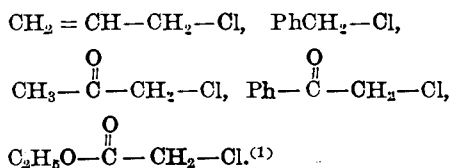


Electronic Interpretation of Organic Reaction Mechanism. VII. Reactions and Structures of Organic Halides in Replacement Reactions

By Masuo MURAKAMI, Shigeru OAE and Sei TAKEUCHI

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Many of the previous workers who have studied on the SN2 type reactions indicate that the following compounds show extremely high reactivities toward nucleophilic reagents:



In order to study why these compounds are highly reactive in the SN2 type reactions, an experiment was made by the present authors using the reaction of ionization mechanism (Pull type). For this type of reaction, the organic halides were interacted on silver nitrate in absolute alcohol. As the previous workers⁽²⁾ have reported that silver nitrates react with alkyl halide by the ionization mechanism (Pull type) and that it exerts too much catalytic activities in the reaction, the same state was recognized also by the authors. However, since it was found that this catalytic action depended chiefly on the sensitized silver chloride, our experiments with silver nitrate were carried out in a dark room in order to avoid the irregular catalytic action. Our experiments show that allyl chloride and benzyl chloride are much more reactive than the ordinary normal alkyl chloride but that chloroacetone, ω -chloroacetophenone and ethyl chloroacetate do not react so easily as *n*-butyl chloride does.

In order to find the effect produced by the second or third chlorine atom of these compounds which have two or three chlorine atoms on the same carbon, the authors made the experiments of the reactions of the polychlorides of *n*-butane and of those of α -polychloroderivatives of toluene with silver nitrate and with

potassium iodide. The results indicate that *n*-butylidene chloride is less reactive than *n*-butyl chloride in both reactions, *i.e.* with silver nitrate and with potassium iodide, while in the series of benzyl chloride, the reactivities decrease with the increase in number of chlorine atoms on the same carbon atom in the case with potassium iodide and increase with the increase in number of chlorine atoms in the case with silver nitrate.

Experimental

Experimental Procedure:—The temperature of the thermostat used for this kinetic measurements was held within 0.1°. The method of determination used in the reaction with silver nitrate was similar to that used by Burke and Donnan^(2a) except the fact that our experiments were performed in sealed tubes in a dark room. A mixture of 5 cc. each of 2 *N* alcoholic solutions of organic chloride and silver nitrate was sealed in a 20 cc. test tube and the test tube was immersed in the thermostat as quickly as possible. At regular intervals, the sealed tube was broken and the content was washed into 25 cc. of 0.05 *N* solution of NH_4SCN and then this mixture was back titrated with 0.2 *N* silver nitrate using iron alum as an indicator. To avoid large catalytic activities produced by silver chloride formed, the reaction was stopped when 30% of the organic chloride had reacted. The velocity constants were obtained from the following equation:

$$k = \frac{1}{t} \left(\frac{1}{C} - \frac{1}{C_0} \right) \quad (i)$$

where *C* is the concentration of silver nitrate at time *t*, while *C*₀ is the initial concentration of silver nitrate.

For the reaction with potassium iodide in acetone, the authors followed the method described by Conant and his co-workers.^(1a) Since this method has been used quite extensively, it is not described here.

Materials:—The solvent used was absolute alcohol which was prepared by boiling dry alcohol with silver nitrate for a few hours. The solution of silver nitrate can be kept in dark without

(1) (a) Conant, Kirner and Hussey, *J. Am. Chem. Soc.*, **66**, 232 (1924); **47**, 478, 488 (1925).

(b) Clarke, *J. Chem. Soc.*, **97**, 416 (1916).

(c) Willson, *Chem. Rev.*, **16**, 149 (1935).

(2) (a) Burke and Donnan, *J. Chem. Soc.*, **85**, 555 (1904).

(b) Senter, *J. Chem. Soc.*, **97**, 343 (1916).

(c) Hammett, "Physical Organic Chemistry" Chapter V.

spoiling for a week, but the authors avoided to use the solution which was prepared more than a week before the experiment. At each time the solution was freshly prepared.

Both allyl chloride and benzyl chloride used were the commercial products. *n*-Butylidene chloride and benzal chloride were prepared from the corresponding aldehyde by reacting these with phosphor pentachloride. Benzotrichloride was prepared by the reaction of benzyl chloride with chlorine. Monochloroacetone and ω -chloroacetophenone were prepared by reacting the corresponding ketone with chlorine, *n*-butyl chloride from *n*-butyl alcohol and hydrochloric acid using zinc chloride as a catalyst, and ethyl chloroacetate by the ordinary esterification of chloroacetic acid with ethanol. All these compounds were washed with dilute sodium carbonate solution, dried over calcium chloride and then distilled for sometimes. The boiling points of these compounds are as follows:

$\text{CH}_2=\text{CH}-\text{CH}_2-\text{Cl}$	45°
$\text{CH}_3-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{CH}_2-\text{Cl}$	119°
$\text{Ph}-\text{CH}_2-\text{Cl}$	179°
$\text{CH}_3-\text{CH}_2-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{CH}_2-\text{CH}_2-\text{Cl}$	77.5°
$\text{C}_2\text{H}_5\text{O}-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{CH}_2-\text{Cl}$	143-4°
$\text{Ph}-\text{CHCl}_2$	88-9° (14 mm.)
$\text{CH}_3-\text{CH}_2-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{CH}_2-\text{CHCl}_2$	114.6°
$\text{Ph}-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{CH}_2\text{Cl}$	m. p. 56°
$\text{Ph}-\text{CCl}_3$	104-5° (25 mm.).

Products were investigated in the case of benzyl chloride. Seventeen g. of silver nitrate and 12 g. of benzyl chloride were reacted in 500 cc. absolute alcohol. After filtering the silver chloride precipitated, alcohol was removed by evaporation, thereby leaving some oily substance. Main parts of this oil (15 g.) distilled over at 95-106° under a reduced pressure of 19 mm. This oil gave a deep violet color when treated with diphenylamine and conc. sulfuric acid, which indicated the presence of $-\text{NO}_2$ group in the molecule. When this oil was treated with caustic soda, benzaldehyde and benzoic acid were obtained. Benzaldehyde was confirmed by converting it to 2, 4-dinitrophenylhydrazone, which melted at 131°, and did not show any fall of its melting point when it was mixed with the known sample. Benzoic acid was confirmed by its melting point and mixed melting point with the known. These experiments indicated that the product obtained in this experiment was benzyl nitrate.

Results

The bimolecular velocity constants obtained by the reaction with silver nitrate of *n*-butyl

chloride, allyl chloride, benzyl chloride, chloroacetone, ω -chloroacetophenone and ethyl chloroacetate are given in Table 1.

Table 1

Bimolecular Velocity Constants in the Reaction of Organic Chloride with Silver Nitrate in Absolute Alcohol at 50°

Compounds	$10^{-5} k$ at 50°C, l., mol., ⁻¹ min. ⁻¹
$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Cl}$	1.2
$\text{CH}_2=\text{CH}-\text{CH}_2-\text{Cl}$	7.9
$\text{Ph}-\text{CH}_2-\text{Cl}$	83.0
$\text{CH}_3-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{CH}_2-\text{Cl}$	0.31
$\text{Ph}-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{CH}_2-\text{Cl}$	0.67
$\text{C}_2\text{H}_5\text{O}-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{CH}_2-\text{Cl}$	0.32

Bimolecular velocity constants of the reaction with silver nitrate for *n*-butylidene chloride, *n*-butyl chloride, benzyl chloride, benzal chloride, and benzotrichloride are summarized in Table 2.

Table 2

Bimolecular Velocity Constants of the Reaction of Organic Polychlorides with Silver Nitrate in Absolute Alcohol

Compounds	Temp. °C	$10^{-5} k$, l., mol., ⁻¹ min. ⁻¹
$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Cl}$	50	1.2
$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CHCl}_2$	50	0.13*
$\text{Ph}-\text{CH}_2-\text{Cl}$	20	8.4
$\text{Ph}-\text{CHCl}_2$	20	76.7*
$\text{Ph}-\text{CCl}_3$	20	102.5*

In the case of polychlorides (these with asterisk in Table 2) the observed values of k obtained from the equation (1) were divided by the number of chlorine atoms present in the molecule in order to get the velocity constants of the splitting of the first chlorine at the initial step of this reaction; therefore the values with asterisk are all treated accordingly. The reason is that the second and the third step of this reaction are very fast as compared to the first.

In Table 3, the velocity constants of polychlorides in the reaction with potassium iodide are summarized.

In order to observe the action of silver chloride formed and of sensitized silver chloride, the reactivities in the following three cases were compared: (a) the ordinary reaction between

Table 3

Bimolecular Velocity Constants of Polychlorides
in the Reaction with Potassium Iodide
in Absolute Acetone

Compounds	Temperature, °C.	k
CH ₃ -CH ₂ -CH ₂ -CH ₂ -Cl	60	0.12
CH ₃ -CH ₂ -CH ₂ -CHCl ₂	60	0.00
Ph-CH ₂ -Cl	25	0.77
	50	(809)
Ph-CHCl ₂	50	0.24
Ph-CCl ₃	50	0.13

silver nitrate and allyl chloride, (b) a reaction of allyl chloride with silver nitrate in the presence of 0.2 *M* freshly prepared silver chloride, (c) a reaction of allyl chloride with silver nitrate in the presence of 0.2 *M* sensitized silver chloride. The data obtained are summarized in Table 4.

Table 4

Percentage of Silver Nitrate Reacted with
Allyl Chloride after 180 Minutes in the
Presence of an Excess of Silver
Chloride in Absolute Alcohol

No.	Reactivities, %		
	(a)	(b)	(c)
1	9.08	11.06	13.3
2	9.21	11.07	15.4

Discussion

According to the currently prevailing theory there are two commonly occurring mechanisms for the nucleophilic substitution reactions: one is the bimolecular, kinetically second order substitution (SN 2) (Push type), or "Walden Inversion"⁽³⁾ and the other is the ionization mechanism (SN 1) (Pull type).^(4, 5, 2c) In the SN2 type mechanism, the driving force is chiefly a "Push" or nucleophilic backside attack by the atom or group having an unshared electron pair which is strongly dominant in the bond formation. On the other hand, in the SN1 type or ionization mechanisms, the main part of the driving force is a "Pull" or front side attack by the solvent or some electrophilic reagent.⁽⁶⁾ This weakens the old bond, allowing

it to ionize in the rate determining step. This reaction is kinetically of the first order when it is with solvent which exists in large excess. The reaction of alkyl halide with silver nitrate is also the reaction of this type, though it is kinetically second order.

From the standpoint of the tetrahedral constitution of carbon atom, a steric hindrance is caused by the other three groups in the back side of the substituted group, therefore except in more complicated cases,⁽⁷⁾ the hindrance must be considered in the SN2 reaction, but not in the ionization or SN1 reaction, when the reagent approaches to the reaction center.

There have been many reports concerning the extremely high reactivities of these compounds such as chloroacetone and benzyl chloride in the SN2 type reaction,⁽⁸⁾ and it might be considered from the authors' experiments that the high reactivities of chloroacetone, *o*-chloroacetophenone and ethyl chloroacetate in SN2 type reaction depend upon a low electron density in the α -carbon atom originated by the strong electron attractive effect of carbonyl group, thus making the approach of nucleophilic reagent easier. This interpretation appears to support the electrostatic hypothesis by Hinshelwood, Laidler and Timm.⁽⁹⁾ The lower reactivities of these compounds in SN1 type reaction (Pull-type) are also ascribed to the same reason — a lower electron density on the α -carbon atom, which attracts a pair of electron toward the carbon atom and makes the splitting of the chlorine anion more difficult. This argument is consistent with the hypothesis given by Hughes and Ingold.⁽¹⁰⁾ The high reactivities of allyl chloride and benzyl chloride might be considered as such: as they have highly unsaturated group at α -carbon atoms, there arises the relatively high resonance energy in their transition states of both types of the reactions in common, thus making the ionization of chlorine easier.

The results obtained from the experiments of polychlorides can be well discussed as follows. The decrease of reactivities with the increase in the number of chlorine atoms in the reaction of polychlorides with potassium iodide might be ascribed to the steric hindrance, because the van der Waals' radius of chlorine is much larger than hydrogen. (Cl = 1.8 Å, H = 1.2 Å, cf., CH₃ = 2.0 Å).⁽¹¹⁾ The authors

(3) (a) Walden, *Ber.*, **28**, 1287 (1875).

(b) Hughes, Juliusburger, Masserman, Topley and Weiss, *J. Chem. Soc.*, **1935**, 1525.

(4) (a) Hughes, Ingold, *Nature*, **132**, 933 (1933).

(b) Hughes, *Trans. Farad. Soc.*, **37**, 602, 612 (1941).

(5) Recently G. Swain indicated that almost all the replacement reactions proceed through concerted mechanism and thereby the meanings of SN1 or SN2 have slightly altered out of their original meanings. Swain, *J. Am. Chem. Soc.*, **70**, 1119, 2969 (1948).

(6) Polanyi, *Endeavour*, **8**, 3 (1949).

(7) such as Brown's F-strain.

(8) Branch and Calvin, "Theory of Organic Chemistry", Prentice-Hall, Inc., 1941, pp. 428-440.

(9) Hinshelwood, Laidler and Timm, *J. Chem. Soc.*, **1938**, 848.

(10) Hughes, *J. Chem. Soc.*, **1946**, 968.

(11) Pauling, "The Nature of Chemical Bond", Cornell University Press, 1940, pp. 189.

consider that in the reactions with silver nitrate, the decreasing tendencies of reactivities of the *n*-butyl chloride series and the increasing trends of the benzyl chloride series with the increase in number of chlorine atoms are due to the following reasons. In the series of *n*-butyl chloride, the one chlorine atom, attaching to the simple alkyl group, cannot resonate largely in its transition state, but has the strong attractive inductive effect, thus making difficult the anionic dissociation of the other chlorine atom. On the other hand, in the series of benzyl chloride, chlorine atoms are attached to the carbon atom which can participate in the resonance system with phenyl group, thus making the electrons of the chlorine atoms resonate easily in its transition state. Therefore the one chlorine atom facilitate the ionization of the other chlorine atom, namely the reactivities are increased. Ingold, Hughes and their co-workers also support⁽¹²⁾ the fact that in the

reactions of alkyl series, the inductive effect is predominant in substitution or elimination, but in the aryl series, the electromeric effect is prominent factor on their reaction rather than the inductive effect. This is quite in agreement with the results of the authors' experiments.

Summary

(1) It was observed in the reaction of organic chloride with silver nitrate that the irregular catalytic action can be avoided by carrying experiments in a dark room.

(2) Silver nitrate was interacted with several organic chlorides which were highly reactive in SN2 type reaction and the kinetic data obtained were fully discussed.

(3) Some organic polychlorides were reacted with silver nitrate and with potassium iodide and rates obtained in these reactions were discussed.

(12) (a) Hughes, Ingold and Taher, *J. Chem. Soc.*, 1940, 949.

(b) Dhar, Hughes, Ingold, Mondour, Mau and Woolf, *J. Chem. Soc.*, 1948, 2093.

The "Critical Thickness" of Organic Thin Films⁽¹⁾

With a Criticism to
Long Range Force Hypothesis of Rothen

By Taro TACHIBANA and Kiyoshige FUKUDA

(Received on September 13, 1950)

Introduction

Several years ago, Rothen⁽²⁾ postulated specific long range forces to explain the specific interaction of an antibody with the antigen layer through the inert screen film of the thickness extending over 150 Å. Since then, his proposal has aroused considerable interest in biologists, chemists and physicists, and has become the focus of much controversy.^{(3),(4),(5),(6),(7)}

But anyone has not been able to formulate any such mechanism that could account for the specificity required to explain Rothen's experimental results. Rothen, himself, has suggested that this specific long range interaction might take place through resonating extended oscillators.

On the other hand, Singer⁽⁵⁾ recently has shown the evidence that strongly suggests that holes in the screen films, permitting such macromolecules as antibody to come into contact and react with antigen, are primarily responsible for the effect observed by Rothen. We have also obtained experimental evidences that appear to suggest that the results of Rothen can be explained by a simpler mechanism that does not require the assumption of specific long range forces. This interpretation has been strongly supported by many facts that had already been obtained through the study of

(1) This paper was partly presented before the regular meeting of the Chemical Society of Japan held at Tokyo, Sept. 24, 1949, and the annual meeting of the Chemical Society of Japan held at Kyoto, Apr. 3, 1950.

(2) A. Rothen, *J. Biol. Chem.*, **168**, 75 (1947); *J. Am. Chem. Soc.*, **70**, 2732 (1948).

(3) F. Karush and B. M. Siegel, *Science*, **108**, 107 (1948).

(4) J. Iball, *Science*, **109**, 18 (1949).

(5) S. J. Singer, *J. Biol. Chem.*, **182**, 189 (1950).

(6) H. J. Trurnit, *Science*, **111**, 1 (1950).

(7) B. Carroll, *J. Am. Chem. Soc.*, **72**, 2763 (1950).

thin film. Then, we have found the "critical thickness" of thin film below which the film could not perfectly cover the substrate. There exist similar phenomena on metallic films. It is a well-known fact that metallic films given by evaporation and cathodic sputtering on non-conducting substrate display, below a certain thickness, different properties from those of the metals in bulk. These results have led us to an opinion that Rothen's results did not necessarily prove the existence of specific long range forces. The present paper describes the results of these experiments and some discussion thereupon.

Experimental Procedure and Results

Experiments have been made on three systems as follows: azo-ovalbumin—rabbit antisera against the haptenic group, azo-ovalbumin—ovalbumin, and cholestanol—digitonin.

1. Azo-ovalbumin—Antisera System.—In order to investigate whether specific long range action is demonstrated in artificial antigen—antiserum system as well as natural antigen—antiserum system used in Rothen's experiments, we have performed an experiment with azo-ovalbumin (ovalbumin coupled with diazotized *p*-amino-phenylarsonic acid) and antibody specifically directed against this haptenic group. After our studies were completed, we found that Singer carried out similar experiments on the same system. His works, however, differ from ours in respect to the condition of the film of antigen; his experiments deal with adsorbed film, while ours with unfolded film.

The techniques used in this experiment will be described elsewhere.⁽⁸⁾ Azo-ovalbumin was prepared by coupling ovalbumin with diazotized *p*-amino-phenylarsonic acid in the usual manner. The number of the diazonium groups introduced in one ovalbumin molecule (assuming the molecular weight as 40,000) was found to be 47 analytically. Rabbit antisera was produced against horse globulin coupled with diazotized *p*-amino-phenylarsonic acid.

In order to prepare the antigen film, azo-ovalbumin was spread on distilled water and then, compressing the monolayer at surface pressure of 15 dynes per centimeter, one double layer of azo-ovalbumin was transferred onto the metal slide covered with an optical gauge of multilayers of barium stearate. Under these conditions, the thickness of the transferred antigen layer (one double layer) was found to be 26–30 Å. Subsequently, films of barium stearate, as screen, were deposited on the antigen films by means of the Blodgett—Langmuir technique. These slides were immersed into undiluted antiserum until the

adsorption of the antibody was completed. After the slides were taken out of the solution, washed and dried, the increase of thickness was measured optically.

The experimental results are given in the curve A of Fig. 1. Each of the points represents an

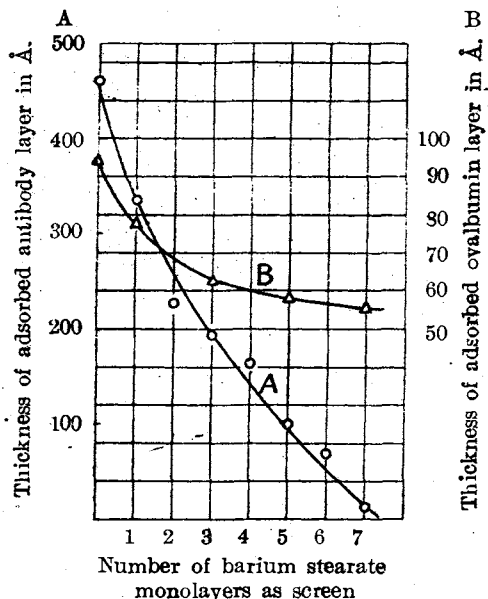


Fig. 1.—Screening action of barium stearate films on one double layer of azo-ovalbumin. Curve A, azo-ovalbumin—antiserum system; curve B, azo-ovalbumin—ovalbumin system.

average of about four independent determinations. Control experiments demonstrated that none of the antibody in the antiserum used in these experiments was adsorbed on the film of original ovalbumin when it was treated in the same manner, and that no measurable amounts of normal serum proteins were adsorbed on the stearate-coated or non-coated films of azo-ovalbumin. These results demonstrate that the antibody specifically directed against the haptenic group was adsorbed on the stearate-covered antigen through the screen in the range of thickness indicated.

Pauling, Pressman and Campbell,⁽⁹⁾ on the other hand, based on the investigations of the hapten-conjugated antigen and the antibody, proposed a mechanism for the antigen-antibody reaction that, over a considerable portion of both molecules having complementary configuration, the short range forces, as van der Waals', electrostatic, hydrogen bond, and other similar forces could cooperate cumulatively to form a sufficiently strong bond.

In the case of azo-ovalbumin and antisera

(8) T. Tachibana, K. Fukuda, T. Ogata, K. Suzuki and S. Yamaoka, unpublished.

(9) L. Pauling, D. Pressman and D. H. Campbell, *Physiol. Rev.*, **23**, 203 (1943).

directed against the diazonium groups, antibody activity is directed specifically against them. If Rothen's interpretation is applied to our experiments, long range forces should operate between antibody and haptenic group of which chemical structure is well known. However, long range forces hypothesis was advanced on the basis of the assumption that holes in the screen films are not responsible for the effect observed. If thin screen films were actually preventing the diazonium groups of azo-ovalbumin and antibody molecules from coming into direct contact, this fact is inconsistent with the consideration put forth by Pauling and his co-workers.

On the other hand, similar phenomena observed by Rothen in immunologic and enzymatic reactions, might occur in the case of the adsorption of large molecule on films of any adsorbent as well. In order to investigate this problem, the following two experiments were performed.

2. Azo-ovalbumin—Ovalbumin System.—Adsorption of ovalbumin on the film of azo-ovalbumin. It was at first reported by Haurowitz⁽¹⁰⁾ that the mixing of azoprotein and ovalbumin in solution of some pH range brought about precipitation reaction. In this case, the interaction would be of electrostatic nature as pointed out by Haurowitz. We found, by monolayer technique, that the ovalbumin molecule was adsorbed on the spread film of azo-ovalbumin when the slide covered with azo-ovalbumin film was brought into contact with the solution of ovalbumin. Then, experiments were extended to detect whether both molecules might not also exert their action throughout a screen film of barium stearate.

As described previously, ovalbumin coupled with diazotized *p*-amino-phenyl arsonic acid was spread on the distilled water and transferred, as one double layer, onto the metal slide covered with an optical gauge of multilayers of barium stearate. The thickness of one double layer was found about 28 Å. The number of the diazonium groups per molecule of the sample was found 58 analytically. Then azo-ovalbumin film was coated with the screen films of barium stearate in the same manner as in the previous experiments. Hereafter the slides to be tested (with or without screen) were immersed into the solution of pH 4 containing one percent of ovalbumin for 45 minutes at room temperature of about 10°C. The thickness increment was measured optically. The results (the thickness increment caused by the adsorption of ovalbumin) are given in curve B of Fig. 1. Ovalbumin molecules were adsorbed on azo-ovalbumin film, despite of the screen films of barium stearate over 100 Å. thick in a manner similar to that found for the antigen-antibody system. Control experiments demonstrated that ovalbumin layer of about 20 Å. thick was adsorbed directly on the stearate films alone, when they were treated in the same manner.

Rothen has performed, on the other hand,

similar experiments with protamin and insulin to demonstrate that barium stearate and Formvar were effective screens for this system. A double layer of barium stearate covering the film of protamin clupein sulfate (10 Å. thick) cut down the adsorption of insulin completely, whereas 220 Å. of insulin could be adsorbed directly on the protamin. This fact was ascribed to the non-existence of holes in screens through which even smaller molecule, such as insulin, than antibody globulin molecule could permit to pass. However, as stated by Singer, the barium stearate screens may not be inert barrier in these experiments, but may rather react with the protamin film.

Such complications are excluded in our experiment with azo-ovalbumin-ovalbumin reaction. Therefore, the present results may show that apparently long range forces also might exert their effect in the reaction system mentioned above. The adsorption of ovalbumin on azo-ovalbumin film is commonly thought to be brought about due to the electrostatic forces between the oppositely charged molecules, since azo-ovalbumin molecule is charged negatively while ovalbumin molecule is positive at pH 4. Consequently, if long range force operates in this case, it may be of electrostatic nature. However, two possibilities may also be considered: 1) that there may be holes to permit the diffusion of ovalbumin molecules in the screens; 2) the electrostatic interaction between azo-ovalbumin film and ovalbumin molecule may take place through induced polarization through the screen. Which possibility is true, would be difficult to decide only from this experiment. At any events, it is important that there could be found a phenomenon that appeared to be caused by long range force, in non-specific reaction also.

3. Cholesterol-Digitonin System.—The deposition of digitonin on cholesterol films was studied by Langumir, Schaefer and Sobotka.⁽¹¹⁾

We have performed experiments to see whether the adsorption of digitonin does not take place through the screen of barium stearate. The techniques used are essentially the same as that described in their paper, except for the covering of cholesterol films with the screen of the built-up films of barium stearate.

The results are summarized in Table 1. It is noticeable that, regardless of the thickness of screens, the thickness increments after treatment with digitonin were found to be about 15 Å. Control experiment demonstrated that the optical gauge of stearate multilayers alone decreased 6 Å. in thickness after being treated with digitonin solution. The amount of digitonin adsorbed on cholesterol films was independent of the number of the monolayers of cholesterol on the slide. Although the amount of digitonin adsorbed on cholesterol film was independent of the thickness of screen films, the surfaces after adsorption of digitonin were, depending upon the thickness of

(10) F. Haurowitz, *Kolloid-Z.*, **74**, 208 (1935).

(11) I. Langumir, V. J. Schaefer and H. Sobotka, *J. Am. Chem. Soc.*, **59**, 1751 (1937).

screen film. markedly different in their adhesion toward water. This is given in column marked "hydro-affinity" in Table 1. When screen films

Table 1

Screening Action of Barium Stearate Film
against the Adsorption of Digitonin
on Cholesterol Film

Cholesterol film		Screen of barium stearate		After treatment with digitonin	
Mode of deposi- tion**	Thickness observed, Å.	Number of layers	Thickness observed, Å.	Thickness increment, Å.	Hydro- affinity of the surface
AB	42	0	0	11	++ θ
(AB) ₂	72	0	0	12.5	++
(AB) ₃	187	0	0	7	++ 64°
AB	34	1	20.5	18.5	++
AB	32	2	48.5	14	++ 76°
AB	37	5	116	15	++ 79°
AB	36	8	195	10	+
AB	41	10	244	{ 7 14.5*	+ 92°

The time of adsorption was 10 minutes in each experiment, but the value marked * was obtained by adsorption of one hour. Symbol ++ indicates to be more hydrophilic than symbol +. θ denotes the contact angle towards water. ** Symbols AB, (AB)₂ and (AB)₃ stand for one, two and five double layers, respectively.

of stearate are less than 5 monolayers, the slide has relatively high hydro-affinity. However, when they are thicker, the slide become less hydrophilic. Cholesterol films and barium stearate films themselves are both originally hydrophobic. Therefore, the effect observed might probably suggest that digitonin molecule, penetrating the screen film of stearate, came into contact directly with the underlying cholesterol film.

If this is the case, there may probably be holes to permit molecule as large as digitonin to diffuse in screen of stearate film.

Discussion

From the present studies, it was found that some kind of chemical reactions involving large molecule, such as the adsorption of ovalbumin on azo-ovalbumin film and the adsorption of digitonin on cholesterol film, as well as the adsorption of antibody on antigen film could occur although the adsorbent films were separated by the screen films of barium stearate. Consequently the phenomena that long range forces appear to operate are not always specific in biochemical reactions alone. Therefore, it seems to be unreasonable for us to require specific long range forces in immunologic and

enzymatic reactions alone. It may be rather plausible to admit the possibility that holes in screen films are responsible for the effect observed, although Rothen attempted to show that the possibility did not exist or in any events was not important. At least, our experiment with the cholesterol-digitonin system might prove that there are holes to permit digitonin molecules to diffuse in screen film of barium stearate, since this system probably reacts by a short range mechanism.

Furthermore, we might show some evidences that the physical state of screen film is of fundamental importance for the explanation of the effect observed. Let us consider the barium stearate alone as screen film for convenience' sake.

If we examine the screening action of barium stearate films from the results of Rothen, Singer and the present authors, we see that there is an almost constant "critical thickness" of barium stearate films to inhibit the combination of antibody on antigen film.

This critical thickness is found around 150 Å. in most systems investigated, as summarized in Table 2. Particularly it would be difficult to explain from the long range forces hypothesis that the same value of critical thickness was obtained independently of whatever the antigens used may be natural or artificial, or whatever the amount of antibody adsorbed directly on antigen film may be (See Table 2).

The critical thickness of stearate film was also observed in other phenomena. The clean glass surface is hydrophilic and gives a zero

Table 2

The Critical Thickness of Barium Stearate
Film to Inhibit the Specific Adsorption
of Antibody on Antigen Layers

Varieties of the system	I One double layers of oval- bumin and anti- oval- bumin system	II One double layers of bovine albumin and anti- bovine albumin system	III Adsorbed layer of Pneumoc. cocci poly- saccharide III and bovine homologous antibody system	IV Adsorbed human albumin and homologous antibody system	V One double layers of azo- oval- bumin and homologous antibody system
Thickness of antibody layer adsorbed directly on antigen film, Å.	26	65	270 125	80	465
Critical thickness of barium stearate film, Å.	70~ 100	150	150~ 160	150~ 160	150~ 170

Critical thickness was observed directly or calculated from the number of layers multiplied by the thickness per monolayer, 24.4 Å. I, II, III, were taken from the results of Rothen; IV from Singer; V from the present authors.

contact angle with water. However, after the stearic acid monolayers have been deposited on glass, the surfaces becomes hydrophobic and the contact angles increase with the number of the stearate monolayers until they attain a critical value, about 115° , where the thickness of stearate films is $70\sim 120\text{\AA}$. ($3\sim 5$ monolayers) as shown in Table 3 (column 3).

Table 3
Screening Action of Stearic Acid Multilayers
on Solid Surface

1 Number of layers	2 Thick- ness, $\text{\AA}$.	3 Contact angle towards water	4 Surface potential, mV.	5 Static friction coeff- cient
0	0	0°		1.0
1	24.4	$66^\circ 11'$	$101^\circ 46'$	0.12
3	73	$115^\circ 23'$	355	0.09
5	122	$115^\circ 56'$	467	0.06
7	171	$112^\circ 10'$	457	0.06
9	220	$117^\circ 36'$		0.06

column 2; calculated from the thickness per monolayer, $24.4\text{\AA}$: column 3; S. Mitsui and T. Sasaki, private communication (1948): column 4; T. Isemura, Private communication (1950): column 5; T. Isemura, this Bulletin, 15, 467 (1940).

The surface potential of stearate monolayers on metal slides shows also a similar behavior. In this case, the critical thickness of stearate monolayers is $120\sim 170\text{\AA}$. ($5\sim 7$ monolayers) as indicated in column 4 of Table 3. It might also be significant to quote the results of Isemura who studied on the effect of monolayers on the static friction of glass surface. We see from his results that the static friction decreases with the increase of the number of stearate monolayers, until it becomes nearly constant in the region of the thickness exceeding five monolayers, *i.e.* about $120\text{\AA}$., as shown in column 5 of Table 3. These results appear to be as if the character of underlying substance was transmitted across the screen film of stearate. Furthermore, as far as stearate films are used as screen, the critical thickness to interrupt the effect of underlying substance is always about $120\text{\AA}$., irrespective of independent phenomena observed. This value of the critical thickness is approximately the same as that found in immunologic and enzymatic reaction. This coincidence is regarded as more than accidental. This seems to indicate that multilayers of stearate, when they are less than $150\text{\AA}$ thick, consist of fragile structure. Namely such a thin film may be such as the network of structure loose enough to permit the diffu-

sion or penetration of a large molecule. The detailed mechanism may be complicated. The present suggestion might be extended to apply to screen films of Formvar and other polymers as well.

Moreover, Rothen showed that in the bovine serum albumin—antiserum system, the amount of antibody adsorbed increased linearly with the number of monolayers of antigen up to eight layers where the thickness of adsorbed layer of antibody is $149\text{\AA}$. We also obtained a similar relation from the experiments with azo-ovalbumin—rabbit antiserum. These results are represented in Fig. 2, the details of which will be described elsewhere.

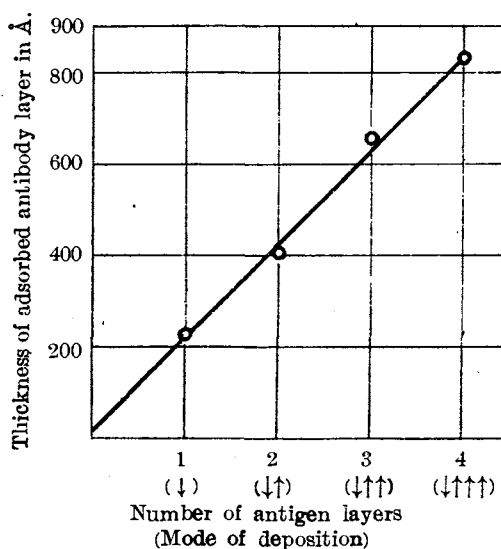


Fig. 2.—Relation between the number of azo-ovalbumin and thickness of antibody layer adsorbed on it.

It is noteworthy that a layer of $800\text{\AA}$. of antibody, which is larger than the major axis of antibody molecule, was adsorbed directly on the four monolayers of antigen (ABBB). At first sight, this result might appear to support long range force hypothesis. However it may be unfavorable to Rothen's hypothesis that the thickness of antibody layer increases linearly with the number of underlying monolayers of antigen, *i.e.* the number of haptenic groups of antigen per unit area. The total haptenic groups of antigen layers should be available to the adsorption of antibody molecules. Let us notice that the thickness of antigen layer, in this experiment, is lower than the "critical thickness."

In this case, the structure of antigen layer may be fragile. Especially, by bringing into contact with antiserum, the structure of protein

layers may become more loose by swelling. Therefore, the antigen layer might conceivably disrupt, exposing all the haptenic groups of antigen molecules in original monolayers to antiserum. Thus, the underlying antigen layer, also, may become available to the reaction by direct contact with antibody molecules. After drying, the layers may become such structure as that in which antigens and antibodies are mixed together or alternated more regularly. Such conditions are probable in consideration of more strong affinity between antigen and antibody than between each antigen monolayers.

Rothen, also, reported that, on optical gauges of octadecylamine, a layer of 700 Å. of antibody was adsorbed on 5 Å. of pneumococcus type III polysaccharide. He explained this facts by long range forces. But, in this case also, as polysaccharide is a chain polymer, it may extend into bulk of antiserum, like seaweeds on the bed of sea, exposing all determinant groups to antibody. Therefore, adsorbed layer of 700 Å. is not a uniform layer of antibody, but instead may be quite complicatedly composed of antigen and antibody. Thus, the large thickness of 700 ~ 800 Å. of adsorbed antibody layer observed by Rothen and us may be explained without long range forces hypothesis.

In conclusion, in view of the considerations and the evidences presented above, we seem to be facing the problem of a "critical thickness" or structure of thin organic films rather than the long range forces postulated by Rothen.

Summary

By studying the reactions of protein with the aid of monolayer technique, Rothen found that antigen and antibody, and also enzyme and substrate molecules, can react in despite of being apparently separated by some inert screen.

He assumed from these results, that the specific long range forces operate in immunologic and enzymatic reactions. We have found that similar phenomena occurred in the following systems: monolayer of hapten-conjugated

protein as antigen and antibody directed specifically against the hapten, azo-ovalbumin and ovalbumin, and even cholestanol and digitonin. Therefore, it leaves some room for consideration to assume specific long range forces in immunologic and enzymatic reaction alone.

Besides, we suggested that there was required an almost constant thickness (about 150 Å.) of barium stearate to inhibit completely the combination of antibody with antigen in transferred film, independent of the variety of the systems.

We have also noticed, from the data of the contact angle towards water, those of surface potential and of static friction coefficient of stearic acid multilayers on glass or metal surface, that the multilayers of stearic acid must have a thickness over about 150 Å. (same as the result of antigen-antibody reaction) to interrupt the effect of underlying substance, regardless of the phenomena concerned.

These facts appear to suggest the fragile nature of screen film which is thinner than the certain thickness which we call the "critical thickness." Such a thin film may conceivably be such as the net-work structure loose enough to permit the diffusion and the penetration of large molecules. Such a physical state of screen film may primarily be responsible for the results of the experiments of Rothen, Singer and the present authors.

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Dipole Moments of Tropolone and Related Compounds⁽¹⁾

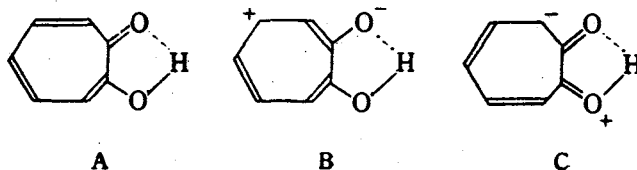
By Yukio KURITA, Tetsuo NOZOE and Masaji KUBO

(Received September 15, 1950)

Introduction

One of us⁽²⁾ carried out extensive studies on the chemical properties of hinokitiol (4-iso-propylcycloheptatriene-2, 4, 6-ol-2-one-1) and assumed its structure to be the resonance hybrid among various electronic structures of

very great. The materials used were prepared by one of us⁽³⁾ and his collaborators. They are:— tropolone, m.p. 51°, tribromotropolone, 126°, hinokitiol, 52°, α -monobromohinokitiol, 56°, α -dibromohinokitiol, 134°, β -dibromohinokitiol, 96°, α -mononitrohinokitiol, 56°, dinitrohinokitiol, 155°.



type A, B and C. He⁽³⁾ also succeeded in synthesizing this compound and its mother substance, tropolone (cycloheptatriene-2, 4, 6-ol-2-one-1). We measured the dipole moments of some of these compounds in benzene solution. The object of the present work is twofold. The first is to obtain some conclusion concerning the positions of substituents in various substituted tropolone and hinokitiols. The second is to investigate the structure of cycloheptatrienolone ring. This is of interest because the ring has odd number of carbon atoms. Wheland and Mann⁽⁴⁾ have measured the dipole moment of azulene, but in general the data on cycloheptatriene ring compounds are very scanty. It will be very desirable to determine whether the cycloheptatrienolone ring is planar like benzene ring or non-planar like cyclooctatetraene ring.

Experimental Method and Materials

Dielectric constants were measured by heterodyne beat method at the wavelength of 300 m. The sum of P_E and P_A was taken to be equal to the molecular refraction for D-line calculated additively from the atomic refractions of constituent atoms and bonds. This did not cause any serious error because orientation polarizations are

Experimental Results

The results obtained are shown in Table 1, where w and P denote the weight fraction and molecular polarization respectively. Other notations used have their usual significances.

Table 1

Dipole Moments of Tropolone and Related Compounds

$w_2(\%)$	ϵ_{12}	d_{12}	$P_2(\text{cc.})$
Tropolone, 25° and 35°			
0	2.273	0.8733	(317.5)
0.621	2.346	0.8749	295.5
1.332	2.421	0.8764	277.2
1.951	2.487	0.8784	268.7
$P_{2\infty} = 317.5 \text{ cc.}, R_D = 32.5 \text{ cc.}, \mu = 3.71 \text{ D}$			
0	2.253	0.8627	(298.0)
0.621	2.321	0.8645	282.1
1.332	2.395	0.8659	272.3
1.951	2.460	0.8682	265.0
$P_{2\infty} = 298.0 \text{ cc.}, R_D = 32.5 \text{ cc.}, \mu = 3.64 \text{ D}$			
Tribromotropolone, 25°			
0	2.273	0.8733	(125.6)
0.604	2.280	0.8769	122.4
1.145	2.291	0.8800	147.5
1.830	2.305	0.8840	157.5
$P_{2\infty} = 125.5 \text{ cc.}, R_D = 55.7 \text{ cc.}, \mu = 1.84 \text{ D}$			
Hinokitiol, 33°			
0	2.257	0.8651	(375)
2.047	2.467	0.8687	351
3.002	2.573	0.8706	350
3.686	2.628	0.8715	334
$P_{2\infty} = 375 \text{ cc.}, R_D = 46 \text{ cc.}, \mu = 4.04 \text{ D}$			

(1) Presented at the Annual Meeting of the Chemical Society of Japan on 2 April 1950 and at the General Discussion on Structural Chemistry held by the society on 8 July 1950.

(2) T. Nozoe, *Yakugaku*, **3**, 174 (1949).

(3) T. Nozoe *et al.*, *Proc. Japan Acad.*, **26**, 38, 43, 47 (1950).

(4) G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 204 (1949).

$w_2(\%)$	ϵ_{12}	d_{12}	$P_2(\text{cc.})$
α -Monobromohinokitiol, 33°			
0	2.257	0.8651	(430)
2.047	2.420	0.8724	411
2.448	2.454	0.8738	404
3.055	2.505	0.8762	402

$P_{2\infty}=430 \text{ cc.}$, $R_D=54 \text{ cc.}$, $\mu=4.32 \text{ D}$

α -Dibromohinokitiol, 33°			
0	2.257	0.8651	(430)
1.208	2.329	0.8710	409
2.334	2.391	0.8756	393
3.941	2.486	0.8832	386

$P_{2\infty}=430 \text{ cc.}$, $R_D=62 \text{ cc.}$, $\mu=4.27 \text{ D}$

β -Dibromohinokitiol, 20°			
0	2.283	0.8790	(269)
0.4351	2.302	0.8809	317
0.6964	2.317	0.8821	342
0.9113	2.332	0.8832	368

$P_{2\infty}=269 \text{ cc.}$, $R_D=62 \text{ cc.}$, $\mu=3.14 \text{ D}$

α -Mononitrohinokitiol, 25°			
0	2.273	0.8733	(847.3)
0.558	2.387	0.8753	824.3
1.212	2.522	0.8769	807.5
1.526	2.582	0.8777	788.7

$P_{2\infty}=847 \text{ cc.}$, $R_D=53 \text{ cc.}$, $\mu=6.19 \text{ D}$

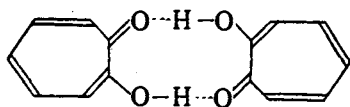
Dinitrohinokitiol, 20°			
0	2.283	0.8790	(537)*
2.450	2.534	0.8874	506

$P_{2\infty}=537 \text{ cc.}$, $R_D=59.5 \text{ cc.}$, $\mu=4.63 \text{ D}$

* Hedestrand's method of extrapolation (*Z. physik. Chem.*, B, 2, 428 (1929).) was used for this as well as for others giving values consistent with those extrapolated graphically.

Discussion

The dipole moments of these compounds are high. Hence the existence of dimers with a vanishing moment such as (I) cannot be con-



(I)

ceivable. The normal dependence of molecular polarization upon concentration also denies such association. The bonds of high moments in the molecules of tropolone and hinokitiol are located in the part of $-\text{CO}-\text{C}(\text{OH})-$. Assuming the bond moments of $\text{C}=\text{O}$, $\text{C}-\text{O}$ and

$\text{O}-\text{H}$ to be equal to 2.5 D, 0.86 D and 1.53 D respectively, the valency angle $\angle \text{C}-\text{O}-\text{H}$ to be 110° and that of $\angle \text{C}-\text{C}-\text{O}$ at the C -atom of carbonyl group to be 130° as in benzophenone,⁽⁵⁾ the resultant moment is calculated as 2.1 D, if the valency angle $\angle \text{C}-\text{C}-\text{O}$ at the C -atom of $\text{C}-\text{OH}$ is equal to the tetrahedral angle. The resultant moment is fairly insensitive to the assumed value of the $\angle \text{C}-\text{C}-\text{O}$ angle. In fact, it is 2.0 D if the latter angle is equal to 115.7° which corresponds to the regular heptagon form of the ring and 1.85 D if the angle is assumed to be 120° . The difference between these and the observed values are too great to be attributable to the solvent effect or induction effect. We must take into account the hydrogen bond between the H -atom in OH and the O -atom in $\text{C}=\text{O}$ and resonance among various electronic structures of the type B with a formal positive charge at one of the seven C -atoms in the ring. There will be fourteen such electronic structures if the two O -atoms can interchange their role. Each of these structures, to be sure, corresponds to an excited state with smaller number of double bonds. Hence its contribution to the normal state will be small. But the number of these dipolar-ionic structures are great and each of these structures has very high moment. These two factors will be sufficient to account for the observed moments. Furthermore the fact that tropolone and its derivatives show fairly strong acidic character and that they are readily attacked by electrophilic reagents giving substitution products suggests the possibility of resonance involving the electronic structures of type C. Their contribution, however, will be small. The rather small contribution of the electronic structures of type C is in agreement with our results concerning the direction of dipoles in the molecules as will soon be evident.

As a result of resonance among these structures, it is supposed that each bond in the ring has a certain amount of double bond character and the cycloheptatriene ring takes a plane form. The valency angle of carbon must deviate from its normal value and consequently internal energy will increase. We calculated the hybridization of $2s$, $2p_x$ and $2p_y$ orbitals giving three hybrid orbitals ψ_1 , ψ_2 , ψ_3 the latter two of which are equivalent and make an angle θ with each other. It was found that, as shown in Table 2, the bond strengths for θ equal to the angle of a regular heptagon $128^\circ 34'$ are weakened about 0.6% in

(5) N. L. Leonard and L. E. Sutton, *J. Am. Chem. Soc.*, 70, 1864 (1948).

Table 2
Bond Strengths of sp^2 -Hybrid Orbitals

θ	ψ_1	ψ_2, ψ_3
109°28'	1.932	2.000
120°	1.991	1.991
128°34'	1.999	1.979

the two equivalent orbitals ψ_2, ψ_3 to be assigned to the bonds in the ring and strengthened about 0.4% in a non-equivalent orbital ψ_1 for the bond to a substituent as compared with the benzene ring. Though in total the bond strengths become weak, the small increase of energy of this magnitude will be overcompensated by high resonance energy⁽⁶⁾ due to a great number of resonating structures stabilizing the molecules. It should be noted that if instead of bond strength, the dependence of bond energy, calculated by Penney⁽⁷⁾ from resonance integrals, upon the angle θ is considered, the formation of heptagon ring becomes more favorable.

Finally the position of substituents in various derivatives must be determined. A difficulty arises because, though the magnitude of dipole moment of hinokitiol has been measured, the direction of dipole in the molecule cannot be obtained experimentally. The approximation is reasonably adequate that the moment of monobromohinokitiol is the vector sum of that of hinokitiol μ_0 and C-Br bond moment ($\mu(\text{C-Br})=1.48$ D). It is highly probable from the consideration on the course of formation⁽¹⁾ of α -monobromohinokitiol that Br-atom is in the position 7. Therefore, a plane heptagon form of the ring being assumed, the C-Br moment points along a line from the center of the ring to the C-atom at the position 7. The angle between this and μ_0 can be determined since their vector sum is known. There are two possibilities in the direction of μ_0 , one to each side of C-Br bond moment. Considering various resonating structures of type B, μ_0 pointing in the direction nearly coincident with the line from the center of the ring to the middle point of two O-atoms with positive end at the ring⁽⁸⁾ is taken to be correct. The other possibility with the dipole nearly pointing in the opposite direction must be rejected.⁽⁹⁾

The magnitude and the direction of the dipole moment of hinokitiol being known, the moment of tropolone can be calculated by subtracting vectorially the bond moment of isopropyl group, which is assumed to be equal to that of isopropylbenzene⁽¹⁰⁾ ($\mu(\text{C-}i\text{-C}_3\text{H}_7) - \mu(\text{C-H})=0.65$ D). The calculated moment is 3.8 D in agreement with the observed value 3.7 D. For bromo- and nitro-derivatives, the conceivable position of substitution are 3, 5 and 7 in analogy to benzene derivatives such as phenol or aniline.⁽¹¹⁾ The calculated moments of dibromohinokitiols are 3.7 D, 4.7 D and 2.9 D for 3,5-, 3,7- and 5,7-dibromohinokitiol respectively. Comparing these values with the observed ones, it is concluded that the position of substituents in α -dibromohinokitiol is 3,7 while in β -dibromohinokitiol it is 5,7.⁽¹²⁾ Assuming the bond moment of nitro-group to be $\mu(\text{C-NO}_2) - \mu(\text{C-H})=3.0$ D, the moment of mononitrohinokitiol is calculated to be 6.0 D, 1.3 D and 5.1 D for 3-, 5- and 7-nitrohinokitiol. Comparing these values with the observed one, the probable positions of a substituent group in α -mononitrohinokitiol is supposed to be 3 or 7. The calculated moments of dinitrohinokitiols are 4.1 D, 5.4 D and 2.6 D for 3,5-, 3,7- and 5,7-dinitrohinokitiol respectively. Comparing these values with the observed one, it is supposed that dinitrohinokitiol under investigation is 3,5- or 3,7-derivative. The reason for the indefinite conclusions are partly connected with the magnitude of C-NO₂ bond moment that must be assumed.⁽¹³⁾ For tribromotropolone, all the three positions 3, 5 and 7 must be substituted by Br-atoms. The moment calculated from that of tropolone and three C-Br bond moments is 2.8 D, which is much higher than the observed value. If, however, the moments of C=O, C-OH are added vectorially together with three C-Br and two C-H moments in accordance with the electronic structure of the type A without

(10) J. W. Baker and L. G. Groves, *J. Chem. Soc.*, **1939**, 1144.

(11) By the molecular orbital treatment already mentioned, it is found that in the molecule of tropolone, π -electron distribution is concentrated at C-atoms 3, 5 and 7, which justifies that only these positions are liable to be attacked by electrophilic reagents.

(12) 3,5-Dibromo derivative can be excluded also from considerations in organic synthesis. Both α - and β -dibromohinokitiol can be obtained from α -monobromohinokitiol by bromination⁽⁷⁾.

(13) Considering the neglect of possible formation of hydrogen bond between the H-atom in OH and the O-atom in the neighboring nitro-group and the consequent existence of tautomers and taking into account the investigations on the rearrangement product of this compound⁽²⁾, we should like to reserve, for a while, definite conclusions concerning the positions of substituent groups. Final decision must be given after investigations are extended to cover wider scope of compounds of related structure.

(6) We (Y. Kurita and M. Kubo, this Bulletin, **24**, 13 (1951)), have carried out molecular orbital treatment on tropolone and obtained high resonance energy.

(7) W. G. Penney, *Proc. Roy. Soc., A*, **146**, 203 (1934).

(8) The molecular orbital treatment on tropolone also gives a moment in the direction along the line from the center of the ring to the middle point of the two O-atoms, with a positive end at the ring.

(9) It can be shown that the latter possibility gives resultant moments for dibromo-derivatives that never agree with experiments.

considering resonance effect, the calculated value is 1.8 D in close agreement with experiment. Probably unshared electron pairs of Br-atoms in competition with that of O-atom decrease the resonance effect and consequently diminish the localization of positive charge on the ring, which is characteristic to tropolone. Furthermore, the electron withdrawal by three electronegative Br-atoms decreases the electron density in the ring, rendering the contribution of the electronic structure of type B more difficult or that of type C more important in conformity to the experimental observations that Br-substituted tropolone and hinokitiol are more strongly acidic than their mother substances.

Summary

The dipole moments of tropolone (cycloheptatriene-2,4,6-ol-2-one-1) and related compounds were measured in benzene solution. The values obtained are:— tropolone, 3.71 D (25°) and 3.64 D (35°); tribromotropolone (3,5,7-tribromo-), 1.84 D (25°); hinokitiol (4-isopropylcycloheptatriene-2,4,6-ol-2-one-1), 4.04 D (33°); α -monobromohinokitiol (7-bromo-), 4.32 D (33°); α -dibromohinokitiol (3,7-dibromo-), 4.27 D (33°); β -dibromohinokitiol (5,7-

dibromo-), 3.14 D (20°); α -mononitrohinokitiol (3- or 7-nitro-), 6.19 D (25°); dinitrohinokitiol (3,5- or 3,7-dinitro-), 4.63 D (20°). The high dipole moments of tropolone and hinokitiol were explained adequately by taking into consideration the contribution of various resonance structures with a formal positive charge at the ring C-atoms. The resonance was supposed to give a certain amount of double bond character to each bond in the ring, causing plane cycloheptatrienolone ring. The position of substituents in the substituted tropolone and hinokitiols were determined and are given immediately after each name of these compounds in parentheses.

We wish to express our cordial thanks to Prof. S. Seto, Mr. Y. Kitahara and Mr. T. Mukai of Tohoku University for collaborating with us in the syntheses of these new compounds and to Prof. A. Kotera for lending us his experimental apparatus. Our thanks are also due to the Ministry of Education in aid of this research.

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Molecular Orbital Treatment of Tropolone⁽¹⁾

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In the previous paper⁽²⁾ we measured the dipole moment of tropolone (cycloheptatriene-2,4,6-ol-2-one-1) and its derivatives⁽³⁾ and discussed the molecular structure of these compounds. We arrived at the conclusion that these molecules resonate among various electronic structures contributing to the normal states of these molecules and that each bond in the ring has a certain amount of double bond character causing plane cycloheptatrienolone ring. We found that the dipole moments of tropolone and hinokitiol (4-isopropyl-

cycloheptatriene-2,4,6-ol-2-one-1) are nearly pointing along the line from the center of the ring to the middle point of two O-atoms with a positive end at the ring. The positions of substituents in the substituted tropolone and hinokitiols were determined, though for a few of them two alternatives were given to be decided finally by further investigations.

The theoretical investigations on the conjugated double bonds by the method of molecular orbitals have already been applied to the molecules of various compounds and have succeeded in the elucidation of the geometrical structures of these molecules, dipole moments, resonance energies, absorption spectra, chemical reactivities, etc. In the present paper we wish to report the results of application of the method of molecular orbitals to tropolone and show

(1) Presented at the General Discussion on Structural Chemistry held by the Chemical Society of Japan on 8 July 1950.

(2) Y. Kurita, T. Nozoe and M. Kubo, this Bulletin, **24**, 10 (1951).

(3) T. Nozoe *et al.*, *Proc. Japan Acad.*, **26**, No. 7, 38, 43, 47 (1950).

that the results obtained experimentally are reasonably correct from theoretical considerations. Finally we shall give the characteristic properties of cycloheptatriene ring.

In the LCAO-molecular orbital method, each electron is considered to be in the self-consistent field due to other electrons and atomic nuclei and the single electron wave function ψ_j is approximated by a linear combination of atomic orbitals φ_k , each belonging to one of the nuclei. We treat the problem as a π -electron system, excluding, for a while, σ -electrons involved in the formation of single bonds.

$$\psi_j = \sum_k a_{jk} \varphi_k$$

The electronic energy E_j of the molecular orbital ψ_j can be obtained as roots $E=E_j$ ($j=1, 2, \dots, l$) of a secular equation,

$$D = |H_{mk} - S_{mk}E| = 0,$$

where l denotes the number of π -electron atomic orbitals and H_{mk} and S_{mk} are given by the following equations respectively.

$$H_{mk} = \int \varphi_m^* H \varphi_k d\tau, \quad S_{mk} = \int \varphi_m^* \varphi_k d\tau.$$

The coefficients a_{jk} can be calculated by solving a set of simultaneous equations,

$$\sum_{k=1}^l a_{jk} (H_{mk} - S_{mk}E_j) = 0, \quad j, m = 1, 2, \dots, l,$$

and normalizing the wave function ψ_j . The wave function for the ground state can be obtained if we allot all π -electrons successively to the molecular orbitals ψ_j of low energy E_j , with the restriction that only two electrons of opposite spin can be adopted by each orbital.

An electron in the molecular orbital ψ spends a fraction a_{jk}^2 of time in the atomic orbital φ_k . Consequently the mean number of π -electrons at k -atom is given by

$$q_k = \sum_j |a_{jk}|^2,$$

where the sum extends over all molecular orbitals ψ_j occupied by electrons in the ground state. The bond order p_{lm} was defined by Coulson⁽⁴⁾ as

$$p_{lm} = \sum_j a_{lj} a_{jm}.$$

The sum of bond orders relating to l -atom, i. e.,

$$N_l = \sum_m p_{lm}$$

expresses the saturation degree of valency of l -atom. Coulson⁽⁵⁾ defined the free valence index of l -atom by

$$F_l = N_{\max} - N_l$$

and gave to $N_{\max}$ (the maximum value of N_l) the value of 1.68 for carbon. The free valence index is a measure of reactivity of the atom towards a free radical. The constitutional formula with the inscription of values of q_k , p_{lm} and F_l is called a molecular diagram.⁽⁶⁾

In actual calculation for a molecule under investigation, we make the approximation that H_{mk} is zero except Coulomb integrals H_{kk} and exchange integrals between neighboring atoms, since exchange integrals will decrease rather rapidly as the distance between the atoms increases. In a similar manner, as for the matrix components of unity, the overlap integrals are assumed to be $S_{mk}=0$, while $S_{kk}=1$. We now introduce, for the convenience of calculation, two quantities δ_k and ρ_{mk} defined by⁽⁷⁾

$$H_{kk} = \alpha_k = \alpha + \delta_k \beta, \quad H_{mk} = \beta_{mk} = \rho_{mk} \beta,$$

where α is the Coulomb integral of an electron in a π -orbital of benzene molecule, and β is the exchange integral between neighboring C-atoms in the same molecule.

The calculation of successive approximation must be carried out until the final result is self-consistent.⁽⁸⁾ First a set of proper values is chosen for δ_k and ρ_{mk} , i. e., for α_k and β_{mk} . These enable us to calculate molecular orbitals, which in turn give q_k and p_{mk} . The total charge Q_k of each atom in the molecule and the interatomic distance r_{mk} between neighboring atoms can be obtained from q_k and p_{mk} respectively. Then α_k and β_{mk} are calculated from Q_k and r_{mk} respectively. The calculated values will not in general be identical with the original set. The calculations are repeated with the new set. This procedure is continued until the assumed set and the calculated set are almost identical. Four functional relations between q_k and Q_k , Q_k and α_k , r_{mk} and β_{mk} , p_{mk} and r_{mk} are required for the calculation. We used the following interrelations. (i) The total charge Q_k belonging to each atom is

(4) C. A. Coulson, *Chem. Abstr.*, **43**, 6877 (1949).

(5) A. Pullman, B. Pullman and P. Rumpf, *Bull. soc. chim. France*, **1948**, 787. B. Pullman and G. Berthier, *ibid.*, **1948**, 788.

(6) G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942).

(7) G. W. Wheland and D. E. Maun, *J. Chem. Phys.*, **17**, 264 (1949).

(8) C. A. Coulson, *Proc. Roy. Soc. (London)*, **A**, **169**, 423 (1939).

equal to the sum of the nuclear charge, the charge of electrons in an inner shell, π -electron density q_k and σ -electron density, which is given by $\sum(l) \mu_{kl}/r_{kl}$, where μ_{kl} and r_{kl} denote respectively the dipole moment of σ -bond and interatomic distance between k - and l -atom. The sum is over all σ -bonds attached to the k -atom. (ii) According to Sandorfy,⁽⁹⁾ α_k is proportional to the electronegativity χ_k of an atom. Assuming $\alpha/\beta=4.1$, the values of δ_k are calculated as shown in Table 1. For an

Table 1
Electronegativity χ_k and δ_k

Atom	χ_k	δ_k
C	2.50	0.00
N	3.15	1.07
O	3.60	1.80
F	4.15	2.70

atom with a charge Q_k correction term must be added. According to Pauling⁽¹⁰⁾ a unit positive formal charge increases the electronegativity of an atom by an amount approximately equal to two-thirds of the difference between the electronegativities of that atom and the next atom to the right in the periodic table, and a negative formal charge similarly decreases the electronegativity value. Hence for an a -atom with a charge Q_k , the electronegativity χ_k is given by

$$\chi_k = \chi_a + \frac{2}{3} (\chi_b - \chi_a) Q_k,$$

where χ_b denotes the electronegativity of a b -atom, the right neighbor of the a -atom. From the proportionality of electronegativity and Coulomb integral, $\alpha_k = (\chi_k/\chi_c)\alpha_c = \alpha_c + (\chi_k/\chi_c - 1)\alpha_c$, and by definition, $\alpha_k = \alpha_c + \delta_k\beta$. Hence

$$\delta_k = \left(\frac{\chi_k}{\chi_c} - 1 \right) \frac{\alpha_c}{\beta}$$

Inserting in this equation the value of χ_k obtained above,

$$\delta_k = \left[\left(\frac{\chi_a}{\chi_c} - 1 \right) + \frac{2}{3} \left\{ \left(\frac{\chi_b}{\chi_c} - 1 \right) - \left(\frac{\chi_a}{\chi_c} - 1 \right) \right\} Q_k \right] \frac{\alpha_c}{\beta} = \delta_a + \frac{2}{3} (\delta_b - \delta_a) Q_k.$$

Hence for carbon

$$\delta_k = \frac{2}{3} \delta_N Q_k = 0.71 Q_k,^{(11)}$$

and similarly for oxygen

$$\delta_k = 1.80 + \frac{2}{3} (\delta_F - \delta_O) Q_k = 1.80 + 0.60 Q_k,$$

$$\delta_k = 1.80 + \frac{2}{3} (\delta_O - \delta_N) Q_k = 1.80 + 0.49 Q_k,$$

for $Q_k > 0$ and $Q_k < 0$ respectively. Considering the polarization of σ -bonds, the value of δ for a C-atom neighboring to a hetero-atom was assumed to be equal to one-tenth of δ of the latter atom. (iii) The exchange integral β_{mk} was assumed by Sandorfy⁽⁹⁾ to be inversely proportional to the fourth power of interatomic distance r_{mk} . (iv) The relation between the bond order p_{mk} and interatomic distance r_{mk} is given by Coulson's curve⁽⁴⁾ for C-C bonds. We calculated the bond order of C-O bonds for various compounds as shown in Table 2. Approximately linear relation is obtained between the bond order and the interatomic distance.

Table 2
Interatomic Distance and Bond Order of C-O Bonds

	Interatomic distance	Bond order
Single bond	1.43	0
Resorcin	1.36	0.28
CaCO ₃	1.31	0.58
NaHCO ₃	1.27	0.68
Double bond	1.22	0.94
Double bond*	1.185	1

* Ideal double bond with no ionic character⁽¹²⁾

Molecular Diagram of Tropolone.—The C-atoms of tropolone are numbered in the same way as the nomenclature "cycloheptatriene-2,4,6-ol-2-one-1." Let us call the two O-atoms attached to the position 1 and 2 respectively by the number 8 and 9. Molecular orbitals are constructed from π -orbitals belonging to these nine atoms. The number of electrons to be put in these orbitals is ten, i. e., eight electrons for double bonds plus two electrons for a lone pair at one of the O-atoms. Though the two O-atoms are not exactly equivalent, they are supposed to be nearly so, owing to the hydrogen bond formation and resonance. Therefore we assign to each of them a charge of $+1.5e$ for the sum of the charge of a nucleus and electrons in an inner shell and a charge $-0.12e$ due to the

(9) C. Sandorfy, *Bull. soc. chim. France*, 1949, 615.

(10) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York (1948), p. 66.

(11) Wheland and Mann⁽⁸⁾, in calculating the dipole moment of fulvene, assumed the coefficient to be equal to 1 instead of 0.71.

(12) R. Cantarel, *Bull. soc. chim. France*, 1949, M 327.

polarization of O-H σ -bond. Consequently the molecule is assumed to be symmetrical across a plane through C-atom 5 and the middle point of C-atoms 1 and 2, and perpendicular to the ring. As a zeroth approximation we put $\rho_{mk}=1$, $\delta_8=\delta_9=2$ and $\delta_k=0$ for C-atoms. Calculation gives for the dipole moment due to π -electrons the value of $\mu_\pi=8.7$ D. The first and the second approximations give 6.7 D and 4.4 D respectively. The molecular orbitals for the last calculation in the order of increasing energy are found to be

$$\begin{aligned}\psi_S(-2.773) &= 0.442(\varphi_9 + \varphi_8) \\ &+ 0.489(\varphi_2 + \varphi_1) + 0.222(\varphi_3 + \varphi_7) \\ &+ 0.114(\varphi_4 + \varphi_6) + 0.084\varphi_5,\end{aligned}$$

$$\begin{aligned}\psi_A(-2.131) &= 0.574(\varphi_9 - \varphi_8) \\ &+ 0.338(\varphi_2 - \varphi_1) + 0.213(\varphi_3 - \varphi_7) \\ &+ 0.104(\varphi_4 - \varphi_6),\end{aligned}$$

$$\begin{aligned}\psi_S(-1.765) &= 0.224(\varphi_9 + \varphi_8) \\ &+ 0.066(\varphi_2 + \varphi_1) - 0.241(\varphi_3 + \varphi_7) \\ &- 0.479(\varphi_4 + \varphi_6) - 0.562\varphi_5,\end{aligned}$$

$$\begin{aligned}\psi_A(-1.137) &= -0.289(\varphi_9 - \varphi_8) \\ &+ 0.061(\varphi_2 - \varphi_1) + 0.465(\varphi_3 - \varphi_7) \\ &+ 0.444(\varphi_4 - \varphi_6),\end{aligned}$$

$$\begin{aligned}\psi_S(-0.572) &= 0.437(\varphi_9 + \varphi_8) \\ &- 0.292(\varphi_2 + \varphi_1) - 0.359(\varphi_3 + \varphi_7) \\ &+ 0.105(\varphi_4 + \varphi_6) + 0.409\varphi_5,\end{aligned}$$

where the suffixes S and A denote the symmetry properties of the wave functions, and the number in the parentheses give $y_j = (\alpha - E_j)/\beta$,⁽¹³⁾ instead of E_j . The results for the ground state,

$$\begin{aligned}\psi_S^2(-2.773)\psi_A^2(-2.131)\psi_S^2(-1.765) \\ \times \psi_A^2(-1.137)\psi_S^2(-0.572)\end{aligned}$$

are given in the molecular diagram depicted in Fig. 1.

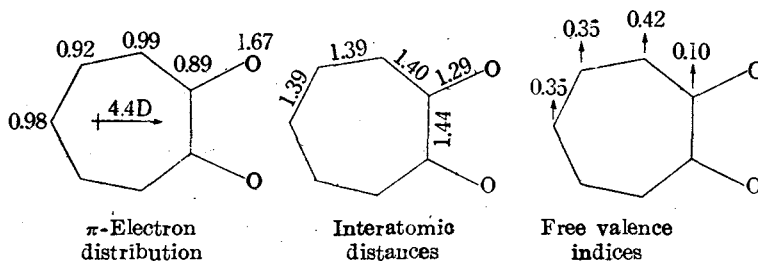


Fig. 1.—The molecular diagram of tropolone.

The direction and the magnitude of the dipole moment of tropolone have been determined in the previous paper⁽²⁾ and is shown in Fig. 2. The π -moment can be obtained by

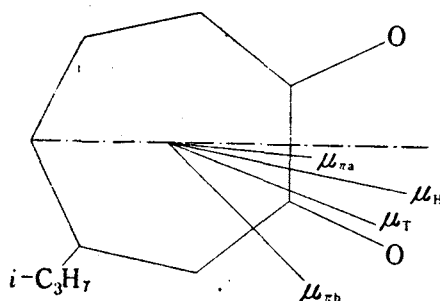


Fig. 2.—Dipole moment of tropolone: $\mu_H=4.04$ D, hinokitiol; $\mu_T=3.7$ D, tropolone; $\mu_{\pi a}=2.4$ D, $\mu_{\pi b}=3.3$ D, π -moment of tropolone.

subtracting two C-O bond moments ($\mu(\text{C-O})=0.86$ D), one O-H bond moment ($\mu(\text{O-H})=1.53$ D), and five C-H bond moments ($\mu(\text{C-H})=0.40$ D). The results is $\mu_{\pi a}=2.4$ D if hinokitiol is 4-isopropylcycloheptatriene-2,4,6-ol-2-one-1, or $\mu_{\pi b}=3.3$ D if the compound is isopropylcycloheptatrienol-1-one-2. The direction of the dipole moment $\mu_{\pi a}$ thus obtained is nearly coincident with the result of molecular orbital treatment. As regards its magnitude, the calculated value is still greater than the observed one. Further approximation will be necessary to reach perfect agreement.

All C-atoms in the ring have a mean number of π -electrons less than unity, indicating that π -electrons are displaced from the ring. The π -electron distribution suggests that electrophilic atoms and radicals will attack the C-atoms 7 (ortho'⁽¹⁴⁾), 3 (ortho) and 5 (para), the former two being more liable to be attacked than the latter. This justifies our assumption made in the previous paper that only C-atoms 7, 3 and 5 are to be considered for the position.

(13) Since β is negative, the lower the energy E_j is, the smaller the value of y_j .

(14) T. Nozoe, *Yakugaku*, **3**, 174 (1949).

of substituents such as a Br-atom or a nitro-group and that α -monobromohinokitiol is 7-bromohinokitiol.⁽¹⁵⁾ The free valence indices indicate that reagents of free radical type will react at C-atoms 7 and 3.

The total energy is found to be $10\alpha + 16.756\beta$, while that of the electronic state represented by an ordinary constitutional formula without taking into account the resonance effect is $10\alpha + 13.664\beta$. Hence resonance energy is 3.09β , as compared with 2β for benzene. This accounts for the aromatic character of tropolone-type molecules.

As has already been mentioned, it is almost certain from the theoretical considerations as well as from experimental results that in tropolone and its derivatives electrons are displaced away from the ring. It seems very probable that the same effect occurs in the case of other compounds with cycloheptatriene ring. In fact, Berthier and Pullman⁽¹⁶⁾ have carried out molecular orbital treatment on methylene-cycloheptatriene and calculated its dipole moment to be equal to 2.35 D with the positive end at the ring. It seems appropriate to mention in this connection that they studied also fulvene with a cyclopentadiene ring, and found a moment of 3 D with the negative end at the ring. In fact, these tendencies reveal

themselves in condensed rings as well as in the case of hyperconjugation. The characteristic electron distribution seems to be the cause of the peculiar properties of tropolone-type compounds in general.

Summary

The molecular orbital treatment was carried out on tropolone. The π -electron distribution, interatomic distances, free valence indices and dipole moment were derived. It was found that the dipole moment is very high (second approximation value of π -electron moment = 4.4 D) owing to resonance and lies along a line from the center of the ring to the middle point between two O-atoms with its positive end at the ring and that the resonance energy amounts to about 1.5 times that of benzene in general agreement with experimental results. It was shown that the substitution by electrophilic atoms and groups are most liable to occur at C-atoms 7, 3 and 5.

We wish to express our thanks to Prof. T. Nozoe of Tohoku University for his interest on this subject and many valuable discussions from organic chemical point of view. Our thanks are also due to the Ministry of Education in aid of this research.

(15) The position 3_o(ortho) will be more difficult to be attacked than 7 (ortho') owing to steric effect.

(16) G. Berthier and B. Pullman, *Bull. soc. chim. France*, 1949, D 467.

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Studies on Amino-hexoses. I. A New Method for Preparing Crystalline D-Arabinose

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The preparation of D-arabinose has been dependent on the methods of Ruff,⁽¹⁾ of Wohl-Zemplén⁽²⁾ or of Weermann⁽³⁾, all of which being consisted of degrading D-glucose.

The author took up D-glucosamine as a starting material which is much accessible in

this country. The author's aim was that D-glucosamine, a sort of α -amino-aldehyde, would undergo an oxidation analogous to the oxidation of α -amino-acids as exhibited by Dakin⁽⁴⁾ and Langheld⁽⁵⁾ who obtained aldehydes with one carbon atom less than the starting amino-acids. In fact, Herbst⁽⁶⁾ has oxidized glucosamine with chloramine-T (*p*-toluenesodium sulfonchloramide) and has

(1) O. Ruff, *Ber.*, **31**, 1573 (1898); R. C. Hockett and G. S. Hudson, *J. Am. Chem. Soc.*, **56**, 1632 (1934).

(2) G. Zemplén, *Ber.*, **59**, 1254 (1926); "Organic Syntheses" **20**, 14, 74.

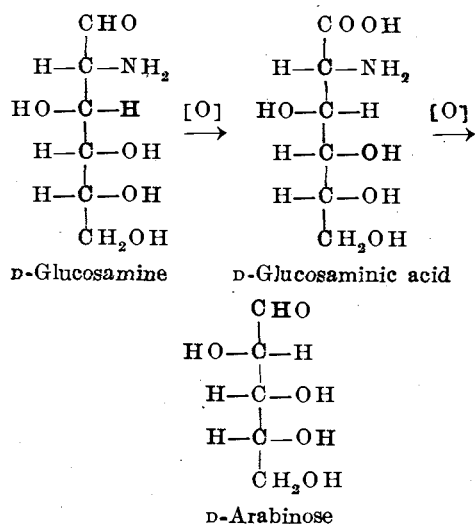
(3) R. A. Weermann, *Rec.*, **37**, 16 (1917); *C. A.*, **12**, 1453 (1918).

(4) H. D. Dakin, *J. Biol. Chem.*, **1**, 171 (1905).

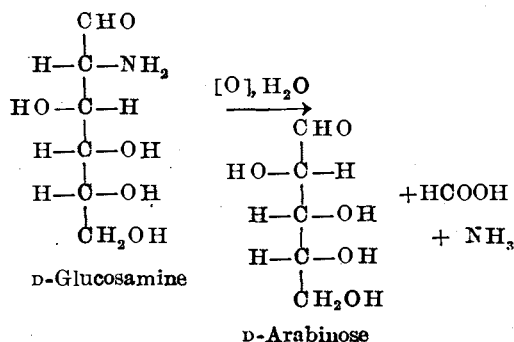
(5) K. Langheld, *Ber.*, **42**, 2380 (1909).

(6) R. M. Herbst, *J. Biol. Chem.*, **119**, 85 (1937).

obtained D-arabinose in the form of benzyl-phenylhydrazone in 20–40% yields. He concludes that the reaction proceeds as below from the fact that the intermediate product, glucosaminic acid, is also oxidized by chloramine-T giving D-arabinose in about 40% yield



The author oxidized D-glucosamine with sodium hypochlorite, the amount of which at first being two oxygen-equivalents, assuming that the reaction would proceed as above. Were the mentioned reaction scheme correct, the first carbon atom of glucosaminic acid should be liberated as carbonic acid. But the fact is that D-arabinose is produced in about 30% yield without liberating any carbonic acid. Then, one must conclude that the reaction formulae described above does not represent the fact and a reasonable interpretation of the reaction may be that glucosamine decomposes into arabinose, formic acid and ammonia with one oxygen-equivalent of the oxidant and water as represented below:



The author's interpretation was confirmed by the experiment in which D-glucosamine was

oxidized with one oxygen-equivalent of hypochlorite under ice-water cooling, where D-arabinose-diphenylhydrazone was isolated in a yield above 70% to the theoretical amount. Furthermore, the production of formic acid was confirmed by its reducing action on mercuric chloride and by the analysis of the calcium salt. The application of the method of sugar analysis proposed by Moore and Link⁽⁷⁾ revealed also the production of D-arabinose in a yield as high as 75% theoretically. The good yield of the reaction enabled the author to isolate directly crystalline D-arabinose, the yield of the specimen melting at above 150° being round 20% and in the most favourable case 27% yield was secured.

From the results mentioned above it is concluded that glucosamine exhibits a novel type of reaction when oxidized with hypochlorite. It may be worth trying to ascertain that other aminoaldehydes, a type of compound not so familiar to us, have the same character with glucosamine. To this purpose the author took up chondrosamine, a naturally occurring aminoaldehyde, as an example from which it is expected that D-lyxose is formed. The author treated chondrosamine with hypochlorite equivalent to one atom oxygen in the like manner as glucosamine and obtained D-lyxose as its *p*-bromophenylhydrazone in a yield of 21% to the theory. The formation of formic acid was also confirmed. The low yield of the *p*-bromophenylhydrazone in comparison with the D-arabinose derivative from glucosamine may be due to the incompleteness of the combination of lyxose and *p*-bromophenylhydrazine.

Experimental Part

Preparation of Glucosamine Hydrochloride.—3 kg. raw dried crab shell is immersed in 20 l. of 2*N*-hydrochloric acid for 3 days with occasional agitation. After washing and drying 1.1 kg. decalcified material is obtained. 500 g. of this material is thrown into 1.5 l. of hydrochloric acid (about 30%) and is heated on a boiling water-bath for 5 hours. To this hydrolysate 1.5 l. water is added and the solution is filtered through Buchner's funnel. The filtrate is concentrated *in vacuo* to about one third of its volume and is placed in a cold room. The colored raw crystals of glucosamine hydrochloride separate and are filtered without washing. The raw crystals are dissolved in as little hot water as possible and are treated with charcoal. The decolorized filtrate is concentrated *in vacuo* until considerable amount of crystals separate which are filtered and washed with a small amount of cold water. The twice

(7) S. Moore and K. P. Link, *J. Biol. Chem.*, **133**, 293 (1940).

repetition of decolorization and concentration of the mother liquor enables above 80% of the raw crystals to be obtained in practically pure state. The yield is 150 g., $[\alpha]_D^{25}$ (final), $+70.15^\circ$.

Oxidation of Glucosamine with Hypochlorite Equivalent to One Atom Oxygen. (a) **Isolation of D-Arabinose as its Diphenylhydrazone.**—5 g. D-glucosamine hydrochloride is dissolved in 200 cc. water and under ice-water cooling and mechanical stirring the solution of 1 g. sodium hydroxide is added. To this, the solution of sodium hypochlorite is added dropwise at the reaction temperatures below 8° . The oxidation takes place very fast and the reaction is almost completely finished as soon as the oxidant is added. The reaction mixture is neutralized with dilute hydrochloric acid to a weak acid reaction and concentrated *in vacuo* at the temperatures below 40° . The syrup thus obtained is filtered from inorganic salts which have separated during the concentration and the salts are washed with 80% alcohol. A definite portion of the alcoholic solution thus obtained is treated with the alcoholic solution of diphenylhydrazine and the diphenylhydrazone formed of D-arabinose is filtered after over-night standing and washed with 50% alcohol. The crystals melt at $197-198^\circ$ with decomposition, the yield of which is 73% theoretically to starting D-glucosamine. Recrystallization from alcohol raises the melting point to $198-200^\circ$ and no melting point depression is observed when mixed with the authentic specimen. Analyses give the following results:

Found: C, 64.88; H, 6.55; N, 8.44.

Calcd. for $C_{17}H_{20}O_4N_2$:

C, 64.54; H, 6.37; N, 8.86.

(b) **Analysis of the Oxidation Mixture by the Method of Moore and Link⁽⁷⁾.**—Using 22.6 g. glucosamine hydrochloride the oxidation is carried out as above. The syrupy product separated from most of the inorganic salts is dissolved in 140 cc. of methanol of which 70 cc. is taken for analysis: 26 g. iodine in 370 cc. methanol is combined with the above methanolic solution of sugar and to this mixture 4% methanolic solution of potassium hydroxide is added dropwise under stirring at 40° until the color of iodine is extinguished. After standing overnight at room temperatures the fine crystals which have separated are collected and washed with methanol. Potassium arabinonate thus obtained melts at $210-212^\circ$ with decomposition and weighs 6.6 g. which corresponds to 62% of theoretical amount to the starting aminosugar. It has a specific rotation $[\alpha]_D^{25} = -6.3^\circ$. The melting point and the specific rotation given in the literature⁽⁷⁾ for the L-isomer is 211° and $[\alpha]_D^{25} + 4.5^\circ$ respectively.

1 g. of potassium arabinonate is condensed with o-phenylene-diamine and 0.9 g. arabo-benzimidazole melting at 235° with decomposition is obtained. After recrystallization from 50% alcohol the specimen melts at $237-237.5^\circ$ and

shows no melting point depression when mixed with authentic specimen. The specific rotation $[\alpha]_D^{25}$ is -48.8° in 5% citric acid solution, while $[\alpha]_D^{25}$ given in the literature⁽⁷⁾ for the L-isomer is $+49.2^\circ$. Analysis gives the following results;

Found: C, 55.14; H, 6.00; N, 11.75.

Calcd. for $C_{11}H_{14}O_4N_2$:

C, 55.45; H, 5.92; N, 11.76.

The calculation from the yield of potassium arabinonate shows a 75% yield of D-arabinose when one takes account of the empirical factor given in the literature⁽⁷⁾.

The distillate of the acidified oxidation mixture gives calcium formate when treated with calcium carbonate in the usual way. The calcium salt in hydrochloric acid solution reduces mercuric chloride to insoluble mercurous chloride and its calcium content is 30.48% while the theoretical value is 30.80%.

Preparation of Crystalline D-Arabinose.—21.6 g. glucosamine hydrochloride dissolved in 100 cc. of water is placed with 200 g. of cracked ice in a beaker surrounded by ice-water. The mixture is then added with 4 g. of sodium hydroxide dissolved in 20 cc. water. Sodium hypochlorite solution (which is prepared by dissolving 7.1 g. of chlorine in a ice-cold solution of 20 g. sodium hydroxide dissolved in 50 cc. water) is run in immediately from the separating funnel under good mechanical stirring. The reaction proceeds smoothly at -3° . After consumption of the oxidant the reaction mixture is neutralized with 6N-hydrochloric acid to pH 3, and is as far concentrated as possible *in vacuo* at the bath temperature below 45° . The syrup thus obtained is filtered from the considerable amount of inorganic salts and the latter is washed with as little methanol as possible. The methanolic solution of the sugar is again concentrated *in vacuo* and the small amount of salts which have deposited is filtered off. The brown colored thick syrup thus obtained is added with 40 cc. of glacial acetic acid and put in an ice-box. Crystallization takes place shortly. After letting it stand for 2 days the crystal cake is filtered and washed completely with glacial acetic acid. The almost colorless crystals thus obtained weigh 6.7 g. and melt at $127-129^\circ$. The raw crystals are dissolved in 4.3 cc. of hot water and then added with 25 cc. of methanol, treated with charcoal, and after seeding put in an ice-box for 2 days. 4.0 g. of D-arabinose melting at $150-151^\circ$ is obtained which is quite free from chlorine ion.

The recrystallized specimen which melts at $155-156^\circ$ has the specific rotation -103.0° (final) and the following composition:

Found: C, 39.84; H, 7.16.

Calcd. for $C_5H_{10}O_5$: C, 40.00; H, 6.71.

Oxidation of Chondrosamine to D-Lyxose.—Chondrosamine was prepared from the cartilage of shark or from bovine trachea through

chondroitin-sulfuric acid following the methods of Kondo⁽⁸⁾, or Fuerth, Bruno, Boyer and Peschek⁽⁹⁾ and Levene and La Forge⁽¹⁰⁾. Chondrosamine hydrochloride obtained was not quite pure though it was a colorless fine crystal.

4.8 g. chondrosamine hydrochloride is dissolved in 100 cc. water and under ice-water cooling and mechanical stirring, 17 cc. of *N*-sodium hydroxide is added. 18 cc. of sodium hypochlorite which is equivalent to one atom oxygen is dropped within the next 10 minutes. After 30 minutes more the reaction mixture is slightly acidified with dilute hydrochloric acid and evaporated *in vacuo* at the temperature below 40°. The distillate contains formic acid. The syrup is freed from inorganic salts and condensed with *p*-bromophenylhydrazine.

The water solution of the syrup is mixed with the alcoholic solution of *p*-bromophenylhydrazine and a small amount of precipitate which is inorganic salts is filtered off after over-night standing. A thick syrup which is obtained by concentrating the filtrate *in vacuo* becomes crystalline when seeded. After letting at stand over-night the crystals are filtered and washed with water to be freed from a syrupy matter. The orange-yellowish crystals thus obtained melt at 148–151° and weigh 1.1 g.

0.5 g. of raw crystals is recrystallized from 30% alcohol. Slightly yellowish needles thus obtained

weigh 0.4 g. and melt at 154–155° and show no melting point depression when mixed with the *p*-bromophenylhydrazone of D-lyxose which is prepared from calcium D-galactonate by the Ruff-degradation. Analyses give the following results:

Found: C, 41.01; H, 4.78; N, 8.43.

Calcd. for $C_{11}H_{15}O_4N_2Br$:

C, 41.39; H, 4.74; N, 8.78.

$[\alpha]_D^{25}$ in pyridine in as follows:

Time after solution	$[\alpha]_D^{25}$	$[\alpha]_D$ in the literature ⁽¹¹⁾
10 min.		+31.8°
15	+33.9°	
60	+27.9	
24 hrs.	+ 9.97	+ 7.8
48		+ 7.8

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(8) K. Kondo *Biochem. Z.*, **26**, 116 (1910).

(9) O. Fuerth, T. Bruno, R. Boyer and K. Peschek, *Biochem. Z.*, **294**, 183 (1937).

(10) P. A. Levene and La Forge *J. Biol. Chem.*, **18**, 123 (1914).

(11) P. A. Levene and La Forge, *J. Biol. Chem.*, **18**, 325 (1914).

Conductometric Titration of Cation Exchange Resins

By Tunetaka SASAKI and Ayako INABA

(Received September 25, 1950)

Introduction

There have been various methods to determine the exchange capacities of exchangers, for example, the analysis of the supernatant obtained from the salt solution added in large excess to exchanger⁽¹⁾ or the analysis of the effluent of salt solution coming from a column of exchanger.⁽²⁾⁽³⁾ But these methods give no

information about the exchange tendency or dissociation degree of exchange groups. The potentiometric method⁽⁴⁾⁽⁵⁾⁽⁶⁾⁽⁷⁾ and some other means⁽⁸⁾ have also been reported for the determination of the above mentioned quantities. But these are often complex in procedure

(1) H. Jenny, *Kolloid-Beihfte*, **23**, 428 (1939).
(2) R. J. Myers, J. W. Eastes and F. J. Myers, *J. Ind. Eng. Chem.*, **33**, 697 (1941).
(3) R. J. Myers and J. W. Eastes, *J. Ind. Eng. Chem.*, **33**, 1206 (1941).

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(5) H. P. Gregor and J. I. Bregman, *J. Am. Chem. Soc.*, **70**, 2870 (1948).
(6) E. G. Cassidy, *J. Am. Chem. Soc.*, **71**, 402 (1949).
(7) L. H. Undergraft and E. G. Cassidy, *J. Am. Chem. Soc.*, **71**, 407 (1949).
(8) E. Heyman and L. J. O'Donnell, *J. Colloid Science*, **4**, 395 (1949).

and the detailed experimental results have not been available for discussion.

The present paper deals with the relatively simple method of conductometry and also with the analysis of its results for the determination of both exchange capacity and tendency of resins.

Experimental

Sample.—The resins used included: (A) Dowex 50; (B) phenoxyacetic acid-formaldehyde; (C) Amberlite IR-C 50; (D) hydroquinone-formaldehyde; (E) phenolsulfonic acid-formaldehyde; (F) sulfonated coal. In these resins each of (A), (B), (C) and (D) had only one kind of exchange group, namely (A) had SO_3H group, (B) and (C) COOH , and (D) phenolic OH . (E) had two kinds of groups, SO_3H and OH , and (F) was supposed to have more than two kinds of groups. (A), (C) and (E) were commercial products and the others were prepared as follows. (B) was prepared by condensation of phenoxyacetic acid and formaldehyde with hydrochloric acid as catalyst, and (D) by condensation of hydroquinone and formaldehyde with sodium hydroxide as catalyst with the subsequent promotion of the polymerization by heating in each case. (F) was prepared from bituminous coal of Takashima coal mine by treating with hot mixture of conc. sulfuric acid and potassium bichromate with a trace of mercuric sulfate as catalyst. These resins were used as grains of 48–100 mesh size excepting (C) of 20–30 mesh which condition was adopted because this resin was easily ground into very minute particles unsuitable for our purpose. The resins were converted into H-form by rinsing with 2 *N* sulfuric acid solution before using.

Titration.—From one to five g. of swollen resin and 50 cc. of conductivity water were introduced in a 200cc. glass vessel and the whole mixture were titrated with 0.5 *N* sodium hydroxide solution conductometrically. In this process, sodium hydroxide solution was gradually added, one cc. at each time, with constant stirring and conductivity of the supernatant was determined after each addition under the equilibrium condition. Time required to attain the equilibrium was about 5–10 min., although in the case of some resins it became as long as 30 min. in the final stage of titration. To avoid the effect of carbon dioxide, air free from it and saturated with water vapor was passed through the solution during the titration. Moreover suitable corrections were made when the case required.

Results and Discussion

(1) Results of measurements for (A), (B) and (C) resins were shown in Fig. 1. Here x was the adsorption value in terms of equivalent of sodium ion per 1000 cc. swollen resin and u was the equilibrium concentration of solution in terms of equivalent of sodium ion

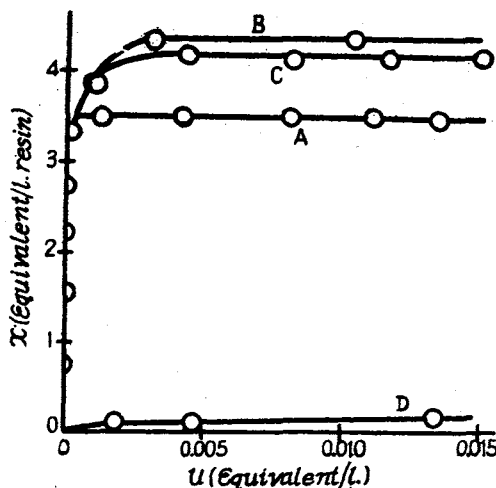


Fig. 1.—Exchange adsorption of NaOH by Dowex 50 (A), phenoxy. resin (B), Amberlite IR-C 50 (C), and hydroquinone resin (D).

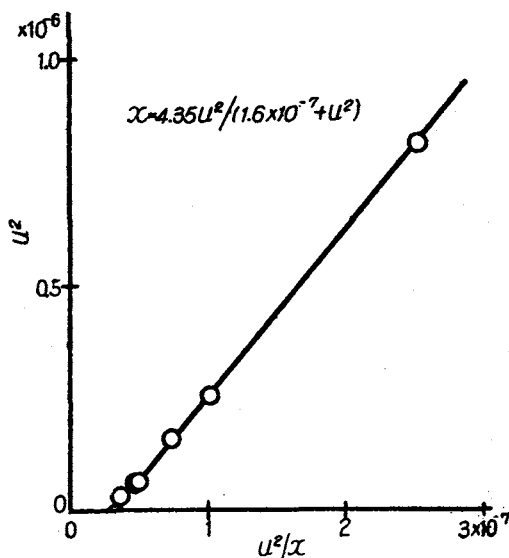
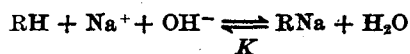


Fig. 2.—Exchange equilibrium for (B) resin.

remaining in 1000 cc. of solution together with resin.

Generally, when the cation exchanger in H-form is treated with sodium hydroxide solution, the equilibrium



is established. Here RH and RNa represent the exchanger in H-form and Na-form respectively, and K denotes an equilibrium constant. In this case if mass action law is applicable, the relation

$$[\text{RH}][\text{Na}^+][\text{OH}^-]/[\text{RNa}] = K$$

is obtained. [] represents the concentration of the substance inscribed. This relation is expressed in the terms of u and x as follows:

$$x = au^2/(K + u^2) \text{ or } u^2 = au^2/x - K \quad (1)$$

Here a denotes a maximum adsorption value. Using the data for (B) resin, u^2 and u^2/x were calculated. A fairly linear relation was obtained between them (Fig. 2). In the cases of (A) and (C) resins, similar relations were obtained. From these relations constant a and K were calculated (Table 1). Theoretical curves cor-

Table 1

Resin	Exchange groups					
	OH		COOH		SO ₃ H	
	k	a	K	a	K	
		eq./l.	eq. ² /l. ²	eq./l.	eq. ² /l. ²	
Amb. IR-C 50		4.22	2.4×10^{-6}			
Phenox. resin		4.35	1.6×10^{-7}			
Dowex 50				3.51	1.2×10^{-11}	
Hydroquinone resin	α	1.7				
Ph. sulf. resin	27			1.34	2.0×10^{-9}	
Sulf. coal	51.5	0.27	3.5×10^{-6}	0.75	1.0×10^{-9}	

responding to the equation (1) were drawn using these a and K values (solid lines in Fig. 1), which showed good coincidence with the experimental results. Thus the adsorption isotherm (1) was considered to be sufficient to account for the results obtained. According to such a reasoning, the exchanger can conveniently be characterized by two factors, namely, a , the exchange capacity and K , the exchange tendency as has been generally accepted.^{(4) (9) (10)} In fact, the value of K for (A) resin having SO₃H group is an order of 10^{-11} , while the values are $10^{-7} \sim 10^{-8}$ for (B) and (C) resins both having only COOH group. From these results it is concluded that SO₃H group has a stronger exchange tendency than that of COOH group, which is of course in accord with results obtained by others.^{(4) (5)} Fluctuation of the value of K for (B) and (C) resins, both having COOH group, may be ascribed to the difference in molecular structure and degree of gelation of these resins.

(2) Results obtained for (D) resin was shown in Fig. 1. $u^2 \sim u^2/x$ curve is linear excepting in the region of small u value. In this connection it is worth while to refer to phenol formaldehyde resin. Novolack resin which was prepared by condensation using acid catalyst and showed low polymerization degree, was soluble in alkaline solution and so it was of no use as an exchanger, while a resin such as Bakelite which was prepared by alkaline catalyst, and which showed high polymerization degree, was insoluble in alkaline solution, but it was again useless as an exchanger because of its no exchange capacity. We can however, expect the existence of the phenol formaldehyde resin having intermediate properties of being insoluble and showing weak exchange tendency. Considering from the results of such a phenol resin and (D) resin, it may be said that OH group of the resin generally shows very weak function, giving large value of K . The value of K may also suffer fluctuation due to the variety in molecular structure of the resin. Such a weak adsorption can conveniently be expressed by $x' = ku$ as shown in gradual increase in x' in the region of large u value in Fig. 1, though the equation (1) rather gives $x = ku^2$ in the case of $K \gg u^2$. It must be noted that the case may not be a mere adsorption, but for the present purpose this is not a matter of importance as the equation $x' = ku$ is sufficient to characterize the behavior of phenolic OH group of the resin.

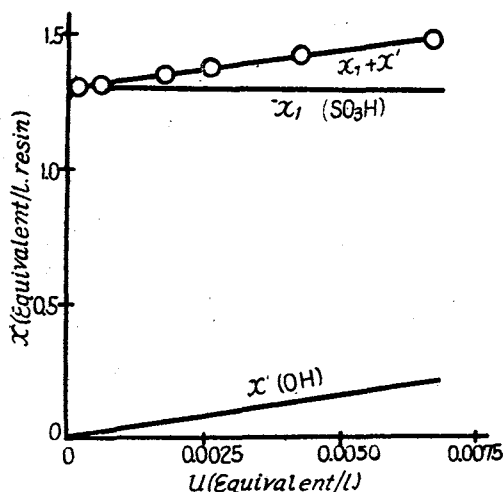


Fig. 3.—Exchange adsorption by phenolsulfonic acid formaldehyde resin (E).

(3) The results of experiments for (E) resin was shown in Fig. 3 (marked with O). This

(4) M. Honda, *J. Japanese Chem.*, **2**, 386 (1948).

(10) G. E. Boyd, J. Schubert and A. W. Adamson, *J. Am. Chem. Soc.*, **69**, 2818 (1947).

adsorption curve shows steep inclination in the small u region with subsequent and abrupt change in direction which can be interpreted as an existence of a strong exchange group perhaps of SO_3H . After the sudden change in direction, the amount of adsorption still increases gradually and linearly with equilibrium concentration. This gradual increase may be ascribed to the existence of OH group, for which the above equation $x' = ku$ ($k=27$) may be given. Then, the remaining part of adsorption, $x-x'$ may be ascribed to SO_3H group and for this part the value of a and K were determined by the similar method as mentioned above (Table 1). The theoretical curves thus obtained for SO_3H and OH were shown in Fig. 3 (x_1 and x' respectively), the resultant curve ($x_1 + x'$) of which fairly coincide with experimental results. It can be concluded from such an analysis of the experimental results, that the (E) resin contains two kinds of exchange groups and no more group of any kind is necessary for the explanation. The value of K for SO_3H of this resin is hundred times greater than that of (A) resin, which is again explained by the difference in structure between these resins as in the case of COOH . We can, however, make clear distinction in order of magnitude of K between SO_3H and COOH .

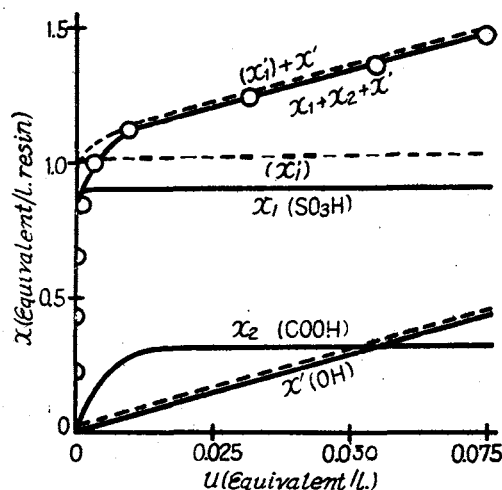


Fig. 4.—Exchange adsorption by sulfonated coal (F).

(4) The results obtained for sulfonated coal (denoted by $\circ$ in Fig. 4) also showed linear increase in adsorption in the region of large equilibrium concentration. From the linear part of this curve we obtained $x' = ku$ ($k=51.5$) for phenolic OH group. Using this value of k , the values of x' and $x-x'$ accordingly were

calculated for each concentration. We then attempted to explain this remainder part by supposing only one kind of exchange group. From the values of a and K thus obtained, and also from k for OH group, two adsorption curves (x_1 and x' respectively) were drawn, the resultant ($x_1 + x'$) of which however did not coincide so well with the experimental results (Fig. 4). Therefore it was considered that at least two kinds of exchange groups other than OH took part in this case. Then, from the initial part of $u^2 \sim u^2/(x-x')$ plot, the constants a_1 and K_1 for stronger group were obtained (Table 1). Using these constants the corresponding adsorption amounts x_1 were calculated by equation (1) and from $u^2 \sim u^2/(x-x'-x_1)$ plot, the constants a_2 and K_2 for another exchange group were determined (Table 1). The adsorption amount (x_2) due to the latter group, was also calculated using a_2 and K_2 , and plotted together with x_1 against u (Fig. 4). The resultant $x_1 + x_2 + x'$ thus obtained plotted against u closely coincided with the experimental results. From such a reasoning it can be concluded that sulfonated coal has two different types of exchange groups in addition to phenolic OH group. These two groups are supposed to be SO_3H and COOH , when we consider the facts that the constant K_1 and K_2 measured fall in the region of the order of magnitude of K estimated in the earlier part of this paper for such exchange groups mentioned.

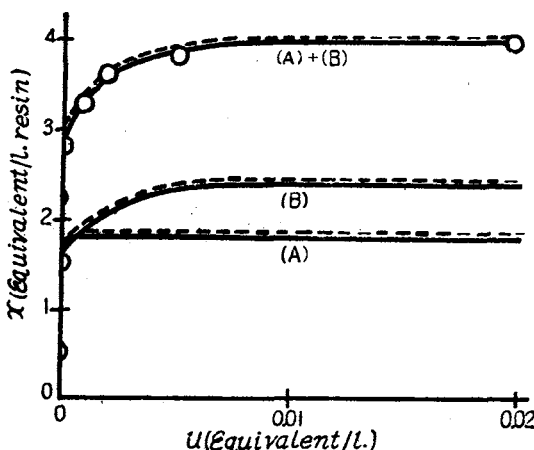


Fig. 5.—Exchange adsorption by a mixture of (A) and (B) resins.

(5) The results of measurement for (A) and (B) resins were shown in Fig. 5. The sum (solid line (A)+(B)) of the each adsorption amount of the two resins (solid lines (A) and (B)) calculated from the constants a and K

Table 2

Exchange Equilibrium Constant of a Mixture of Dowex 50 and Phenoxo. Resin

	Values calcd. from the separate determination	Values calcd. by the analysis of the results for mixed resin
Phenoxo. resin (COOH)	$\alpha = 2.18$ eq./l. $K = 1.6 \times 10^{-7}$ eq. ² /l. ²	$\alpha = 2.39$ $K = 1.0 \times 10^{-7}$
Dowex 50 (SO ₃ H)	$\alpha = 1.75$ $K = 1.2 \times 10^{-11}$	$\alpha = 1.76$ $K = 3.2 \times 10^{-11}$

which were previously determined by the separate measurement, agreed well with the experimental results (indicated by circles) for their mixture. The values of α and K obtained by the analysis of the experimental results for the resin mixture and the adsorption curves corresponding to them (dotted lines in Fig. 5) also coincided well with those obtained by the separate determination. These circumstances have some bearing upon the fundamental assumption in the present experiment that the total exchange capacity of an exchanger is the sum of the exchange capacities of each component exchange groups, although the lack of similarity between mechanical mixture of two different types of resins and the mixture of two different exchange groups in molecular scale, still leaves some questions behind.

(6) Finally, we should like further to note a few points. It is inevitable that the basic assumption made for the derivation of equation (1), namely, the substitution of the analytical concentration of sodium hydroxide, which was determined directly from conductometry in this experiment, for the concentrations of Na⁺ and OH⁻, introduces considerable error in the dilute region of sodium hydroxide. From this point, direct potentiometric determination of OH⁻ concentration is rather desirable. However, this paper emphasizes the applicability of the simple conductometric method generally applied to the solution of a larger concentration.

Consideration of activity in place of concentration is neglected for simplicity, which must be taken into account for precise discussion.

It has been reported that the dissociation constant of polymer electrolyte should be very complex in character,⁽¹¹⁾ however, the existence of the mean dissociation constant might still be considered. With the change in molecular structure and the degree of gelation of the resin, mutual effects of exchange groups are affected and the dissociation constant of the groups or the equilibrium constant K fluctuates. However, the fluctuation due to these factors is small compared with that due to the variation in exchange groups. The exchange group can therefore be identified by the value of K .

Summary

Cation exchange resins in H-form each having only one kind of exchange group were titrated with sodium hydroxide solution conductometrically. The results were analysed, and exchange capacity and tendency of each exchange group were determined. A mixture of two resins, each having one kind of exchange group was titrated. The analysis of the results gave adsorption values which agree well with that expected from the determination for the separate resin. From the titration results for more complex cation exchange resins the number of the sorts of exchange groups was estimated and each group was identified.

The cost of this research has been defrayed from the Grant in Aid for Publishing Research Results of the Ministry of Education, to which the authors' thanks are due.

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(11) I. Kigawa and K. Tsumura, *J. Soc. Chem. Ind., Japan*, 47, 463, 574 (1944).

Etudes spectroscopiques des complexes métalliques du diphénylthiocarbazone. II⁽¹⁾

Par Seinosuké MIYAKAWA et Taku UÉMURA

(Reçu le 14 octobre, 1950)

Introduction

Nous avons déjà publié sur les recherches des spectres d'absorption des complexes du diphénylthiocarbazone (dithizone) formés avec l'argent, le cuivre, le zinc, le cadmium, le plomb et le bismuth dans notre mémoire précédent⁽²⁾. Le présent compte-rendu inclut une méthode spectrochimique pour déterminer les structures des complexes du dithizone formés avec le cobalt, le nickel et l'or. Le mécanisme d'absorption lumineuse par le dithizone est aussi expliqué dans la publication actuelle.

Procédé expérimental

Nous avons appliqué "la méthode de variation continue" présentée par P. Job⁽³⁾ pour déterminer la constitution chimique des complexes du diphénylthiocarbazone. En changeant un peu seulement à la fois la quantité d'ion métallique qui forme le complexe, nous pouvons l'extraire avec la quantité définie de la solution normale du dithizone dissous dans le tétrachlorure de carbone et séparer le mélange du complexe dissous avec le dithizone non réactif de la couche aqueuse. Pour mesurer, à ce moment, l'absorption en utilisant une longueur d'onde spéciale, nous avons à choisir la longueur d'onde qui peut donner la variation maxima par la formation du complexe. Au cas du dithizone, sa première bande d'absorption ($\lambda = 620 \text{ m}\mu$), la longueur d'onde qui montre le pouvoir absorbant minimum donné par le point du fond dans la courbe d'absorption et la bande d'absorption produite par le complexe nouvellement formé ont été choisies.

Les réactifs et les dissolvants qui sont utilisés à nos expériences ont été purifiés par les indications déjà montrées dans notre publication précédente. Les sels métalliques employés pour la préparation des complexes sont les trois suivants: sulfate de cobalt dérivé du carbonate de cobalt (marque allemande "Kahlbaum"), acétate de nickel (marque "Kahlbaum") et chloro-aurate de sodium purifié obtenu par la dissolution le fil

d'or pur dans l'eau régale. Nous avons préparé la solution aqueuse acide du sel cobaltique et celui du nickel, tous les deux tamponnés par l'acide acétique et l'acétate de sodium en donnant $\text{pH} = 6.0$. Nous étions encore prêts pour la solution aqueuse neutre du sel aurique. Nous nous sommes servis du spectrophotomètre Nutting construit par Hilger et de celui du modèle Spekker et du spectrographe en quartz "type QF-60" construits par Shimazu pour la mesure des bandes d'absorption. Dans nos études actuelles, la concentration du dithizone était $6.28 \times 10^{-5} \text{ mol/l}$ et la longueur du tube d'absorption, 1 cm.

Spectres d'absorption

Nous avons montré dans la Fig. 1 les courbes d'absorption dans la région visible produite par les complexes du dithizone et des résultats numériques dans la table suivante.

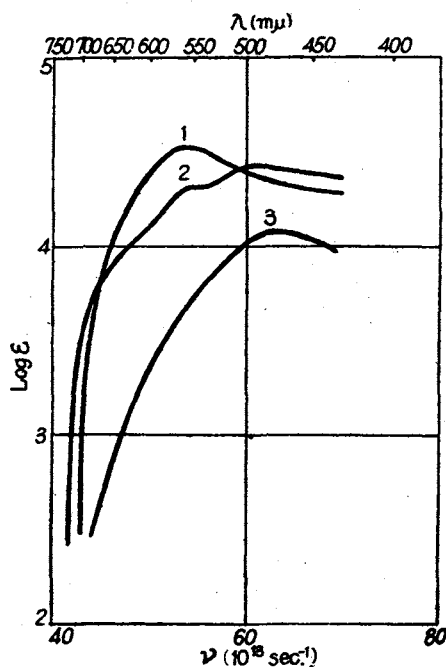


Fig. 1.—Absorption des complexes.
1, CoD_2 ; 2, NiD_2 ; 3, AuD .

La Fig. 2 nous expose la variation des extinctions quand les complexes se forment.

(1) Exposé fait lors de la Séance de Tokai-shibu (Nagoya) de la Société chimique du Japon, le 13 novembre, 1949.

(2) T. Uémura et S. Miyakawa, *Bull. Chem. Soc. Japan*, **22**, 115 (1949).

(3) P. Job, *Ann. chim.*, [10], **9**, 113 (1928).

Table

Absorption lumineuse par le dithizone et ses complexes métalliques

Formule chimique	λ , m μ	ν , sec. ⁻¹	ϵ
D	620	51.0×10^{13}	3.05×10^4
CoD ₂	560	53.5	3.52
NiD ₂	480	61.3	2.76
AuD	486	62.5	1.24

ϵ = des coefficients d'extinction moléculaire
D = dithizone λ = longueur d'onde
 ν = fréquence

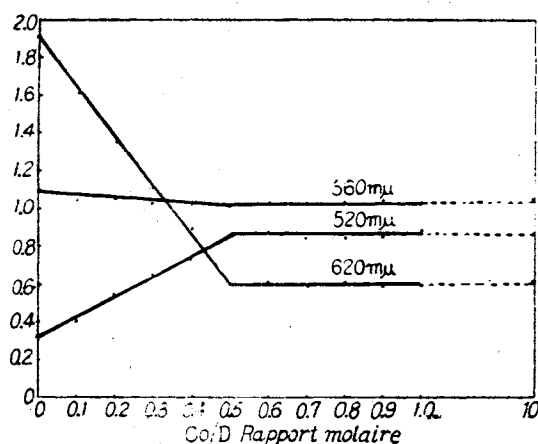


Fig. 2.

Nous mettons l'extinction en axe des ordonnées, et en abscisse le rapport de concentration molaire du dithizone contre la quantité de cobalt dans la solution aqueuse. Les trois lignes dans la Fig. 2 présentent respectivement les longueurs d'onde 620 m μ , 520 m μ et 560 m μ que comporte chaque extinction.

L'absorption maxima du dithizone à 620 m μ diminue graduellement par la formation de complexe et son extinction se trouve invariablement au-dessus du rapport molaire 0.5. Le pouvoir absorbant minimum du dithizone à 520 m μ augmente peu à peu et ne change plus de 0.5. L'extinction de bande à 560 m μ est à peu près égale à celle du dithizone lui-même et, dans ce cas, il est très difficile de trouver sa variation. En augmentant la quantité de cobalt, on fait la réaction entre le dithizone et ce métal et on arrive au rapport Co:D = 1:2, la formation du complexe se complète et par conséquent sa composition doit être CoD₂.

La Fig. 3 donne la courbe de réaction entre le dithizone et le nickel. On peut semblablement assigner NiD₂ au sel complexe du nickel. La réaction entre le sel aurique et le dithizone exposée dans la Fig. 4 montre une apparence

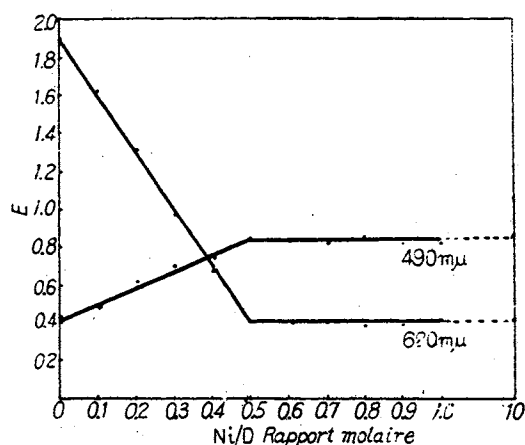


Fig. 3.

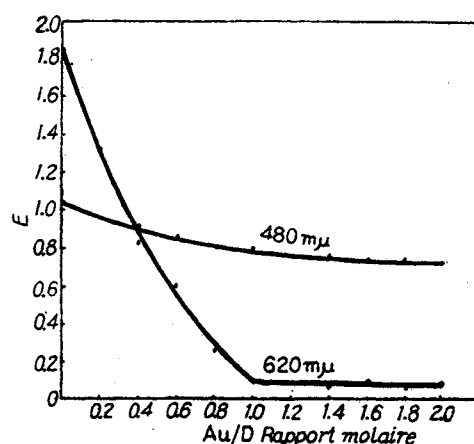


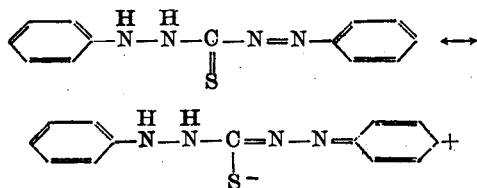
Fig. 4.

différente des deux cas précédents. La bande d'absorption du dithizone à 620 m μ diminue rapidement par l'augmentation de la quantité d'or qui indique la valeur définie minima au-dessus du rapport 1. La bande d'absorption du complexe aurique à 480 m μ nous montre, au contraire, une tendance à diminuer au rapport au-dessus de 1, et elle n'a pas de point de détournement très clair. Cela nous explique que le AuD formé se change partiellement lorsque le sel aurique augmente. Dans le cas de la formation de AuD₃, le point de détournement assez clair doit se trouver au moins à une des deux courbes dans la Fig. 4 à l'endroit rapport molaire 0.33. La décomposition de AuD est donc due à employer une partie de dithizone en dehors de la formation du complexe lorsque le sel aurique est oxydé en sel aurique.

Mécanisme d'absorption lumineuse par le dithizone

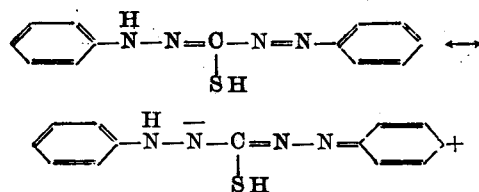
Le dithizone cétonique a une bande d'absorp-

tion très intense en région de longueur d'onde élevée (620 $m\mu$) et cette bande déplace en longueur d'onde plus courte en formant le complexe, ce que nous avons déjà exposé dans notre mémoire précédent.⁽²⁾ Nous supposons que cette bande intense se produit à cause de la liaison $S = C <$, où le soufre est considérablement électro-négatif et a une relation intime avec la résonance suivante.



En formant le complexe, deux électrons émis de l'atome d'azote qui se trouve dans le radical azoïque, voisin de celui benzène, s'entremêlent dans la liaison de coordination et la migration de charge électrique indiquée se contrarie. Dans ce cas, la résonance déjà montrée s'affaiblit et la première bande d'absorption du dithizone subira peut-être l'effet hypsochromique. Quant au type énolique, l'effet du soufre contre l'atome du carbone central diminue, et le type dipolaire (constitu-

tion droite dans la résonance suivante) exigera probablement une énergie plus élevée.



Par cette raison, on peut prévoir que la première bande d'absorption du composé énolique est remarquablement hypsochromique en comparant celle du type cétonique.

Résumé

(1) Nous avons trouvé les constitutions complexes métalliques (Ni, Co et Au) du dithizone par le procédé spectrochimique.

(2) La première bande d'absorption du dithizone subit l'effet hypsochromique par la formation du complexe ou la production d'isomère énolique. Nous avons expliqué ce résultat expérimental par la constitution résonante.

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The Wet Oxidation and the Structure of Carbon

By Hideo AKAMATU, Hiroshi TAKAHASHI and Kenzi TAMABU

(Received on November 18, 1950)

Introduction

In recent years, the view that the so-called amorphous carbon consists of minute crystallites of graphite has been modified⁽¹⁾ in the strict sense of the word. Most kinds of carbon give the characteristic X-ray powder photographs known as "carbon pattern." This shows that the molecular structure of carbon is made of a layer plane of condensed aromatic rings. However, it is thought that the plane

molecules do not arrange themselves in a regular manner as in graphite, namely, it is thought that they are paralleled to each other in layers equally spaced along the *c* axis, but are otherwise disordered along the *a* and *b* axis. Thus, the true three-dimensional atomic lattice as in graphite is not built up in amorphous carbon. Such a structure is called by the term of "turbostratic."

Associating with physico-chemical properties of carbon, measurements of the sizes of their crystallites have been carried out by the X-ray examination. The dimension of the crystallite is the order of 10 ~ 60 Å. along the *a* axis, and 10 ~ 40 Å. along the *c* axis, for most industrial carbon. Now, there remains a problem which must be investigated hereafter;

(1) U. Hofmann and D. Wilm, *Z. Elektrochem.*, **42**, 504 (1936); A. H. White and L. H. Germer, *J. Chem. Phys.*, **9**, 492 (1941); J. Bischoe and B. E. Warren, *J. Appl. Phys.*, **13**, 364 (1942); H. Akamatu, *J. Chem. Soc. Japan*, **64**, 1251 (1943); H. Akamatu and K. Nagamatsu, *J. Colloid Science*, **2**, 593 (1947).

that is, in what manner do these crystallite micelles aggregate themselves? For the larger part of the properties, by which types of carbon are characterised, is considered to be attributed to those inter-micellar aggregations.

H. L. Riley and his co-workers,⁽²⁾ for example, have carried out a series of experiments on the measurements of the change of dimensions of crystallites by heat treatment of carbon. Their results gave much informations about the inner structure of carbon which can not be expressed merely by the statements of the crystallite sizes. We have also carried out a series of experiments on the wet oxidation of carbon, that is, on the reactivity of carbon for the oxidizing solution, and also followed the changes in dimensions of crystallites under the oxidation process by the X-ray examination.

Reactivity to the Wet Oxidation and the Types of Carbon

Carbon is oxidized to carbon dioxide by the solution of potassium dichromate in phosphoric acid. The velocity of this reaction is very slow at the room temperature, but accelerated by moderate heating. It also varies widely depending upon the kind of carbon. This fact can be used to compare the features of carbon with each other.

The oxidizing solution was made by dissolving 20 g. of potassium dichromate into 100 cc. of phosphoric acid of which density is 1.75. Each experiment was carried out with 0.03 ~ 0.05 g. of carbon, which had been powdered below 140 mesh, and 7 cc. of the oxidizing solution. A small glass vessel containing the reactants was dipped into a water

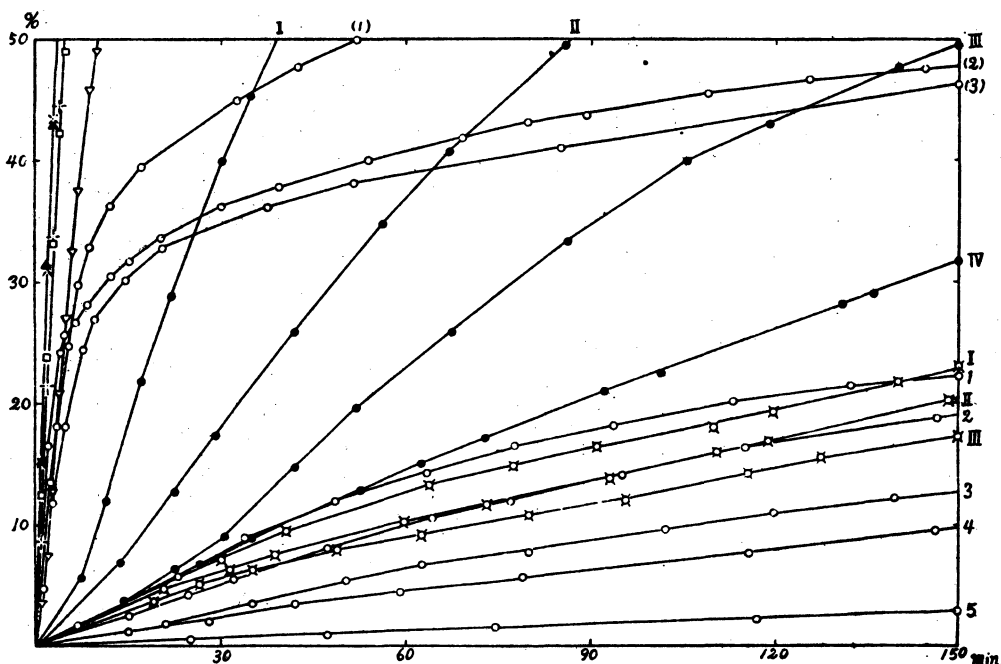


Fig. 1.—The rate of oxidation of various kinds of carbon by the solution of potassium dichromate in phosphoric acid. The fraction of carbon oxidized is shown in percentage against the reaction time in minutes.

Carbon Black: —x—x—, Micronex; —▲—▲—, Tokyo Gas Co.; —□—□—, Nippon Kasei Co.; —+—+—, Nippon Sekiyu Co.; —▽—▽—, acetylene black. Graphite: —●—●—, I, Acheson graphite; II, a natural graphite in Japan; III, flake graphite in Japan; IV, Ceylon graphite. Active carbon: —○—○—, (1), Norit; (2), Active carbon Takeda; (3), Supra-Norit. Pitch coke: —□—□—, I, an industrial product in Japan; II, Great Lake; III, an industrial product in Japan. Charcoal: —○—○—, 1, char prepared from filter paper at 390°C.; 2, char prepared from filter paper at 500°C.; 3, wood charcoal; 4, carbonaceous substance prepared from cane sugar and sulfuric acid; 5, carbosaccharose Kahlbaum.

(2) J. Gibson, M. Holohan and H. L. Riley, *J. Chem. Soc.*, 1946, 450.

bath at 100°, and then the volume of carbon dioxide produced was measured by a gas

burette following the time.

The results are shown in Fig. 1, where the fraction of carbon oxidized are plotted against the time.

The types of carbon which were used in this experiment are as follows. (1) Carbon blacks, containing several kinds of commercial carbon black made in Japan and also "Micronex" made in U. S. A. (2) Active carbons, containing "active carbon Takeda," "Norit" and "Supra-Norit." (3) Charcoals, containing wood charcoal, chars prepared at 390° and 500° from filter paper, and "Carbosaccharose-Kahlbaum." It also contains carbonaceous matter prepared from cane sugar and concentrated sulfuric acid. (4) Pitch cokes, containing commercial products in Japan and U. S. A. (5) Graphites, containing Acheson graphite, Ceylon graphite and two kinds of natural graphite in Japan.

Of all these types of carbon, carbon blacks were oxidized with the highest rate of reaction. Most of them have the same order of the reactivity to the oxidizing solution. The samples of graphite were oxidized with moderate velocities. We can not estimate the crystallite sizes of these samples, because they are all infinitely large under the X-ray scale. However, the curves seem to be arranged in the opposite order of the apparent crystallization, namely, the velocity of artificial Acheson graphite is the highest and that of Ceylon graphite is the lowest. Between them two kinds of natural graphite in Japan are situated.

The charcoal group has the lowest reactivity to the oxidizing solution, nevertheless the crystallites of these carbons are very small as it is well known. Hence, the fact that they have a large resistance to the wet oxidation, suggests that there must be some important difference in the inner structure between charcoals and carbon blacks. The reactivity of pitch cokes is in the same order as that of charcoals. This suggests that these two kinds of carbon have common characteristics in the inner structure.

The curves of active carbons are distinguishable from others by their shapes. At the first part of the reaction, active carbons were oxidized with the velocity as rapidly as carbon blacks were. After 20 ~ 30 per cent of carbon was oxidized, however, the velocity dropped down to the value of charcoals. These activated carbons must not be different substantially from charcoals in their main structures, but it seems, from these results, that they have certain portions of which structure and that of carbon black are alike. This is supposed to be attributed to the process by which these

carbons were activated.

H. L. Riley assumed,⁽³⁾ in his paper, that the resistance of carbon to the oxidizing solution is attributed mainly to the presence of the bonding of hydrogen between the layer planes of crystallites, and that the rate of oxidation will be higher as the species is progressively graphitized. In the series of his experiments, however, data on carbon blacks have not been found.

Our results will be interpreted, at least qualitatively, by the following assumptions. The reaction to carbon dioxide proceeds through the formation of intermediate compounds as graphitic oxide, of which structure has been investigated by U. Hofmann.⁽⁴⁾ Hence, the first step of the reaction is the entrance of oxygen atoms between the layer planes of crystallites. This is accompanied by the swelling of the crystallite micelles along *c* axis. An effect, caused by the formation of graphitic oxide and the swelling, can be presumed, by which the aggregations of micelles will be destroyed and crystallites will be dispersed into the solution. In reality, in the case of carbon black and graphite, it was found always that carbon was dispersed into the colloidal state in the process of the wet oxidation. In consequence of the dispersion, the surface area of carbon in contact with the oxidizing solution becomes larger, and it will progressively increase as the carbon is made of smaller crystallites. The order of the rate of oxidation from carbon black to Ceylon graphite will be interpreted by this assumption.

In the case of charcoals and pitch cokes, on the other hand, we could not find any dispersion of carbon into the colloidal solution. The small reactivity of these substances to the oxidizing solution will be attributed to the fact that their crystallite micelles seem to be prevented to dispersion. It is further assumed that this restriction is due to the binding of micelles with some cross-linkages between them. These cross-linkages are supposed to be caused by the residual carbon atoms, or some others, which are not completed to the aromatic condensation under the carbonisation process.

The assumption that carbon black is made of independently mobile micelles as in graphite and that charcoal is made of non-mobile micelles bridged to each other with cross-linkages, seems to be plausible when we

(3) H. L. Riley, *Trans. Faraday Soc.*, **34**, 1011 (1938); Blayden and H. L. Riley, *J. Soc. Chem. Ind.*, **54**, 159 T (1935).

(4) U. Hofmann, A. Frenzel and E. Omlán, *Ann. Chem.*, **510**, 1 (1934).

remember the origin of these kinds of carbon. Carbon black or soot is prepared from substances of low molecular weight through the gas phase, on the other hand, charcoal or pitch coke is prepared in liquid or solid phase, from materials or at least through certain intermediate substances of high molecular weight.

X-ray Examination of the Oxidizing Process

To get further informations, we carried out the X-ray examination of carbon following the process of the wet oxidation. The results support the assumption described in the preceding section. Experimental procedure was as follows.

By controlling the amount of potassium dichromate in the oxidizing solution, it is able to stop the reaction at any desired step of oxidation, before all the amount of carbon is consumed. Thus, after a part of carbon which is equivalent to the amount of potassium dichromate in the solution disappeared, a certain amount of carbon still remains in the solution. This residual part of carbon was used as the specimen of the X-ray examination, after being purified from salts by repeated decantation with water or by dialysis.

X-ray powder photographs were made by using a cylindrical camera (radius is 50.4 mm.) and copper- K_{α} radiation filtered by nickel foil. Powder photographs of carbon consist of diffused bands. By measuring the half-peak widths of the diffraction bands, *i. e.* its width at half the peak intensity, it is possible to know the dimensions of the crystallites. The intensities of the patterns have been found for this purpose from the photographic film using a microphotometer. In this case, however, as the blackening on the photographic film is not simply proportional to the X-ray intensity curve. Several devices have been proposed for the means of this correction. The procedure which was devised by us was as follows. The cover of the photographic film was made of three parts side by side in the X-ray camera, the two parts were covered with aluminium foils differing in thickness to each other, in

addition with a paper envelope which was commonly used in all three parts. In consequence, a photograph is divided into three parts such as shown in plate 1.

From the value of the coefficient of absorption of aluminium, $\mu = 180.3$,⁽⁵⁾ and the thickness of the foils used, 0.036 and 0.082 mm. respectively, the relative values of the intensities at the corresponding points in the three parts of a photograph can be known, as in ratio of 1:0.625:0.344. The further procedure is the same as that described by G. P. Thomson,⁽⁶⁾ in its principle. The patterns were then microphotometered and groups of densities of the corresponding points on the three parts were tabulated. Each group of densities was plotted with density as ordinate and differences of abscissa equal to $\log 0.625$ and $\log 0.344$ respectively. Each group of points was then shifted parallel to the axis of abscissa until the whole lie on a smooth curve, which gives the relation between the blackening and the logarithm of the relative intensity of X-ray. From this a second curve was drawn giving density against the relative intensity itself. Basing on this curve, the corrected intensity distribution curve was obtained from a microphotometer curve.

For the calculation of the crystallite size from the value of half-peak width (B), the Laue-Brill-Pelzer's formula was used,

$$\eta = 0.0884 \left\{ B \cos \theta - \frac{1}{B} \left(\frac{\pi r}{R} \right)^2 \cos^3 \theta \right\}$$

where r and R is the radius of the cylindrical specimen and camera respectively, and θ is half the diffraction angle as defined in the Bragg law. η is a pure number related to the crystallite size by the expression $\eta = \lambda / 4\pi ma_i$, where λ is the wave length and ma_i represents the extension of crystallite along the a or c axis in our case. From the (002) diffraction band we can estimate the c -dimension, *i. e.* the average height of layer lattices or of piles of plane molecules, and from the (100) diffraction band, the a -dimension⁽⁷⁾ *i. e.* the average diameter of the plane molecules.

In Figs. 2 and 3 the c and a dimensions are shown respectively, plotted against the degree of oxidation which is shown as the fraction of carbon disappeared by the wet oxidation. Each figure shows a process which has been



Plate 1.—Powder photograph of pitch coke "Great Lake," 60% oxidized. Photograph is divided into three parts, the intensities at the corresponding points in these parts are in ratio 1:0.625:0.344, theoretically.

(5) E. W. Pike, *J. Appl. Phys.*, **12**, 206 (1941).

(6) G. P. Thomson, *Proc. Roy. Soc.*, **A125**, 352 (1929).

(7) If Warren's formula (*Phys. Rev.*, **49**, 693 (1942)), $B = 1.84\lambda / L \cos \theta$ where L is the dimension of crystallite, is used for the calculation of the a -dimension, the value becomes larger than that calculated by L. B. P.'s formula in the amount of about 70–90 percent.

followed by crystallite micelles, when a solid disappeared by a chemical reaction.

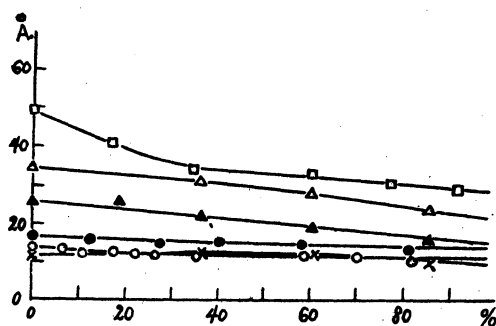


Fig. 2.—The crystallite dimension in Å. along the c -axis is plotted against the fraction of carbon oxidized in percentage.

□, acetylene black; △, pitch coke "Great Lake"; ▲, pitch coke, an industrial product in Japan; ●, carbon black "Miike"; ○, carbon black "Nippon Kasei"; ×, Supra-Norit.

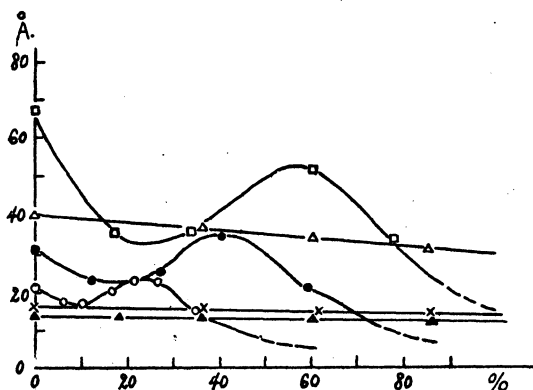


Fig. 3.—The crystallite dimension in Å. along the a -axis is plotted against the fraction of carbon oxidized in percentage. The same symbols as in Fig. 2.

In these figures, changes in the c -dimensions are small all over the degree of oxidation and for all the species of carbon, on the other hand, changes in the a -dimensions are remarkable. Namely, the a -dimension curve of carbon black has a minimum and a maximum. It seems to be a common character of carbon black.

For example, while the first twenty per cent of carbon was lost, the a -dimension of acetylene black decreased from 68 Å. to 35 Å. Such rapid decreasing in the a -dimension will not be expected when we conceive crystallites as small discs and the consumption takes place uniformly along the circumference inward. It is rather logical to assume, from

this result, that a disc was split into smaller discs through cracking. Crystallite micelles may contain in their net planes unstable bonds as well as stable bonds. Consequently it is plausible to consider that the reaction proceeds preferentially along weak bonds, and micelles will be split into smaller ones. To interpret the next step, from the minimum to the maximum, it must be remembered that the reaction is an irreversible one, and the growth of crystallite consequently can not be conceived. It must be further remembered that the dimensions measured by the X-ray diffraction method are not other than the average values of the sizes of crystallites, which are even limited to the ordered parts of the micelles, overlooking the disordered parts. The apparent increasing of the a -dimension curve can be attributed to the fact that minute crystallites will be consumed preferentially leaving stable larger micelles behind, in consequence the average values of the dimensions increase. At the maximum point, there remain crystallites with relatively uniform dimensions, and thereafter they are consumed uniformly following the progressive reaction. The results of chemical analysis are shown in Fig. 4. Corresponding to the minimum and the maximum point of the a -dimension curve, there appeared also the minimum and maximum in the oxygen content curve. This supports the above interpretation of the a -dimension curve, because the oxygen content observed can be assumed to be proportional to the total surface of crystallites which can be combined with oxygen.

The behaviors of carbon black can be understood from the assumption that their micelles

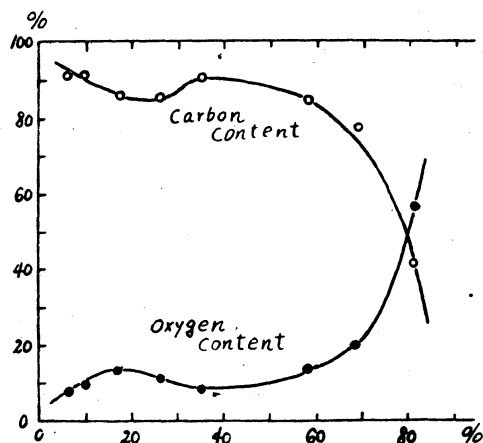


Fig. 4.—Carbon and oxygen content in percentage is plotted against the fraction of carbon oxidized. The sample is carbon black "Nippon Kasei."

are mobile and can be dispersed into the oxidizing solution. Furthermore each micelle can be attacked simultaneously by the oxidizing agent. On the other hand, the α -dimension of pitch-coke and Supra-Norit almostly did not change, even when about eighty per cent of carbon had been lost by the reaction. This fact suggests that some micelles at the preferable positions of the total numbers of micelles are consumed preferentially leaving others unchanged, rather than that the total micelles are attacked simultaneously as in the case of carbon black. If the micelles are rigidly bridged with each other to a conglomeration, in which micelles can not move for dispersion and into which the oxidizing solution hardly penetrate, then the micelles being consumed by the reaction are limited to the outer ones of this conglomeration and inner micelles remain unchanged until the outer micelles are completely lost. In consequence, the constancy of the dimensions will be held all over the degree of oxidation.

In Table 1, the observed values of the half-peak widths of (002) and (100) band of Acheson graphite under the process of the wet oxidation are shown. The half-peak widths of the c -dimension increased rapidly rather than that

of the a -dimension. This suggests that the crystallites of graphite split along the layer planes into thinner crystallites in the process of the reaction. The values of the spacings did not change through the reaction, until about 80 per cent of carbon was lost, when a new additional band at about 8 Å. appeared. The sample which remained after 99 per cent of carbon had been lost showed a pattern consisting of only two highly diffused halos at the position of 4.1 and 3.5 Å. respectively. This is a kind of amorphous carbon.

Summary

The reactivity of various kinds of carbon to the solution of potassium dichromate in phosphoric acid was examined. The samples investigated contained carbon blacks, graphite, pitch cokes, and charcoals. The rate of the reaction varied depending on the types of carbon, and the order of the reactivity was found to be in the order shown above. This is attributed to the modes of aggregation of crystallites. It was assumed that, in carbon blacks the crystallites are mobile individually for dispersing or swelling, on the other hand, in pitch cokes as well as charcoals there are some linkages to bridge the micelles with each other. This is supported by the results of the X-ray examination which was carried out following the steps of the wet oxidation.

In conclusion, the authors wish to express their sincere thanks to Prof. J. Sameshima for his encouragement through the experiment. A part of the cost of this study was defrayed from the grant of the Ministry of Education, to which the authors' thanks are due.

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Table 1

The Half-peak Widths of (002) and (100)
Band of Acheson Graphite, in the
Process of the Wet Oxidation

Fraction of oxidized carbon	0%	25%	50%	80%	98%
	mm.	mm.	mm.	mm.	mm.
(002)	1.25	2.55	2.95	3.15	3.6
(100)	1.35	1.55	1.70	1.85	3.1

(Copper K_{α} -radiation, the radius of the cylindrical sample is 0.6 mm., the radius of the camera is 50.4 mm.)

Fluorometric Microdetermination of Uranium. IV. Measurement of the Fluorescence Intensity and Determination of the Uranium Content in Natural Substances

By Masaki NAKANISHI

(Received March 9, 1950)

Measurement of the Fluorescence Intensity

In the way successively described in the foregoing papers, uranium is extracted from the sample in question and mixed with sodium fluoride to prepare the fluorescent material. The prepared fluorescent bead produces a vivid yellow luminescence under the excitation of ultraviolet ray.

This report will recount the particulars in measuring the fluorescence intensity. As shown in the first report of this series, the fluorescence intensity varies with the uranium content of each fluorescent bead, and the larger the content is, the more intense becomes the fluorescence within the range of uranium 10^{-4} to 10^{-9} g.

The bead from an unknown sample is compared on its luminescence intensity with those of known content of uranium, and the uranium content of the former is determined by interpolation.

The high tension mercury lamp was used as the source of ultraviolet light, in combination with the glass filter prepared for this purpose.

The measurement is performed, as a rule, with the aid of the photographic spectral photometry, but the visual observation is also often applied expediently.

By the Photographic Spectral Photometry.—As is often available in the measurement of a faint gleam, the photographic spectral photometry is the effective means for measuring the fluorescence intensity.

On the same photographic plate, fluorescence band spectra of both known and unknown beads are photographed in parallel, and the blackness of these bands is compared at the corresponding wave length. In order to avoid the effect of ultraviolet light, which is reflected on the surface of the bead, on the photographic plate, it is necessary to disperse the fluorescence into a spectrum, making use of a spectrograph.

Procedures.—The fluorescent bead is supported at a fixed position on the optical axis closely before the widely opened slit of the spectrograph,

and is irradiated from a fixed slant direction with the ultraviolet light condensed with a quartz lens of short focus.

As the direction and the position of the discal bead settled in its place affect considerably the density of the photographic plate, they must strictly be fixed.

In order to determine the uranium contents of the unknown beads, the observation of the fluorescence spectra of at least two different known beads are necessary. Spectra of the known and the unknown are taken successively on the same plate, where the time of exposure must be constant for every spectrum, in accordance with the rule of the photographic photometry. The exposure is usually about 10 minutes for the bead containing 10^{-6} g. of uranium, provided that an ordinary panchromatic plate is used. But the time of exposure should be decided by the trial run, for it is subjected to the nature of the plate, as well as the optical system, the intensity of fluorescence and the breadth of the slit.

After the photographing, the plate is developed and the photographic density of each spectrum is estimated at $555\text{ m}\mu$ with the microphotometer.

The obtained values of photographic density for known beads are referred to their contents of uranium, and the relation between content and density is established in a convenient way, say, graphically. The particulars of the photographic spectral photometry are omitted here.⁽¹⁾

By the Visual Observation.—In estimating the intensity of the fluorescence, the photographic photometry has the superiority above other methods, especially for such a faint luminescence as in the present case. But the procedures are somewhat tedious, and if they are faultily followed in any point unexpected results are likely to be obtained. In these respects the following method facilitates the course and provides the satisfactory results.

In this method the intensity comparison of the unknown beads with the known is made with the naked eye, instead of the spectrograph. It is of course possible to make the comparison in the simple way, in which the intensity of the unknown bead is observed in the ultra-

(1) H.B. Dorgelo, *Physik. Z.*, **26**, 756 (1925); R. Frerichs, "Handbuch der Physik", Berlin, 1928, Vol. 19, Chapter 23.

violet light and compared with those of several known beads containing different quantities of uranium. But more accurate results are expected by the following device based on the same principle.

Procedures.—The colorimeter of the Duboseq type is used for this purpose for the sake of convenience. Any turbid solution of an arbitrary concentration is applied to the absorbing layer in the vertical cylinders. Just under each cylinder the fluorescent bead is placed severally. In the one position under one cylinder an arbitrary bead for comparison is settled and kept fixed during the process, and in the other position known and unknown beads are placed one after another. These two beads are compared by the balancing method in the ultraviolet light.

As the fluorescence is in general fairly faint, the microscopic part of the colorimeter is removed to eliminate the absorption and to make the loss of light due to magnification minimum. The fluorescent beads are arranged in such a way that those two images are observed side by side in the scope.

The uranium content in the bead in question is determined as follows.

According to the absorption law of light, the intensity I of the fluorescence in question after passing through the layer d of the turbid solution is given by

$$I = I_0 e^{-kd},$$

where I_0 and k represent the initial intensity and the absorption constant respectively.

On the other hand, we obtain a similar equation for an arbitrary bead for comparison,

$$I' = I'_0 e^{-k'd'},$$

where each figure has the corresponding meaning.

When the apparent intensities of both images come equal,

$$I = I'$$

$$\text{or} \quad I_0 e^{-kd} = I'_0 e^{-k'd'}$$

$$\text{therefore} \quad I_0 = I'_0 e^{-k(a'-a)}.$$

To obtain the values of the two unknown constants, I'_0 and k , more than two beads containing different amounts of uranium are compared on their luminescence intensity with the arbitrary bead for the comparison in the manner as given above. Then the uranium content of an unknown bead is obtained from these values of constants in the same procedure.

The above calculation is valid only within the range in which the fluorescence intensity is linearly proportional to the content of uranium of the bead.

This visual observation method has the advantages, in spite of its simplicity, over the photographic photometry in several points. The latter method is not free from imperfections for the purpose of this kind in the following points.

(a) The fluorescence is too faint to make an image on the photographic plate in case the content of uranium is small. In consequence, the time of exposure must necessarily be prolonged. Meanwhile the bead may be wet by the atmospheric moisture especially in the damp weather, and consequently the fluorescence intensity is likely made feeble.

(b) The procedures following after the photographing, e.g., the development of the plate and the measurement of the photographic density, are not easy.

(c) Each operation is subjected to the influences of many factors, and this presumably makes the possibility of the experimental error much.

The visual observation method overcomes these difficulties for all the simplicity in comparison with the photographic photometry. The writer therefore takes the former from his experiences for a suitable method in routine works, and he has got the satisfactory results by the method.

Determination of the Uranium Content in Natural Substances

On the uranium contents of various natural substances which are not regarded as radioactive, almost no direct determination has been carried out so far in this country. Since these nonradioactive substances usually contain such an amount of uranium as is most suitably determined by the fluorometric method, this procedure must furnish the useful means to manifest the geochemical circumstances of radioactive elements.

In dealing with rocks in which uranium is expected to be in the state of equilibrium with radium, the amount of the former is easily estimated indirectly from that of the latter.

The microdetermination of uranium is necessary, especially for the samples in which radioactive elements of the uranium series do not yet reach their equilibrium condition. In these circumstances the fluorometric method is an effective measure.

Included among these are samples from the hydrosphere as well as the biosphere. Furthermore some minerals of which ages are less than a million years from their formation, weathered minerals or rocks, etc. must be treated in the direct microdetermination method to determine

uranium, because uranium is not expected to be in equilibrium with the disintegration products. The following sections will deal with some examples of natural substances treated with the fluorometric method of analysis.

The Uranium Contents of Rocks

Experiment.—The particulars of the treatment are omitted here, for the full description of the analytical procedures appeared in the previous papers.

About 1g. of the sample suffices for the analysis. In case the sample is first fused with sodium carbonate and leached with hot water as recommended from the writer's experiences, the procedure must be repeated at least three times to make the complete extraction of uranium.

The leached solution containing a considerable amount of sodium carbonate is made acid with hydrochloric acid and evaporated to dryness. From this residue remove silica in the usual way, and to the resulting solution add a little ferric chloride (corresponding to about 20 mg. Fe_2O_3) and ammonium chloride. Boil the solution, make it ammoniacal, continue the boiling for a few minutes, and then filter the precipitate. The filtrate is treated two times more in the same way repeating the precipitation. The first precipitate generally contains some aluminum hydroxide.

Three precipitates are brought together. The combined mass must necessarily be reprecipitated, for it includes much impurities, especially sodium chloride derived from the mother liquor.

The obtained precipitate of iron hydroxide contains the total amount of uranium in the original sample. The after treatments run in the same way as already described.

The interferences of impurities are satisfactorily avoided even in such a normal course of procedures, so far as the common igneous rocks are concerned.

The results obtained on some examples of the rock are listed in Table 1.

Table 1

No.	Sample	Location	Uranium content, 10^{-6} g. U/g.
(1) {	Sinter deposit (ferruginous) {	Masutomi (Yamanashi Prefecture)	0.05
(2) {	Sinter deposit (calcareous) {	"	0.004
(3)	Greywacke	"	{ 2.15 2.06
(4) {	Shale (average sample) {	Europe	0.67

The first sample (1) shows the uranium content of the sinter deposit at one of the chalybeate mineral springs in Masutomi district (Yamanashi Prefecture), which is widely known

as one of the strongest radioactive spring regions in Japan.

The spring A 8 (as named by earlier investigators),⁽²⁾ from which the ferruginous sinter grew, is very radioactive owing to its large contents of radium and radon, but the uranium content of the spring water itself (0.3×10^{-6} g. U/g.) is not so large as expected. A part of the dissolved uranium in the spring water must be coprecipitated with iron near the orifice, but the larger part of the element is likely to remain in the solution, because the spring water contains some noticeable amount of carbonate.

The sample (2) is an example of calcareous sinter deposits formed from mineral waters of old times. It consists mainly of calcium carbonate. This sample was obtained in October, 1936, by Dr. Toshio Nakai, who found in it the extraordinarily large content of radium amounting to 1.75×10^{-10} g. Ra/g.⁽³⁾ The writer is much obliged to him for affording facilities to make use of the sample.

As the result of analysis a very small amount of uranium was found as given in Table 1. If uranium be present to the equilibrium amount to radium, the content would reach 5.15×10^{-4} g. U/g. On the contrary, however, the observed value of uranium is 10^5 times smaller than the expected. This fact shows that uranium and radium are brought into the sinter deposits independently to each other by different mechanisms. Further, it would be natural that uranium does not behave in the same manner as calcium, when considered that uranium forms a soluble complex salt with carbonate. The uranium found in the calcareous sinter deposit will presumably have originated from the permeating mineral water.

The analysis of the sample (3) was attempted to know the uranium content of the ground, from which the strong radioactive springs arise. The sample was taken at the spot between B and C areas⁽²⁾ of Masutomi district.

The sample (4) is an average sample of various European shales, which the writer received by courtesy of Professor Eiichi Minami. The value obtained corresponds to that of mean basic igneous rocks.

Summary

Details of the methods of measuring the relative intensity of the fluorescence were described, in which the photographic spectral photometry and the visual observation method were related.

(2) S. Oana and K. Kuroda, this Bulletin, 17, 400 (1942).

(3) T. Nakai, this Bulletin, 15, 420 (1940).

Several examples of uranium contents in rocks and sinter deposits determined by this method are treated from the geochemical interest in the course of this study.

The writer's thanks are due to Professor Kenjiro Kimura of the University of Tokyo for his continual advice and encouragement

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Fluorometric Microdetermination of Uranium. V. The Uranium Content of Sea Water

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(Received March 9, 1950)

Experimental

A sample of 200 ml. of sea water is enough to determine the uranium content by the present fluorometric method.

The sample water is treated in the way as described in the foregoing papers. For fear that the organic substances are present in the original sample, the residue of the first evaporation is dealt with nitric acid and evaporated again. Then the residue is dissolved in dilute hydrochloric acid and the insoluble matters are separated.

The iron hydroxide precipitate obtained as the carrier of uranium must be re-precipitated, because it probably includes a certain amount of sodium chloride.

Even in the case when the treatments are carried out along the normal course as given before, almost no noticeable interference of impurities comes about. Consequently no special procedures of removing impurities are required in the analysis of sea water. For this reason the particulars of the processes are omitted here to avoid the repetition.

Results

The uranium content of sea water obtained in several samples are given in Table 1 and 2.

Table 1

No.	Location	Depth, m.	Content of U, 10 ⁻⁶ g./l.	Salinity, ‰
(1)	{ Mutsu-wan (Aomori Prefecture) }	0	0.46	28.8
(2)	{ Sagami-nada (Shizuoka Prefecture) }	29	{ 1.36, 1.04 1.20, 1.30 1.06, 1.12 mean: 1.18 }	34.7

Table 2

Depth, m.	(3) 32°39.1' N 135°27.0' E		(4) 31°49.0' N 135°23.7' E	
	Content of U, 10 ⁻⁶ g./l.	Salinity, ‰	Content of U, 10 ⁻⁶ g./l.	Salinity, ‰
0	—	—	1.96	34.72
500	3.37	34.33	2.98	34.61
1000	2.65	34.31	—	—
1500	2.76	34.40	2.55	34.54
2000	2.79	34.52	2.44	34.58
3000	3.06	34.60	—	—
4000	2.70	34.61	—	—

Depth, m.	(5) 31°50.0' N 133°08.2' E	
	Content of U, 10 ⁻⁶ g./l.	Salinity, ‰
0	1.75	34.45

The sample (1) was taken from the surface water in Mutsu Bay one kilometer off Asamushi (Aomori Prefecture) on April 27, 1946, and the determination was carried out several weeks after the sampling.

The sample (2) was obtained at the mouth of Ito Bay (eastern side of the Izu Peninsula, Shizuoka Prefecture) at the depth of 29 m. from the surface, close to the sea-bottom. This was sampled on April 29, 1947, and the treatment followed soon after.

The samples (3), (4) and (5) were examined in the attempt to find the uranium content of the ocean water, which is less affected by the influences of land. For using these materials as analytical samples the present writer is much obliged to the Hydrographical Department, Ministry of Transportation. Sampling was performed on December 5, 1947, and the treatment came off in June (1948), in

January (1949) and in June (1949) for the sample (3), (4) and (5) respectively. All these samples were kept preserved in the glass bottles.

Discussion

On the uranium content of sea water several reports have been published in foreign countries. Among them Hernegger and Karlik⁽¹⁾ first applied the fluorometric method to this purpose. The results they obtained are given in Table 3.

Table 3

Location	Depth, m.	Content of U, 10^{-6} g./l.	Salinity, ‰
Gullmar Fjord	0	0.36	23.9
"	60	0.98	34.1
"	100	1.17	34.3
Skagerak	500	1.90	35.2

The sample water for analysis was taken near the western coast of Sweden. According to their later report,⁽²⁾ they obtained the values from 2.0 to 2.2×10^{-6} g. U per l. for the uranium content of coast and ocean water.

Later on Föyn and others⁽³⁾ reported 1.5×10^{-6} g./l., and this value was approved by Wattenberg.⁽⁴⁾

The present writer intends to compare his results with those given in Table 3.

The sample (1) taken from the surface water close to the coast of a bay is an example of those which are much affected by the inland water. Therefore it is of little importance from the geochemical point of view to discuss in detail on the uranium content of sea water from this result. In this sample of sea water, the uranium content was found to be considerably small just as it was expected, and in the same degree of magnitude as reported previously by Hernegger (Table 3). The only conclusion is that the uranium content will probably be higher in sea water than in common inland water.

Similarly the sample (2) was subject to the influences of land, though a less degree, and can not be looked on as the typical sea water. But the result obtained from this sample shows a fairly large value, which nearly

corresponds to that of Hernegger's which was collected at 100 m. depth. In the present case the depth (29 m.) of sampling is of no great importance, because it is also the depth of the sea-bottom. The value obtained will be equivalent to that of the deeper layer of the open sea.

Quite different from these two, the samples (3), (4) and (5) are the true sea water, belonging to the Kuroshio Current, and are supposed to give the uranium content of sea water in various depths.

In these samples the values obtained are in general somewhat larger than expected, except that taken at the depth of 0 m. (surface). The blank test was carried out and the standard fluorescent beads of known content were examined on the correctness. Moreover the relatively high values obtained above are not attributed to the substance contaminated from the glass bottles, though Hoffmann⁽⁵⁾ told about the unexpectedly large uranium content of some sorts of glass and porcelain. This is because the uranium in the sample (4), which was treated about half a year later after the sample (3) had been treated, shows no increase in content during the interval.

The concentration of uranium in the surface water is evidently lower than that in the deeper layer. In order to search into the biological concentration of this element, the sample (5) was first filtered through a filter paper, and the remaining residue was ignited to ash. Then the ash was treated by the fluorometric method. But no trace of uranium was found in it, and this fact means that the remains of the dead micro-organisms stayed by the filter paper do not play any important part to concentrate the element. The smaller value in the sample (5) is also consistent with that of the sample (4), though the reason why the sea water is poorer in uranium in the surface layer is not yet finally given.

Even though there comes out a peak at the depth of 500 m., the uranium content of deeper layers seems to be approximately constant, as the determination method involves the error amounting to 10%. Provided that uranium finds itself in the same concentration throughout the deeper layers, the average value comes up to 2.82×10^{-6} g. U/l., and this is the most probable value for the deep ocean water.

This result will be contributive to the problem of the radioactive elements in sea water.

Evans and others⁽⁶⁾ made an investigation

(1) F. Hernegger and B. Karlik, *Sitz. Akad. Wiss. Wien, Abt. IIa*, 144, 217 (1935).

(2) F. Hernegger and B. Karlik, *Göteborgs K. Vetensk.-Saml. Handl.*, V. B. 4, No. 12.

(3) E. Föyn, B. Karlik, H. Pettersson and E. Rons, *Medd. Oceanogr. Inst. Göteborg*, Nr. 2, (1939).

(4) H. Wattenberg, *Z. anorg. allgem. Chem.*, 251, 86 (1943).

(5) J. Hoffmann, *Sprechsaal*, 75, 214 (1942).

(6) R. D. Evans, A. F. Kip and E. G. Moberg, *Am. J. Sci.*, 36, 241 (1938).

on the radium content of sea water at the western coast of North America, and gave the information of the variation in depth shown in the first column in Table 4.

Table 4

Depth, m.	(I) Content of Ra, 10^{-12} g./l.	(II) Equilibrium amount of U (calc.), 10^{-6} g./l.	(III) U (obs.) U (calc.) (approximate)
0	0.3 ± 0.1	0.09	20
600	1.5 ± 0.1	0.44	7
1300	3.2 ± 0.2	0.94	3

The amount of uranium which is in the radioactive equilibrium to radium is calculated in the second column. And the last column represents the ratios of the observed values given in Table 2 to the corresponding calculated values. As shown clearly in the table the ratios rapidly decrease with the depth; in other words, it is obviously sure that radium is gradually precipitated in some mechanism,⁽⁷⁾ for the concentration of uranium is approximately constant to the depth.

In regard to the thorium content of sea water, several reports have been published, among which the values $<2\gamma/\text{l.}$ ⁽⁸⁾, $\leq 0.5\gamma/\text{l.}$ ⁽⁹⁾, $0.5\gamma/\text{l.}$ ⁽⁴⁾ and $0.66\gamma/\text{l.}$ ⁽¹⁰⁾ were displayed. The last one was determined with the surface water of the Seto Inland Sea, and this is no more than one third of the corresponding uranium amount. Therefore the relation between uranium and thorium in sea water is in direct opposition to that in common igneous rocks.

Other investigations of the writer show that the largest uranium content of the inland waters ever found in Japan belongs to the water of Shin-arima hot spring (Hyogo Pre-

fecture) amounting to 0.95×10^{-6} g.U/l., which has also the largest content of radium (381.14×10^{-12} g. Ra/l.).

Simple springs generally have less contents, for example, less than 2×10^{-9} g.U/l. for Shuzenji hot spring (Shizuoka Prefecture).

Even Masutomi springs (Yamanashi Prefecture), which are told to be the most radioactive spring group in this country, contain rather a small amount of uranium, that is, from 0.4 to 0.04×10^{-6} g.U/l. as far as the writer has examined.

He also failed to find any noticeable amount of uranium in the analyses of some sorts of river and underground waters.

Although we have received some papers⁽¹¹⁾ from abroad reporting of finding more uranium in some mineral springs than in sea water, we may conclusively maintain that the sea water in general has the greatest concentration of uranium in the hydrosphere.

Summary

Coast and ocean water sample were analysed on their uranium contents by the fluorometric method.

The variation to the depth of 4000 m. was also examined in the ocean water sample. The content is likely to be constant even to the deep, though a little decrease appears in the surface water.

The obtained values in the deeper layer (average 2.8×10^{-6} g.U/l.) are somewhat higher than those by foreign investigators.

The writer is indebted to the Ministry of Education for grants which has made this work possible. He also wishes to express his gratitude to Professor Kenjiro Kimura of the University of Tokyo for his invaluable advice and comment.

(7) C. S. Piggot and Wm. D. Urry, *Am. J. Sci.*, **239**, 81 (1941); H. Hamaguchi, *J. Chem. Soc. Japan*, **62**, 839, (1941).

(8) H. Wattenberg, *Z. anorg. allgem. Chem.*, **236**, 339 (1938).

(9) E. Föyn, D. Karlik, H. Petterson and E. Rona, *Nature*, **143** 275 (1939).

(10) M. Ishibashi and S. Azuma, *Chemistry and Chemical Industry*, **2**, 14 (1949).

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(11) J. Hoffman, *Monatsh.*, **74**, 38 (1941).

Studies on the Separation of Arsenic from Iron by Ion-Exchange Resin

By Yukichi YOSHINO

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Although arsenic is an amphoteric element, it has been said that aqueous or dilute hydrochloric acid solution contains arsenic as arseneous or arsenic acid. For the purpose of separating arsenic from iron using cation-exchange resin, the author has made a series of fundamental experiments. It was proved that the trivalent arsenic could be separated quantitatively from ferrous iron, while the separation of quinquevalent arsenic from ferric iron, though theoretically possible, was unpracticable, which seemed perhaps due to the formation of unstable ferric-arseno complex. As an example of practical applications of the method, the content of arsenic as well as iron and sulfur in an arsenopyrite was determined using ion-exchange resin. The results obtained agreed with those of hydrogen sulfide method of separation.

Experimental

The Resin: Cation-exchanger of commercial phenolsulfonic acid type. Ten grams of 30 meshed resin was conveniently equipped in a 50 cc. burette. The flow method was adopted and the rate of flow was 2–3 cc. per minute throughout the experiments. The exchange capacity of the resin was 1.84 milliequivalents per gram with respect to hydrogen ion.

Experiment I. The Behavior of Arsenic Solution in Passing through the Column of Resin.—The resin was previously saturated with 1*N*-sodium chloride or 1*N*-hydrochloric acid and washed thoroughly with distilled water. Various amounts of standard solutions of arseneous and arsenic acid respectively were added to the column of resin. The filtrate and washing water were received in a measuring flask of 150 or 250 cc. of capacity and the flask was filled up to the mark. The aliquot portions of the filtrate were taken and the amount of arsenic was determined iodometrically as follows:

In case of arseneous acid: The sample solution is neutralized with an excess of sodium bicarbonate and then titrated with 0.01*N*-iodine solution using starch as an indicator.

In case of arsenic acid: The method of determination of arsenic acid⁽¹⁾ is just the reverse of the case of arseneous acid, that is, an excess of

potassium iodide is added to the strongly acid solution of quinquevalent arsenic and liberated iodine is titrated with 0.01*N*-sodium thiosulfate solution. In this case, however, the strong acidity of the sample solution is apt to promote the decomposition of potassium iodide and to give the intermediate pink color at the end point of titration. Therefore, special cautions were taken as follows.

Concentrated hydrochloric acid and distilled water are previously boiled and freed from chlorine and air. To ten cc. of the sample solution, add concentrated hydrochloric acid so as to give 6*N* with respect to acidity. Throughout the procedure, a stream of carbon dioxide is led to the solution. Add 1 g. of solid potassium iodide and keep it on standing for five minutes. The liberated iodine is titrated with 0.01*N*-sodium thiosulfate solution. When the end point is near, the solution is diluted with water to 2*N* of acidity and 5 drops of 0.5 per cent starch solution is added and titration is carried out to the end point indicated by the change of color from blue to pink. Using this procedure, the blank value can be kept within 1 or 2 drops in every titration.

The results of such experiments are given in Table 1.

Table 1
Titrated Values of Arsenic after Passing through the Column of Resin

	No. of Expts.	pH	Amts. of arsenic, mg. As		Error, %	Remarks
			taken	found		
AsO ₃ ---	1	2.4	93.64	93.57	-0.07	Na-R*→ 250 cc.**
	2	1.8	56.18	55.91	-0.51	Na-R → 150 cc.
	3	1.8	56.18	56.29	+0.20	H-R → 250 cc.
AsO ₄ ---	4	1.8	102.0	101.8	-0.20	Na-R → 250 cc.
	5	1.0	102.0	100.8	-1.18	Na-R → 250 cc.
	6	1.4	102.0	102.4	+0.39	H-R → 250 cc.

* Na-R and H-R show the types of resin saturated with Na⁺ or H⁺ respectively.

** Total volume of effluent.

Table 1 shows that both trivalent and quinquevalent arsenic can be passed out through the bed without any loss. Moreover their behavior seems to be independent of the types of resin (Na-R or H-R). These results may enable us to

(1) L. Rosestaler, *Z. anal. Chem.*, **45**, 596 (1906); **61**, 222 (1922); I. M. Kolthoff, *Z. anal. Chem.*, **60**, 368 (1921); **62**, 137 (1923).

conclude that arsenic of both valency in the dilute hydrochloric acid solution can be treated as anions.

Experiment II. Separation of Arsenic Acid from Ferrous Iron.—The mixed solution of various amounts of arsenic acid and ferrous ammonium sulfate solution was flowed into the column of resin and the filtrate and washing water were collected and made up to a definite volume, say 250 cc., aliquot portions of which were taken and arsenic acid was determined by titrating with 0.01*N*-iodine solution. Distilled water of 100 to 150 cc. was proved to be sufficient for washing. The test of iron in the effluent with dimethylglyoxime or ammonium thiocyanate revealed no reaction at all.

These results show that arsenic acid could be quantitatively separated from ferrous ion as is given in Table 2.

Table 2

Separation of Arsenic Acid from Ferrous Iron

No. of Expts.	pH	Iron added, mg. Fe	AsO ₃ --- taken, mg. As	AsO ₃ --- found, mg. As	Error, %
1	<1	94.69	18.73	18.60	-0.69
2	1.9	59.53	37.46	37.58	+0.32
3	0.9	59.53	37.46	37.31	-0.30

Experiment III. Separation of Arsenic Acid from Ferric Iron.—A mixture of ferric chloride (94.41 mg. as Fe) and arsenic acid (100 mg. as As) was poured into the column of resin and, to prevent the formation of ferric arsenate precipitate, washed with 0.01*N*-hydrochloric acid solution. But, in this case, the amount of arsenic found in 250 cc. of effluent was about 80 per cent of that originally present. Successive washing with distilled water showed the gradual flowing-out of arsenic remained in the column. Table 3 gives the amounts of arsenic found in the filtrate at each step of washing.

About 2000 cc. of water was necessary for washing until the filtrate ceased to show blue coloration with ammonium molybdate reagent.⁽²⁾

Table 3

Relation between the Volume of Washing Water and the Amount of Arsenic Found in the Filtrate

cc. of washing water	250	500	750	
AsO ₄ ---found, %	~250	~500	~750	~1000
	80.33	15.84	2.25	1.31
cc. of washing water	1000	1250	1500	Total As found
AsO ₄ ---found, %	~1250	~1500	~2000	
	0.13*	0.01*	0.01*	99.88

* determined colorimetrically with "molybdenum blue" method.

The amount of iron in the filtrate when tested by means of ammonium thiocyanate in the dilute nitric acid medium proved to be trace amount. Between pH 0.9 and 2.0, a number of experiments was made varying mixing ratio Fe/As, flow rate and the types of resin (H-R, Na-R or NH₄-R), but none of them proved to be effective for complete separation of arsenic acid from ferric ion. These results seem to suggest that such behavior of arsenic acid might be attributed to some interaction between ferric ion and arsenic acid.

To clarify the state of affairs, following experiment was carried out. Into the column of 5 g. of resin which was previously saturated with ferric ion, a definite amount of arsenic acid (30 mg. as As) was poured. The filtrate and washing water were collected to a definite volume. The arsenic found in the effluent was 71.8 and 81.3 per cent respectively when the volume of the latter reached to 550 cc. and 1050 cc. On the other hand, a little iron (about a few mg. of ferric ion) was found in the filtrate.

In contrast to above mentioned case, when 56.18 mg. (as As) of arsenic acid passed through the column of 5 g. of resin which was previously saturated with ferric ion, the amount of arsenic acid in 150 cc. of filtrate was found to the extent of 98.2 per cent.

We may hereby conclude that a part of arsenic acid might form some complex ion⁽³⁾ with ferric iron in the solution. But owing to the relatively weak linkage, the complex ion is gradually dissociated along with the adsorption of ferric ion by the resin and consequently the flowing-out of arsenic acid takes place.

Even in case of oxidized state of arsenic and iron, it was shown that the separation of arsenic from ferric ion was possible when treated previously with sulfur dioxide. The process is as follows. The solution containing both ferric ion and arsenic acid, after being reduced by leading a stream of sulfur dioxide, is poured into the column of resin. The filtrate and washing water are collected to a definite volume, an aliquot portion of which is oxidized with bromine water. The excess of the latter is expelled by heating.

When cooled, 1 g. of potassium iodide is added and the liberated iodine is titrated with 0.01*N*-sodium thiosulfate solution as mentioned in Experiment I. Table 4 gives the results of such experiments.

Table 4

Separation of Arsenic Acid from Ferric Ion after Reducing with Sulfur Dioxide

Fe+++ added, mg. Fe	Amts. of arsenic acid, mg. As		Error, mg. As
	taken	found	
94.4	102.0	102.3	0.3
94.4	15.3	15.7	0.4

(2) Denigès, *Compt. rend.*, 171, 802 (1920); Emil Trug and A. H. Meyer, *Ind. Eng. Chem., Anal. Ed.*, 1, 136 (1929).

(3) L. Dede, *Z. anorg. Chem.*, 125, 28 (1922).

Analysis of Arsenopyrite using Ion-Exchange Resin.—As mentioned above, the separation of arsenic acid from ferrous ion is quantitatively carried out. As an example of practical applications, the analysis of an arsenopyrite⁽⁴⁾ was tried using ion-exchange resin.

About 0.7 g. of fine powdered sample is weighed out and transferred into a casserol. After digesting with 5 cc. of conc. nitric acid, 5 cc. of bromine is added in portions, while the solution is warmed on a water-bath. When all the sulfur is converted to sulfate, 5 cc. of conc. hydrochloric acid is added and dried up. This is repeated once more. Then, the residue is treated with a small volume of dilute hydrochloric acid and water. The insoluble matter and silica are filtered off. The filtrate is made up to 100 cc.

Determination of Arsenic: An aliquot portion of the sample solution, say 20 cc., is taken and treated with sulfur dioxide. The same procedure as mentioned in the preceding paragraph is adopted.

Determination of Iron: The adsorbed iron is eluted out with about 100 cc. of 4*N*-hydrochloric acid. The elute is evaporated to a small volume, to which a few drops of 1 per cent potassium permanganate solution are added. The solution is heated and the iron is reduced with stannous chloride and then determined volumetrically with 0.05*N*-potassium permanganate solution using Zimmermann-Reinhardt's solution.⁽⁵⁾

Determination of Sulfur: Another portion of the sample solution is poured directly into the column of resin and washed with 150 cc. of water. The sulfate ion in the filtrate is precipitated with 10 per cent barium chloride solution and weighed as barium sulfate.

In order to check the results obtained, the sample was analysed by the usual method as follows:

After separating arsenic from iron with hydrogen sulfide, the element was determined volumetrically by conversion to silver arsenate and titration as in Volhard's method.⁽⁶⁾

From the filtrate of arsenious sulfide, iron was determined volumetrically with 0.05*N*-potassium permanganate solution as in the case of resin method. Sulfur was estimated gravimetrically as barium sulfate after separating it from iron with ammonia. Table 5 shows the data of these experiments. The results obtained are in fairly good agreement with each other.

Table 5

Data of Analysis of an Arsenopyrite	
Resin method, %	Common method, %
As..... 43.89	43.64
Fe..... 34.13	34.30
S 21.11	21.25
Total 99.13	99.19

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(4) The sample is from the Iname mine, Aichi Prefecture.

(5) C. Zimmermann, *Ber.*, 14, 779 (1881); C. Reinhardt, *Z. anal. Chem.*, 36, 794 (1897).

(6) W. Eschweiler and W. Böhrs, *Z. angew. Chem.*, 36, 464 (1923).

On the Critical Concentration of *n*-Aliphatic Acid Salts and Similar Compounds

By Shunsuke SHISHIDO

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I. Introduction

It has been widely accepted that molecules of the soap dissolved in water are associated into grand molecules or micelles, owing to the cohesive interaction between their aliphatic long chain groups. However, properties of

the micelle have little been studied theoretically, for examples, the form, dimension or electrolytic behaviour. Therefore, we can hardly explain the experimental facts and are troubled with complicated behaviours.

The aqueous solution of long chain fatty acid salts and the similar compounds (alkyl-

sulfonic, alkylsulfuric, alkylpyridium, alkyltrimethyl-ammonium salts, etc.) changes their properties complicately with increasing concentration and there appear some nick points on the curve of the properties against the concentration. The nick point which appears in the most dilute region among these nick points is understood tacitly as the formation of comparatively small micelles from the monomolecularly dissolved systems. This concentration is called the critical concentration, which can be determined from this nick point.

In actual case, the critical concentration can be obtained from the observation of the nick point in the density, electric conductivity, viscosity, refractive index, optical absorption, and surface tension against the concentration of a salt. When these experimentally observed values are compared quantitatively with the theoretical ones and the reasonable coincidences are obtained, the circumstances of this micelle formation can be more discretely explained. Therefore, it is valuable to discuss the critical concentration theoretically.

II. Electric Energy of a Monomolecular and an Associated Ion of Soap

A soap molecule is considered to be consisted of three parts, R, $-\text{COO}^-$, and M^+ . R is an aliphatic long chain group which is strongly hydrophobe, so that in aqueous solution they are apt to associate with each other. On the other hand, carboxyl radical, as well as, metal ion M^+ are hydrophile and they disperse in water. The net work of these associating and dispersing forces induces the formation of the stable micelle.

In water, the hydrophile property of carboxyl radical prevents itself from embedding in the alkyl group R, therefore it exists contacting directly with the water molecule (Fig. 1). Now the electrostatic energy of a spherical ion (radius ρ) charged with ϵ in water (dielectric constant $\mu = 80$ at 20°), is

$$\epsilon_0 = \frac{\epsilon^2}{2\mu\rho}$$

If we assign the analogous energy to a carboxyl radical ion, the electrostatic energy of a fatty acid ion is expressed as follows:

$$\epsilon_1 = \epsilon_0 + \epsilon_1(\text{A}) \quad (1)$$

where $\epsilon_1(\text{A})$ is the extra electrostatic energy caused by the alkyl group ($\text{C}_n\text{H}_{2n+1}$) with low dielectric constant ($\mu_3 = 2.30$). First, we must estimate this extra energy. When the point charge exists on a point P, as shown in Fig.

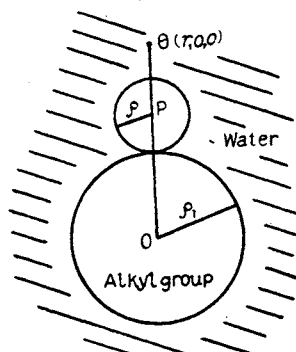


Fig. 1.

1, the potential at a point excluding the point P is obtained by the expansion of the spherical harmonics (Appendix (I)). For example, the potential energy at Q in Fig. 1 is

$$\psi = \frac{\epsilon}{\mu(\rho + \rho_1)} \left\{ \frac{\rho + \rho_1}{r - (\rho + \rho_1)} + \sum_{\nu=0}^{\infty} \frac{\nu(\mu - \mu_3)}{\nu(\mu + \mu_3) + \mu} \frac{\rho_1^{2\nu+1}}{(\rho + \rho_1)^{\nu+1}} \right\} \quad (2)$$

The first term of this equation becomes infinite as $r \rightarrow (\rho + \rho_1)$, and if $r = \rho_1 + 2\rho$, it becomes $\epsilon/\mu\rho$. Therefore we should consider that the first term is concerned of the self electrostatic energy ϵ_0 and the other terms represent extra $\epsilon_1(\text{A})$ due to alkyl group. That is,

$$\epsilon_1(\text{A}) = \frac{\epsilon^2}{2\mu(\rho + \rho_1)} \times \sum_{\nu=0}^{\infty} \frac{\nu(\mu - \mu_3)}{\nu(\mu + \mu_3) + \mu} \frac{\rho_1^{2\nu+1}}{(\rho + \rho_1)^{\nu+1}} \quad (3)$$

The estimated values are almost trivial (Table 1). The form of associated molecule is also considered to be spherical at the first approximation. The energy ϵ_n can be written,

$$\epsilon_n = n\epsilon_0 + \epsilon_n(\text{A}) \quad (4)$$

where $\epsilon_n(\text{A})$ is the extra energy relating to the centrally associated alkyl groups. Hereupon,

$$\epsilon_n(\text{A}) = \frac{1}{2} n\epsilon \sum_{i=1}^n \psi_n + n\epsilon_1(\text{A}, \rho_n) \quad (5)$$

in which ψ_n is the electrostatic potential at point P, due to the n -th $-\text{COO}^-$ radical and $\epsilon_1(\text{A}, \rho_n)$ is the value of Eq. (3) in which ρ_1 is replaced with ρ_n .

$\epsilon_n(\text{A})$ approaches rapidly to the value of

$$\frac{n^2\epsilon^2}{2\mu(\rho + \rho_n)} \quad (6)$$

in the larger degree of association (Appendix (II)).

III. The Association of *n*-Fatty Acid Ions

The energy of a *n*-fatty acid ion in aqueous solution depends mainly on the interfacial energy between aliphatic group and water and on the electrostatic energy. Therefore fatty acid ions should be associated into a grand ion with appropriate degree of association owing to the counterbalancing action of the interfacial and electric energy in water. If we assume that the grand ion with *n* degrees of association is formed spherically, then the radius of this sphere, ρ_n , is

$$\frac{4\pi}{3} \rho_n^3 = nv, \quad \frac{4\pi}{3} \rho_1^3 = v \quad (7)$$

where *v* is the volume of an alkyl group. The interfacial energies are

$$\epsilon_1' = 4\pi\rho_1^2\sigma^* - \Delta \quad \text{for an ion,} \quad (8)$$

$$\epsilon_n' = 4\pi\rho_n^2\sigma^* - n\Delta \quad \text{for an associated ion,} \quad (9)$$

where σ^* is the microscopic interfacial free energy between alkyl group and water, and Δ is the contribution due to the connection part of alkyl group to $-\text{COO}^-$ radical.

The total energies are

$$\sum \epsilon_1 = \epsilon_0 + \epsilon_1(A) + 4\pi\rho_1^2\sigma^* - \Delta \quad \text{for an ion,} \quad (10)$$

$$\sum \epsilon_n = n\epsilon_0 + \epsilon_n(A) + 4\pi\rho_n^2\sigma^* - n\Delta \quad \text{for an associated,} \quad (11)$$

and the energy difference per molecule is

$$\begin{aligned} \Delta\epsilon &= \sum \epsilon_1 - (\sum \epsilon_n/n) \\ &= 4\pi\rho_1^2\sigma^* - 4\pi\rho_n^2\sigma^*/n + \epsilon_1(A) \\ &\quad - n\epsilon^2/2\mu(\rho + \rho_n) \end{aligned} \quad (12)$$

The most probable degree of association is defined by

$$\partial(\Delta\epsilon)/\partial n = 0 \quad (13)$$

and is reduced to

$$\frac{4\pi}{3} \left(\frac{3}{4\pi} v \right)^{\frac{2}{3}} \sigma^* = \frac{\epsilon^2}{2\mu} \frac{n}{\left(\frac{3v}{4\pi} \right)^{\frac{1}{3}} + \frac{\rho}{n^{\frac{1}{3}}}} \times$$

$$\left\{ 1 - \frac{1}{3} \frac{\left(\frac{3}{4\pi} v \right)^{\frac{1}{3}}}{\left(\frac{3v}{4\pi} \right)^{\frac{1}{3}} + \frac{\rho}{n^{\frac{1}{3}}}} \right\} \quad (14)$$

From this condition, $n(\rho_n)$ is determined for the appropriate σ^* , and $\Delta\epsilon$ can be calculated with Eq. (12).

There are many molecules with various degrees of association in an aqueous solution of fatty acid salt, and the equilibrium schemes are



where A_n is the molecule with *n*-degree of association. If the partition functions of these molecules write Z_n , the equilibrium conditions are given as follows according to the statistical thermodynamic way to the dilute solution,

$$\begin{aligned} \frac{Z_{n-1}Z_1}{Z_n} &= \frac{N_{n-1}N_1}{N_0N_n}, \quad \frac{Z_{n-2}Z_1}{Z_{n-1}} = \frac{N_{n-2}N_1}{N_0N_{n-1}} \\ \therefore \frac{Z_1^n}{Z_n} &= \frac{N_1^n}{N_0^{n-1}N_n} \end{aligned} \quad (15)$$

in which N_0 is the number of the water molecules in the system and N_n is the number of the associated molecule A_n .

When the concentration *C* is expressed in mol/l., N_n is C_nN and N_0 is $1000 \times N/18$, in which *N* is the Avogadro's number, Eq. (15) is reduced to

$$\frac{C_n}{C_1} = \left(\frac{C_1}{\frac{1000}{18} \left(\frac{Z_1^n}{Z_n} \right)^{\frac{1}{n-1}}} \right)^{n-1} = \left(\frac{C_1}{C_0} \right)^{n-1},$$

$$\text{where} \quad C_0 = \frac{1000}{18} \left(\frac{Z_1^n}{Z_n} \right)^{\frac{1}{n-1}}. \quad (16)$$

We define the critical concentration C_c for the most probable degree of association as the apparent concentration at $C_n = C_1$ ($C_1 = C_0$),

$$C_c = (n+1)C_0 = (n+1) \frac{1000}{18} \left(\frac{Z_1^n}{Z_n} \right)^{\frac{1}{n-1}} \quad (17)$$

Then, the behaviour of C_n/C_1 versus C ($C = C_1 + nC_n$) is very characteristic. In the case of $C_1 < C_0$ ($C < C_c$), C_n/C_1 is far smaller than unity, but in the case of $C_1 > C_0$ ($C > C_c$), C_n/C_1 is far larger than unity, since *n* is usually far larger than unity. The property which depended mainly on the associated molecule is not distinguishable until *C* reaches to C_c but predominant beyond C_c . It is the nick point on the curve of property against concentration as shown in Fig. 3.

Rewriting the partition function Z as below

$$Z = Z_0 e^{-\sum \epsilon/kT} \quad \text{etc.,} \quad (18)$$

$\exp(-\sum \epsilon/kT)$ is the part owing to the energy of electrostatic and interfacial free energies, and Z_0 is the other part which is not mainly depended on the degree of association. C_c is expressed as

$$C_c = \frac{1000}{18} (n+1) e^{-\frac{n}{n-1} \frac{\Delta \epsilon}{kT}} \quad (19)$$

where $\Delta \epsilon$ is the value for the most probable degree of association.

IV. Calculated and Observed Values

Critical Concentration.—The values dotted in Fig. 4 are the experimental results which have been proceeded at various temperatures (18° – 60°)⁽¹⁾. Fortunately, the critical con-

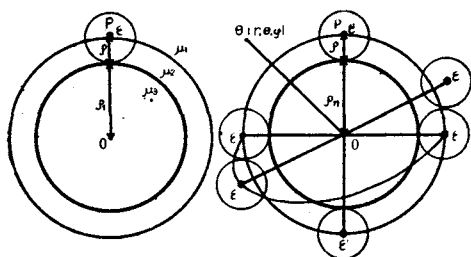


Fig. 2.

Table 1

No. of C atoms in alkyl radical R	5	6	8	10	12	14	16	18
Density of hydrocarbon HR at 20°C.	0.621	0.655	0.694	0.723	0.752	0.765	0.775	0.777
$\rho_1 \times 10^8$, cm.	3.58	3.73	4.02	4.26	4.47	4.67	4.86	5.05
$\epsilon_1(A) \times 10^{14}$, erg	0.7		0.9		1.0			1.1
$4\pi\sigma^*\rho_1^2 \times 10^{14}$, erg								
$\sigma^* = 40$, dyne/cm.	64.3	69.8	81.0	91.2	101	110	119	128
$\sigma^* = 42.5$	67.3	74.2	86.1	97.0	107	117	126	136
Degree of Association n								
$n = 40$	9.0	10	12.5	15	17	19	21.5	24
$n = 42.5$	9.5	11	13	15.5	18	20.5	23	25.5
$\rho_n \times 10^8$, cm.								
$\rho_n = 40$	7.5	8.0	9.3	10.3	11.4	12.5	13.5	14.5
$\rho_n = 42.5$	7.7	8.2	9.5	10.6	11.6	12.7	13.8	14.8
$\frac{4\pi\sigma^*\rho_n^2}{n} \times 10^{14}$, erg								
$n = 40$	30.9	32.2	34.9	37.2	39.5	41.1	42.5	44.5
$n = 42.5$	31.4	33.7	36.3	38.9	40.9	42.8	44.5	46.4
$\frac{n\epsilon^2}{2\mu(\rho+\rho_n)} \times 10^{14}$, erg								
$n = 40$	14.1	14.7	16.3	17.3	18.3	19.3	20.2	21.0
$n = 42.5$	14.7	15.4	16.9	18.0	19.0	20.1	21.0	22.0
$\Delta \epsilon \times 10^{14}$, erg								
$\Delta \epsilon = 40$	20.0	23.5	30.5	37.5	44.0	50.5	57.0	63.5
$\Delta \epsilon = 42.5$	22.0	26.0	33.5	41.0	48.0	55.0	61.5	69.0
Crit. conc.								
$C_c = 40$	2.5	1.0	0.25	6×10^{-2}	1.3×10^{-2}	3×10^{-3}	7×10^{-4}	1.7×10^{-4}
$C_c = 42.5$	1.5	0.9	0.10	2.5×10^{-2}	5×10^{-3}	1.3×10^{-3}	2.0×10^{-4}	5×10^{-5}

(1) K. Hess, *Kolloid Z.*, **88**, 40 (1939); *J. Am. Chem. Soc.*, **61**, 322, 539, 544, 549 (1939); Jander and Weitendorf, *Z. anorg. Chem.*, **41**, 197 (1934); Bury and Parry, *J. Chem. Soc.*, 629 (1935); Howell, *Proc. Roy. Soc. A* **115**, 386 (1936);

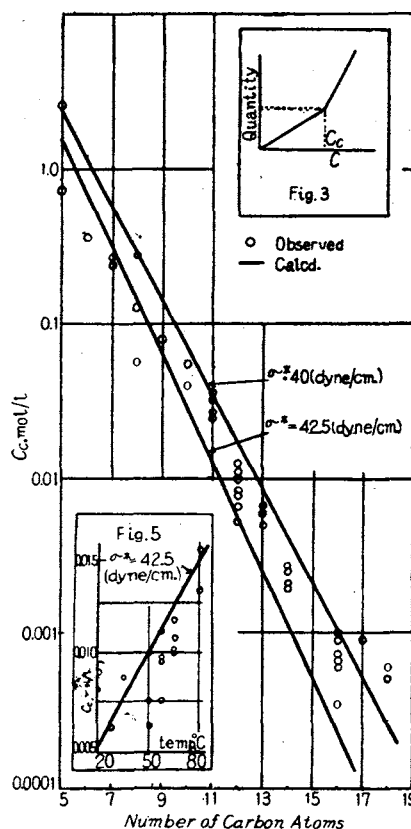


Fig. 4.

Lottermoser, *Kolloid Z.*, **63**, 175 (1935); Hartley, *Trans. Faraday Soc.*, **34**, 799, 1298, 2348 (1938); Ekwel, *Z. physik. Chem.*, **A** **161**, 195 (1932); Ulmann, *Z. physik. Chem.*, **A** **182**, 18 (1938).

Table 2

Temp. °C	Density of HR	μ	C_c equiv./l. calc.
20	0.752	80.0	0.005
40	0.738	73.0	0.008
60	0.722	66.8	0.011
80	0.708	61.8	0.015

($\sigma^* = 42.5$ dyne/cm.)

centrations are not so greatly changed in these temperature intervals, that we can plot these observed values without serious consideration about temperature at which the experiments were proceeded.

In order to calculate the critical concentration with Eq. (17), we are to assign the appropriate value for the volume of an alkyl-group. This is done by the calculation of molecular volume of the corresponding *n*-hydrocarbon at 20°. In Table 1, the calculated values are listed and the critical concentration at 20° for $\sigma^* = 40$ dyne/cm. and 42.5 dyne/cm. are shown by straight lines in Fig. 4.

Dependence on Temperature.—Since observed interfacial tension between water and hydrocarbon scarcely varies with temperature, we assume that the microscopic interfacial tension is also constant with temperature. Now dependence on temperature of critical concentration can be calculated easily, on which dielectric constant of water and temperature are mainly effecting. Observed and calculated values for dodecyl $C_{12}H_{25}$ -group derivatives are shown in Table 2 and Fig. 5.

Generally, the coincidences between observed and calculated values are satisfactory. The slope of the curve for calculated values is steeper than the observed. This would be caused from the fact that the observations for higher homologues ($C_{15}H_{31}$ -, $C_{16}H_{33}$ -, $C_{17}H_{35}$ -, $C_{18}H_{37}$ -, etc.) were done at higher temperature ($\sim 60^\circ$) than the calculation (20°), so that the observed critical concentrations are larger. It can be very easily accepted also that the microscopic interfacial tension between *n*-octane and water is as large as 42 dyne/cm., because the interfacial tension between *n*-octane and water is as large as 50 dyne/cm. at 20° .

I think that the procedure mentioned above is valuable for the estimation of microscopic interfacial free energy between water and aliphatic groups.

Appendix

(I) There is an electric system as shown in Fig. 2, in which the point charge exists at a outer point P. The potential at the point

(r, θ, φ) excluding P, is the solution of Laplacian equation $\nabla^2 \phi = 0$. Namely,

$$\phi = \sum_{\nu} \left(A_{\nu} r^{\nu} + \frac{B_{\nu}}{r^{\nu+1}} \right) S_{\nu} \quad (20)$$

where A_{ν} and B_{ν} are coefficients and S_{ν} is spherical harmonics.

When we divide the space into three parts; outer ($r \geq \rho + \rho_1$), mediate ($\rho + \rho_1 \geq r \geq \rho$) and inner ($r \leq \rho_1$), the potential in these regions are respectively

$$\left. \begin{aligned} \phi_1 &= \sum_{\nu} \frac{{}_1B_{\nu}}{r^{\nu+1}} P_{\nu}(\cos \theta) \\ \phi_2 &= \sum_{\nu} \left({}_2A_{\nu} r^{\nu} + \frac{{}_2B_{\nu}}{r^{\nu+1}} \right) P_{\nu}(\cos \theta) \\ \phi_3 &= \sum_{\nu} ({}_3A_{\nu} r^{\nu}) P_{\nu}(\cos \theta) \end{aligned} \right\} \quad (21)$$

where S_{ν} is replaced by P_{ν} , because the potential is completely symmetrical about Z axis. Of course, the electric charge should be considered as distributed on the sphere surface with radius $\rho + \rho_1$, which is expanded with spherical harmonics. Therefore, the surface charge at ($\rho + \rho_1, \theta, \varphi$) is expressed as

$$\sigma = \sum_{\nu} \frac{(2\nu+1)\epsilon}{4\pi(\rho+\rho_1)} P_{\nu}(\cos \theta) \quad (22)$$

The boundary conditions are

$$\left. \begin{aligned} \phi_1 &= \phi_2, -\mu_1 \frac{\partial \phi_1}{\partial r} + \mu_2 \frac{\partial \phi_2}{\partial r} = -4\pi\sigma \\ &\quad \text{at } r = \rho + \rho_1 \\ \phi_2 &= \phi_3, -\mu_2 \frac{\partial \phi_2}{\partial r} + \mu_3 \frac{\partial \phi_3}{\partial r} = 0 \\ &\quad \text{at } r = \rho_1 \end{aligned} \right\} \quad (23)$$

where $\mu_1 = \mu_2 (= \mu)$ and μ_3 are dielectric constants. From these boundary conditions and orthogonality of P_{ν} , the following equations are obtained:

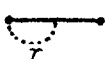
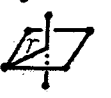
$$\left. \begin{aligned} {}_1A_{\nu}(\rho+\rho_1)^{\nu} + \frac{{}_2B_{\nu}}{(\rho+\rho_1)^{\nu+1}} &= \frac{{}_2B_{\nu}}{(\rho+\rho_1)^{\nu+1}} \\ \frac{(\nu+1){}_1B_{\nu}}{(\rho+\rho_1)^{\nu+2}} + \nu{}_2A_{\nu}(\rho+\rho_1)^{\nu-1} &= -\frac{(\nu+1){}_2B_{\nu}}{(\rho+\rho_1)^{\nu+2}} = -\frac{(2\nu+1)\epsilon}{\mu(\rho_1+\rho)^2} \\ {}_3A_{\nu}\rho_1^{\nu} &= {}_2A_{\nu}\rho_1^{\nu} + \frac{{}_2B_{\nu}}{\rho_1^{\nu+1}} \\ \mu_3{}_3A_{\nu} - \mu \left\{ {}_2A_{\nu} - \frac{(\nu+1){}_2B_{\nu}}{\rho^{\nu+2}} \right\} &= 0 \end{aligned} \right\} \quad (24)$$

Solving these simultaneous equations, we get

the values for coefficients A and B . Potential at point Q ($r \geq \rho + \rho_1$) is

$$\phi_1 = \frac{\epsilon}{\mu(\rho + \rho_1)} \times \left\{ \frac{\rho + \rho_1}{r \sqrt{1 - \frac{2(\rho + \rho_1)}{r} \cos \theta + \left(\frac{\rho + \rho_1}{r}\right)^2}} + \sum_{\nu=0}^{\infty} \frac{\nu(\mu - \mu_3)}{\nu(\mu + \mu_3) + \mu^2(\rho + \rho_1)} \frac{\rho_1^{2\nu+1} P_{\nu}(\cos \theta)}{r^{\nu+1}} \right\} \quad (25)$$

Table 3

Charge	Point charge system		Surface charge system	Ratio (S/P)
	Figure	Energy (P)	Energy (S)	
2e		$\frac{1}{2} \frac{\epsilon^2}{r}$	$2 \frac{\epsilon^2}{r}$	4.00
3e		$\sqrt{3} \frac{\epsilon^2}{r}$	$4.5 \frac{\epsilon^2}{r}$	2.60
4e		$\frac{3\sqrt{3}}{\sqrt{2}} \frac{\epsilon^2}{r}$	$8 \frac{\epsilon^2}{r}$	2.18
6e		$(6\sqrt{2} + 1.5) \frac{\epsilon^2}{r}$	$18 \frac{\epsilon^2}{r}$	1.80
8e		$(6\sqrt{3} + 3\sqrt{2} + 2) \frac{\epsilon^2}{r}$	$32 \frac{\epsilon^2}{r}$	1.65
12e		$(6\sqrt{2} + 8\sqrt{3} + 27) \frac{\epsilon^2}{r}$	$72 \frac{\epsilon^2}{r}$	1.46

From this equation, (2) can be derived for $\theta = 0$, $\cos \theta = 1$.

(II) We may compare the electrostatic energy of the point charge system with that of the spherical surface charge. The ratio approaches to unity when the number of charges becomes larger, as shown in Table 3. Now let us estimate the electrostatic energy of the system shown in Fig. 2, which is the degree of association 6, $\rho_6 = 6.03 \text{ \AA}$. (for oenanthylic acid ions), and $\rho = 1.80 \text{ \AA}$.

The estimation is easy, because $P_{\nu}(\cos \theta)$ in Eq. (25) are simple for $\theta = 0$, $\pi/2$ and π . The potential energy at P due to the other five charges is

$$\psi = 4\phi_6(\cos \theta = 0) + \phi_6(\cos \theta = -1)$$

in which ϕ_6 is the value for $r = \rho + \rho_6$ and $\rho_1 \rightarrow \rho_6$ in Eq. (25) and therefore the electrostatic energy is

$$\frac{1}{2} 6\epsilon \psi + 6\epsilon_1(A_1\rho_6) = 18.1 \frac{\epsilon^2}{\mu(\rho + \rho_6)}$$

for $\mu = 80$ and $\mu_3 = 2.3$.

Comparing it with the case of $\mu_3 = \mu = 1$ (Table 3), this value is more close to the surface charge 6ϵ on the sphere with radius $\rho + \rho_6$, i. e., $18.0 \epsilon^2 / \mu(\rho + \rho_6)$

Therefore, we may safely replace the point charge system with the spherical surface charge for much larger degree of association.

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Adsorption of Carbon Dioxide on Metal Catalysts

By Takao KWAN and Yuzaburo FUJITA

(Received November 13, 1950)

One of the present authors recently investigated the adsorption of carbon monoxide on platinum catalyst⁽¹⁾ with special reference to its state on platinum, and concluded that it was dissociated into statistically independent atoms. Developing the method further, carbon dioxide

adsorption was now investigated on reduced nickel, cobalt and iron respectively.

Adsorption isotherm of carbon dioxide is derived by introducing a set of functions p , q and θ due to Horiuti,⁽²⁾ respectively for the undissociative adsorption $\text{CO}_2 \rightleftharpoons \text{CO}_2(\text{a})$, for the

(1) Kwan, *J. Res. Inst. Catalysis*, Vol. 1, No. 2, 110 (1949).

(2) Horiuti, *J. Res. Inst. Catalysis*, Vol. 1, No. 1, 8 (1949).

partially dissociative one, $\text{CO}_2 \rightleftharpoons \text{CO(a)} + \text{O(a)}$, and for the completely dissociative one into three statistically independent atoms, $\text{CO}_2 \rightleftharpoons \text{C(a)} + \text{O(a)} + \text{O(a)}$, as follows;

$$\frac{\theta}{1-\theta} = \frac{q^{\text{CO}_2(\text{a})}}{p^{\text{CO}_2(\text{a})}} \quad (1.1)$$

$$\frac{\theta}{1-2\theta} = \frac{q^{\text{CO}(\text{a})}}{p^{\text{CO}(\text{a})}} = \frac{q^{\text{O}(\text{a})}}{p^{\text{O}(\text{a})}} \quad (1.2)$$

$$\frac{\theta}{1-3\theta} = \frac{q^{\text{C}(\text{a})}}{p^{\text{C}(\text{a})}} = \frac{q^{\text{O}(\text{a})}}{p^{\text{O}(\text{a})}} = \frac{q^{\text{O}(\text{a})}}{p^{\text{O}(\text{a})}} \quad (1.3)$$

where θ is the covered fraction of the surface and $q^{\text{CO}_2(\text{a})}$, $q^{\text{CO}(\text{a})}$, $q^{\text{C}(\text{a})}$ and $q^{\text{O}(\text{a})}$ are the functions particular to the adsorbed states $\text{CO}_2(\text{a})$, CO(a) , C(a) and O(a) expressed as,

$$q^{\text{CO}_2(\text{a})} = \prod (1 - e^{-\frac{h\nu_i}{kT}})^{-1} e^{-\frac{\epsilon_0 + \frac{1}{2}h\nu_i}{kT}}, \text{ etc.} \quad (2.g)$$

and $p^{\text{CO}_2(\text{a})}$, $p^{\text{CO}(\text{a})}$, $p^{\text{C}(\text{a})}$ and $p^{\text{O}(\text{a})}$ are related with the chemical potentials $\mu^{\text{CO}_2(\text{a})}$, $\mu^{\text{CO}(\text{a})}$, $\mu^{\text{C}(\text{a})}$ and $\mu^{\text{O}(\text{a})}$ of $\text{CO}_2(\text{a})$, CO(a) , C(a) and O(a) as,

$$\mu^{\text{CO}_2(\text{a})} = -RT \log p^{\text{CO}_2(\text{a})}, \text{ etc.} \quad (2.p(a))$$

and p^{CO_2} with the chemical potential of gaseous carbon dioxide μ^{CO_2} and hence with the ordinary partition function Q and its concentration N as,

$$\mu^{\text{CO}_2} = -RT \log p^{\text{CO}_2} = -RT \log Q/N \quad (2.p).$$

At adsorption equilibrium we have

$$\mu^{\text{CO}_2} = \mu^{\text{CO}_2(\text{a})} \quad (3.1)$$

$$\mu^{\text{CO}_2} = \mu^{\text{CO}(\text{a})} + \mu^{\text{O}(\text{a})} \quad (3.2)$$

$$\mu^{\text{CO}_2} = \mu^{\text{C}(\text{a})} + \mu^{\text{O}(\text{a})} + \mu^{\text{O}(\text{a})} \quad (3.3)$$

respectively for the case when CO_2 molecule is undissociated, partially dissociated or completely dissociated at the adsorbed state. From Eqs. (1), (2) and (3) we have

$$\frac{\theta}{1-\theta} = \frac{N q^{\text{CO}_2(\text{a})}}{Q} \quad (4.1)$$

$$\left(\frac{\theta}{1-2\theta} \right)^2 = \frac{N q^{\text{CO}(\text{a})} q^{\text{O}(\text{a})}}{Q} \quad (4.2)$$

$$\left(\frac{\theta}{1-3\theta} \right)^3 = \frac{N q^{\text{C}(\text{a})} q^{\text{O}(\text{a})} q^{\text{O}(\text{a})}}{Q} \quad (4.3)$$

Eqs. (4.1), (4.2) and (4.3) are expressed further in terms of the measurable quantities such as

the equilibrium pressure P and the differential heat of adsorption per mole $\Delta \epsilon$ neglecting the contribution from the higher vibrational levels of gaseous carbon dioxide molecules and for the case $\theta \ll 1$ as⁽⁴⁾

$$\theta = \frac{q^{\text{CO}_2(\text{a})} e^{\frac{T}{\partial T} \log q^{\text{CO}_2(\text{a})}}}{Q_0} P e^{\frac{\Delta \epsilon}{RT}} \quad (5.1)$$

$$\theta^2 = \frac{q^{\text{CO}(\text{a})} q^{\text{O}(\text{a})} e^{\frac{T}{\partial T} \log q^{\text{CO}(\text{a})} q^{\text{O}(\text{a})}}}{Q_0} P e^{\frac{\Delta \epsilon}{RT}} \quad (5.2)$$

$$\theta^3 = \frac{q^{\text{C}(\text{a})} q^{\text{O}(\text{a})} q^{\text{O}(\text{a})} e^{\frac{T}{\partial T} \log q^{\text{C}(\text{a})} q^{\text{O}(\text{a})} q^{\text{O}(\text{a})}}}{Q_0} P e^{\frac{\Delta \epsilon}{RT}} \quad (5.3)$$

where

$$Q_0 = kT \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \frac{8\pi^2 I kT}{sh^2} e^{\frac{1}{2}}$$

The investigation of the factors

$$q^{\text{CO}_2(\text{a})} e^{\frac{T}{\partial T} \log q^{\text{CO}_2(\text{a})}}, \text{ etc.}$$

in the above equations shows that every one of them is generally greater than 1 and approaches 1 as $h\nu_i \gg kT$. Assuming that the latter condition is fulfilled, we have

$$\theta \left. \begin{array}{l} \theta^2 \\ \theta^3 \end{array} \right\} = P e^{\frac{\Delta \epsilon}{RT}} / Q_0 \quad (6.1)$$

$$\theta^2 \left. \begin{array}{l} \theta^3 \end{array} \right\} = P e^{\frac{\Delta \epsilon}{RT}} / Q_0 \quad (6.2)$$

$$\theta^3 \left. \begin{array}{l} \theta^2 \end{array} \right\} = P e^{\frac{\Delta \epsilon}{RT}} / Q_0 \quad (6.3)$$

The above equations give relations between θ and P respectively appropriate to the three different adsorbed states affording a method of experimental determination of them.

Materials

Reduced Nickel.—1 g. of nickel oxide obtained by igniting the basic carbonate at 500° was thoroughly reduced at 350° similarly as described in the previous paper⁽⁴⁾ under several cm. Hg hydrogen for several days keeping the catalyst from volatile matter which might be evolved from stop-cock grease by means of liquid air trap attached directly to the catalyst vessel. The reduced nickel powder thus prepared was then subjected to the adsorption experiment of carbon dioxide and thereafter to the determination of the surface area by B. E. T. method using nitrogen at liquid oxygen temperature and the surface area was found to be 20 m^2 .

(3) The ϵ must be equal because of the stoichiometrical relation for CO(a) and O(a) or for C(a) , O(a) and another O(a) .

(4) Cf. Kwan, *J. Res. Inst. Catalysis*, Vol. 1, No. 2, 81 (1949).

Reduced Cobalt.—Reduced cobalt prepared by reducing 0.5 g. of cobalt oxide at 450° and once used for hydrogen adsorption was used again. The B. E. T. area of the catalyst was 7 m².

Reduced Iron.—Reduced iron prepared by reducing 2 g. of magnetite at 500° and once used for hydrogen adsorption and then for carbon monoxide adsorption as well was used again. The B. E. T. area of the catalyst was 4.2 m².

Carbon Dioxide.—Carbon dioxide was prepared by igniting sodium bicarbonate in an evacuated tube and traces of air and water vapors were removed by fractionation with liquid air.

Experimental Procedure

The apparatus and the general procedure for the measurement of adsorption equilibrium are identical with those of the previous paper.⁽⁴⁾ After any of the reduced metal catalysts has been prepared, U-trap is surrounded by copper gauge filled with copper powder whose bottom being slightly dipped into liquid air, then the temperature of U-trap can be kept at about -60° avoiding the condensation of carbon dioxide inside the U-tube on one hand and freezing out traces of volatile matter from stop-cock grease on the other.

The catalyst is then evacuated by means of mercury diffusion pump for one hour at 350°, one hour at 400° and one hour at 500° for nickel, cobalt and iron respectively. The known quantity of carbon dioxide is then admitted into the reaction vessel, which is maintained at a desired temperature by the electric furnace through the U-trap and the decrease in pressure is followed by McLeod gauge. After letting it stand for about 20 hours the equilibrium pressure is determined both from adsorption and desorption side by lowering or raising the temperature of the furnace.

Adsorbed quantity x is given by

$$x = P_0 V_0 / RT - \alpha P,$$

where $P_0 V_0 / RT$ is the quantity of carbon dioxide initially taken and P the equilibrium pressure. α is the constant depending on the temperature of the reaction vessel and is determined preliminarily keeping any part of the apparatus precisely the same but without a catalyst.

Additional portion of carbon dioxide is then successively admitted and the corresponding equilibrium pressure is similarly determined in respective cases.

Results

Nickel.—The rate of adsorption and of desorption as well were found appreciably quick as was in the case of hydrogen adsorption on this catalyst, suggesting that adsorption equilibrium was instantaneously attained. Any of equilibrium pressures was however

determined, after being left standing for about 20 hours, by approaching it both from adsorption and desorption side. Adsorption isotherms thus determined at 150° and 200° and at pressure ranging from 10⁻⁴ to 10⁻¹ mm. Hg are shown by the plot of logarithm of the adsorbed quantities against logarithm of the equilibrium pressure in Fig. 1. As shown in

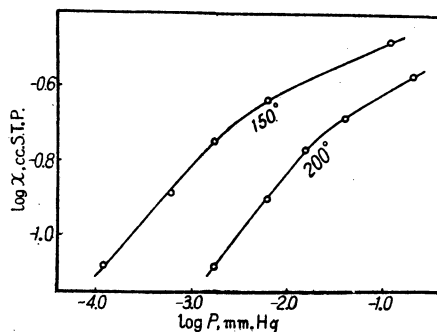


Fig. 1.—Adsorption isotherms of CO₂ on reduced nickel.

Fig. 1 the adsorbed quantity was found to be proportional to 1/3 power of the equilibrium pressure at the lower degree of adsorption, decreasing rapidly with increasing adsorption. It is apparent from the result that carbon dioxide adsorption takes place according to Eq. (6.3) viz. with completely dissociative adsorption at least in the lower pressure region.

Differential heat of adsorption $\Delta \epsilon$ calculated from the isotherms according to the usual expression $\Delta \epsilon = RT^2 (\partial \log P / \partial T)_x$ was almost constant at 22 kcal./mole over the range of the smaller adsorption.

Using the heat of adsorption derived, the covered fraction θ_{calc} was now calculated at 200° according to Eqs. (6.1), (6.2) or (6.3) and compared in Fig. 2 with θ_{obs} derived from the adsorbed quantity and the B. E. T. area of the adsorbent assuming that 10¹⁵ nickel atoms per square centimeter were available and each atom was equally capable of adsorbing CO₂(a), CO(a), C(a) or O(a)⁽⁵⁾.

It is obvious that θ_{obs} agrees fairly well with θ_{calc} derived from Eq. (6.3) and not with that from Eq. (6.1) or (6.2), hence showing that carbon dioxide molecule dissociates into three statistically independent atoms. Somewhat small value of θ_{calc} may be probably attributed to the simplification that $h\nu \gg kT$ in q_s .

(5) In the case of undissociative or partially dissociative adsorption, θ_{obs} may be more or less different according as whether CO₂ (a) or CO (a) occupies how many atoms of nickel. But this would be rather ignored as far as three adsorbed states, mentioned above, concern where θ_{calc} 's in interest are much more differed with each other.

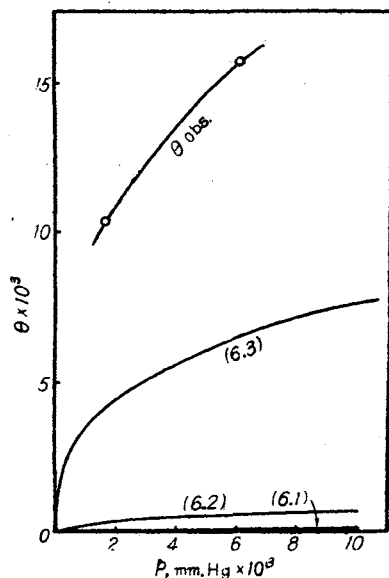


Fig. 2.—The relation between θ and P on reduced nickel, $T=200^\circ\text{C}$.

although we have no available data with respect to ν_{ts} of C(a) or O(a).

In the case of the adsorbed hydrogen atom H(a) on reduced nickel, Horiuti and co-workers⁽⁶⁾ obtained three vibrational frequencies by calculation as

$$417 \text{ cm.}^{-1} \quad 479 \text{ cm.}^{-1} \quad 1900 \text{ cm.}^{-1}$$

taking into consideration the potential of the surrounding nickel atoms upon the adsorbed hydrogen atom for the (110) plane.

On the basis of these values the calculation of the factor $q^{\text{H(a)}} e^{-\frac{T \partial \log q^{\text{H(a)}}}{\partial T}}$ was carried out, affording 7, 5 and 2 at 300° , 200° and 20° respectively. The experimental facts on reduced nickel or cobalt⁽³⁾ however revealed, as reported previously, that the above factor was approximately 1, giving no temperature effect below 300° . It seems likely that the assumption $h\nu_i \gg kT$ in q 's hold enough as far as the hydrogen adsorption on these catalysts concerns.

Reduced Cobalt.—Adsorption isotherms of carbon dioxide on reduced cobalt were determined similarly, as those of reduced nickel at 0° and 40° and below 0.1 mm. Hg as shown in Fig. 3. The isotherms appear to obey nearly Freundlich's type in this case, probably missing such a lower degree of adsorption as

proportional to $1/8$ -power of the equilibrium pressure.

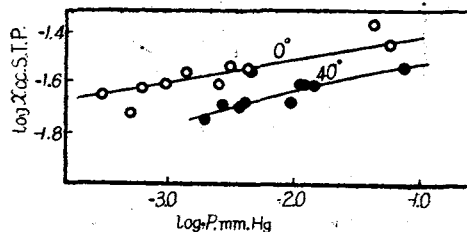


Fig. 3.—Adsorption isotherms of carbon dioxide on reduced cobalt.

Differential heat of adsorption calculated therefrom was found to be 14 kcal./mole. Using the heat of adsorption derived, θ_{calc} s were calculated at 0° similarly as in the case of nickel and were compared in Fig. 4 with θ_{obs} showing the satisfactory agreement of the latter with θ_{calc} derived from Eq. (6.3) at a very low degree of adsorption and θ_{obs} rapidly flattened with increasing adsorption.

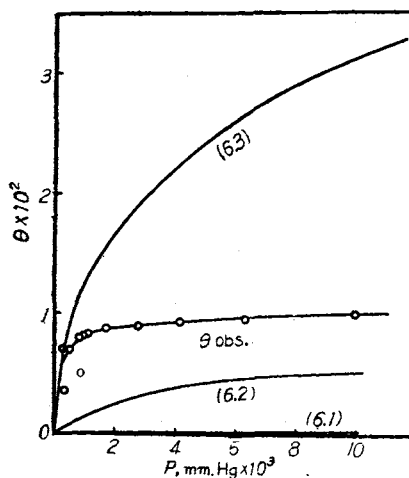


Fig. 4.—The relation between θ and P on reduced cobalt. $T=0^\circ\text{C}$.

Reduced Iron.—The adsorption isotherms on reduced iron determined at 0° and 25° similarly as in the case of nickel or cobalt are shown in Fig. 5. Differential heat of adsorption calculated therefrom was found to be 15.5 kcal./mole at the lower degree of adsorption. The plot of the covered fraction θ_{obs} against the equilibrium pressure P in the present case lies without agreeing with any θ_{calc} given by Eqs. (6.1), (6.2), (6.3) as shown in Fig. 6, being more or less differed from the results given by the two catalysts cited above.

(6) Horiuti, Okamoto and Hirota. *Sci. Rep. Inst. Phys. Chem. Res. Tokyo*, **29**, 223 (1933).

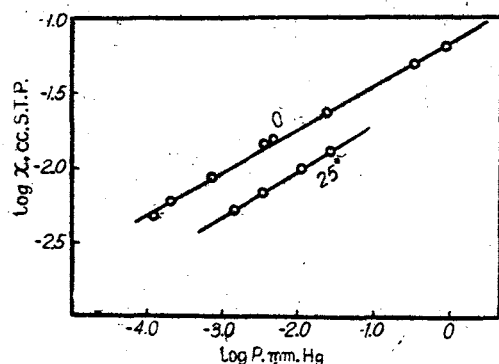


Fig. 5.—Adsorption isotherms of carbon dioxide on reduced iron.

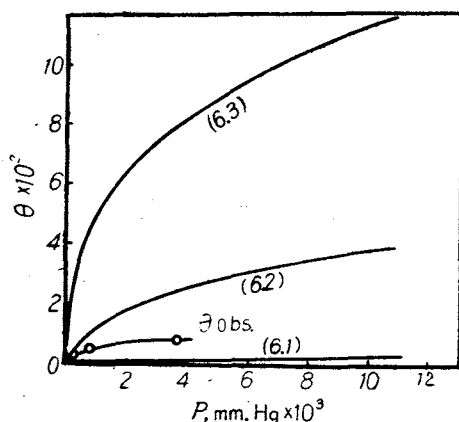


Fig. 6.—The relation between θ and P on reduced iron. $T=0^\circ\text{C}$.

It should be however remembered that the surface of the reduced iron is not homogeneous on the basis of the statistical mechanical investigation of hydrogen adsorption,⁽⁷⁾ exposing at least two crystal planes. We hereby have to take into consideration quantitatively the extent of heterogeneity of the surface.

It is now assumed that two crystal planes 1 and 2 are exposed and every iron atom at the surface behaves physically identical even in the case of carbon dioxide adsorption, namely, the corresponding heats of adsorption of carbon dioxide $\Delta\epsilon_1$ and $\Delta\epsilon_2$ appear iden-

tically with those of hydrogen adsorption. The observed heat of adsorption of carbon dioxide $\Delta\epsilon$ at a very low degree of adsorption would hence reveal $\Delta\epsilon_1$ of the plane 1 provided that $\Delta\epsilon_1 \gg \Delta\epsilon_2$.

The ratio of $\theta_{\text{obs.}}$ to $\theta_{\text{calc.}}$ calculated statistically mechanically using the observed heat of adsorption $\Delta\epsilon$ means the fraction of that "active" plane 1 as described in the previous paper, i. e.

$$\frac{\theta_{\text{obs.}}}{\theta_{\text{calc.}}} = \frac{N_1}{N_1 + N_2}$$

where N_1 and N_2 are the numbers of iron atom respectively belong to the plane 1 and 2. $N_1/N_1 + N_2$ is about 1/100 according to the previous investigation of this catalyst. Hence multiplying 100 to $\theta_{\text{obs.}}$, $\theta_{\text{calc.}}$ we find a better agreement between $\theta_{\text{obs.}}$ and $\theta_{\text{calc.}}$ derived from Eq. (6.3) with regard to the order of magnitude, leading to the same conclusion on the adsorbed state of carbon dioxide as in the case of nickel or cobalt.

Summary

Differential heat of adsorption of carbon dioxide on reduced nickel, cobalt or iron catalyst was determined by the indirect method at the lower degree of adsorption with particular precaution for securing thermodynamical equilibrium, being found at 22, 14 and 15.5 kcal./mole respectively. Using the heat of adsorption derived adsorption isotherms were investigated statistically mechanically with reference to the adsorbed state of carbon dioxide molecule, leading to the conclusion that the molecule dissociates into three statistically independent atoms in any case of the catalysts.

The authors express hearty thanks to the Director of the Institute J. Horiuti for his kind and valuable direction on this work. The cost of this research has been defrayed from the Scientific Research Encouragement Grant from the Ministry of Education, to which the authors' thanks are due.

(7) Kwan, *J. Res. Inst. Catalysts*, Vol. 1, No. 2, 100 (1949).

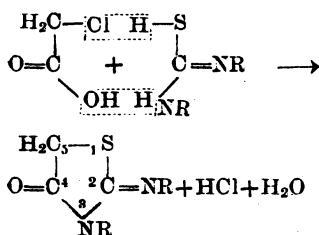
Synthesis of 2-Arylimino-3-aryl-4-kefo-tetrahydrothiazoles by Condensing Di-Arylthioureas with Monochloroacetic Acid

By Prithwi Nath Bhargava

(Received November 18, 1950)

A number of sulfathiazoles have been known for their therapeutic properties and have been universally used as drugs. Amidothiazoles and their isomers were reported by Jacobson⁽¹⁾ and Jacobson and Ney.⁽²⁾ Nitroso-compounds of thiazoles were synthesised previously by Hantzsch⁽³⁾ and Hantzsch *et al.*⁽⁴⁾ Goldberg and Kelley⁽⁵⁾ synthesised 2- ω -aminoalkyl- and 2- ω -sulfanilamidoalkyl derivatives of thiazoles. Gregory and Wiggins⁽⁶⁾ studied 2:4-dimethylthiazole derivatives and 2:4:5-trimethyl thiazole. Recently Alexander R. Surrey has prepared 3-alkyl (and aralkyl) -2-aryl-4-thiazolidones⁽⁷⁾ and 3-alkylaminoalkyl-2-aryl-4-thiazolidones.⁽⁸⁾

The author has carried out the condensations of monochloroacetic acid with diphenylthiourea, di-*o*-tolylthiourea, di-*p*-tolylthiourea, di- α -naphthylthiourea, di- β -naphthylthiourea, di-*p*-anisylthiourea, and di-*p*-phenethylthiourea. The general method of preparation is analogous to the formation of 2-imino-4-keto-tetrahydrothiazole^{(9),(10)} by condensing thiourea with monochloroacetic acid and subsequently dehydrating by heating with glacial acetic acid.



The synthesis has been accomplished on standard lines, thereby showing the constitution of the compounds. All these condensation products are solids of high melting points.

The formation of semicarbazones of the respective compounds gives evidence regarding the presence of a keto-group.

Experimental

2-Phenylimino-3-phenyl-4-keto-tetrahydrothiazole.—To a mixture of thiocarbanilide (22.8 g.), monochloroacetic acid (12.0 g.) and finely powdered anhydrous sodium acetate (12.3 g.) in a dry flask was added 50 cc. of absolute alcohol and the above boiled on a water-bath for 2 hours. Towards the end of the condensation, some of the product separated in leaflets. The major portion of the alcohol was distilled off and the contents of the flask were poured out into a porcelain dish to crystallise. The crystals were washed with cold water to remove excess of monochloroacetic acid. It was purified by recrystallising three times from hot absolute alcohol. Colorless laminae (23.76 g.), m. p. 176° (Found: N, 10.45. Calcd. for $C_{15}H_{12}N_2OS$: N, 10.44%).

Semicarbazone.—The above 2-phenylimino-3-phenyl-4-keto-tetrahydrothiazole (250 mg.) was dissolved in 95% alcohol (20 cc.) and to this semicarbazide hydrochloride (300 mg.) and anhydrous sodium acetate (500 mg.) were added. The whole mixture was refluxed for 15 minutes and poured into water. The crystals were collected and recrystallised from absolute alcohol in needles, m. p. 194° (Found : N, 21.58. Calcd. for $C_{16}H_{15}N_5OS$: N, 21.53%).

2-*o*-Tolylimino-3-*o*-tolyl-4-keto-tetrahydrothiazole.—A suspension of di-*o*-tolylthiourea (12.4 g.) in absolute alcohol (50 cc.) was heated under reflux with monochloroacetic acid (6.0 g.) and anhydrous sodium acetate (6.0 g.) for 2 hours. The condensation was effected, and the product was isolated as described above. The residue on crystallisation from absolute alcohol and drying in vacuum at 110° over phosphorus pentoxide yielded white needles (12.18 g.), m. p. 154–155° (Found: N, 9.44. Calcd. for $C_{17}H_{15}N_2OS$: N, 9.46%).

Semicarbazone.—2-*o*-Tolylimino-3-*o*-tolyl-4-keto-tetrahydrothiazole (260 mg.) was dissolved in 95% alcohol (20 cc.) and refluxed with semicarbazide hydrochloride (300 mg.) and anhydrous sodium acetate (300 mg.) for 20 minutes. On pouring the mixture into water (80 cc.) a precipitate was obtained, which was crystallized from absolute alcohol in leaflets, m. p. 18° (Found: N, 19.85; calcd. for $C_{15}H_{13}N_5OS$: N, 19.83%).

2-*p*-Tolylimino-8-*p*-tolyl-4-keto-tetrahydro-

- (1) Jacobson, *Ber.*, **19**, 1067 (1896).
- (2) Jacobson and Ney, *ibid.*, **22**, 904 (1889).
- (3) Hantzsch, *Ann.*, **262**, 250 (1889).
- (4) Hantzsch *et al.*, *ibid.*, **265**, 108 (1889).
- (5) Goldberg and Kelley, *J. Chem. Soc.*, **1947**, 1372.
- (6) Gregory and Wiggins, *ibid.*, **1947**, 1400.
- (7) Alexander R. Surrey, *J. Am. Chem. Soc.*, **70**, 4262 (1948).
- (8) Alexander R. Surrey, *ibid.*, **71**, 3564 (1949).
- (9) P. N. Bhargava, *Proc. Ind. Sci. Cong. Chem. Sec. Abstr.*, **1949**, 78.
- (10) R. D. Desai, R. F. Hunter and L. G. Koppa, *Rec. trav. chim.*, **54**, 118 (1935).

thiazole.—A mixture of di-*p*-tolylthiourea (12.0 g.), monochloroacetic acid (6.2 g.), anhydrous sodium acetate (6.0 g.) and absolute alcohol (45 cc.) was refluxed on a water-bath for 3 hours. The condensation was effected as above and the residual product was crystallised three times from absolute alcohol in cream colored feathery crystals (12.2 g.), m. p. 128° (Found : N, 9.49. Calcd. for $C_{17}H_{16}N_2OS$: N, 9.46%).

Semicarbazone.—A mixture of 2-*p*-tolylimino-3-*p*-tolyl-4-keto-tetrahydrothiazole (270 mg.), semicarbazide hydrochloride (300 mg.), anhydrous sodium acetate (500 mg.) and 95% alcohol (20 cc.) was refluxed for 15 minutes and then poured into water (60 cc.). The precipitate was crystallised two times from absolute alcohol in needles, m. p. 152° (Found: N, 19.78. Calcd. for $C_{18}H_{19}N_5OS$: N, 19.83%).

2- α -naphthylimino-3- α -naphthyl-4-keto-tetrahydrothiazole.—A mixture of di- α -naphthylthiourea (6.8 g.), monochloroacetic acid (3.0 g.), anhydrous sodium acetate (4.0 g.) and absolute alcohol (50 cc.) was heated on a steam-bath under reflux for 3 hours. The reaction was effected as above and the residue after washing free from acid was crystallised four times from absolute alcohol in grey leaflets (6.25 g.), m. p. 172–173° (Found : N, 7.63. Calcd. for $C_{23}H_{16}N_2OS$: N, 7.6%).

Semicarbazone.—The above compound (300 mg.) was treated with 95% alcohol (20 cc.), semicarbazide hydrochloride (280 mg.) and anhydrous sodium acetate (450 mg.) and refluxed for 15 minutes. The mixture was poured into water (60 cc.) and the precipitate crystallised two times from absolute alcohol in leaflets, m. p. 186° (Found : N, 16.45. Calcd for $C_{24}H_{19}N_5OS$: N, 16.47%).

2- β -Naphthylimino-3- β -naphthyl-4-keto-tetrahydrothiazole.—Di- β -naphthylthiourea (7.0 g.) was suspended in absolute alcohol (50 cc.) and refluxed with monochloroacetic acid (3.0 g.) and finely powdered anhydrous sodium acetate (5.0 g.) for 3 hours on a steam-bath. The condensation was effected as above and the product after washing free from acid was crystallised three times from absolute alcohol in dark red needles (6.28 g.), m. p. 192–193° (Found : N, 7.56. Calcd. for $C_{23}H_{16}N_2OS$: N, 7.6%).

Semicarbazone.—A mixture of the above compound (320 mg.), 95% alcohol (20 cc.), semicarbazide hydrochloride (290 mg.) and finely powdered anhydrous sodium acetate (420 mg.) was refluxed for 15 minutes. The mixture was poured into water and the precipitate crystallised from absolute alcohol in brown needles, m. p. 208° (Found: N, 16.5. Calcd. for $C_{24}H_{19}N_5OS$: N, 16.47%).

2-*p*-Anisylimino-3-*p*-anisyl-4-keto-tetrahydrothiazole.—A suspension of di-*p*-anisylthiourea

(5.5 g.) in absolute alcohol (40 cc.) was treated with monochloroacetic acid (3.0 g.) and finely powdered anhydrous sodium acetate (4.0 g.) and refluxed for 3 hours on a steam-bath. The product after condensation was filtered rapidly while hot. The solvent was recovered by distillation and the residue crystallised three times from absolute alcohol in black needles (5.16 g.), m. p. 107–108° (Found: N, 8.56. Calcd. for $C_{17}H_{16}N_2O_2S$: N, 8.53%).

Semicarbazone.—The above compound (320 mg.), 95% alcohol (20 cc.), semicarbazide hydrochloride (300 mg.) and finely powdered anhydrous sodium acetate (400 mg.) were refluxed for 20 minutes. The mixture was poured into water and the precipitate crystallised from absolute alcohol in dark brown needles, m. p. 120° (Found: N, 18.26. Calcd. for $C_{18}H_{19}N_5O_2S$: N, 18.18%).

2-*p*-Phenylimino-3-*p*-phenetyl-4-keto-tetrahydrothiazole.—Di-*p*-phenethylthiourea (7.0 g.) was dissolved in absolute alcohol (50 cc.) and refluxed with monochloroacetic acid (3.0 g.) and anhydrous sodium acetate (4.0 g.) for 4 hours on a steam-bath. The resulting product after condensation was crystallised from absolute alcohol in brown needles (6.6 g.), m. p. 105–106° (Found : N, 7.84. Calcd. for $C_{19}H_{20}N_2O_2S$: N, 7.86%).

Semicarbazone.—A mixture of 2-*p*-phenylimino-3-*p*-phenetyl-4-keto-tetrahydrothiazole (350 mg.) in 95% alcohol (22 cc.), semicarbazide hydrochloride (260 mg.) and finely powdered anhydrous sodium acetate (450 mg.) was refluxed on a steam-bath for 25 minutes. It was then poured into water and the precipitate crystallised from absolute alcohol in dark brown leaflets, m. p. 140° (Found: N, 16.98. Calcd. for $C_{20}H_{23}N_5O_2S$: N, 16.95%).

Summary

(1) 2-Arylimino-3-aryl-4-keto-tetrahydrothiazoles were prepared by condensation of di-arylthioureas with monochloroacetic acid in the presence of anhydrous sodium acetate and absolute alcohol.

(2) The formation of semicarbazones of 2-arylimino-3-aryl-4-keto-tetrahydrothiazoles has revealed the presence of a keto-group.

The author is indebted to the Uttar Pradesh Government Scientific Research Committee for a grant which made this work possible and also to the authorities of the Banaras Hindu University for providing facilities in the Laboratory of Organic Chemistry.

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Determination of Dielectric Constant and Loss Factor by Free Wave Method. I. Theoretical Part

By Masasi YASUMI⁽¹⁾

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Introduction

Recently microwave technique has been developed rapidly, and the determination of dielectric constant and loss factor in microwave region has become important. Great variety of methods has been devised for this purpose among which the wave guide method is used generally. However earlier experiments were made by means of free wave method. The reason why the free wave method is not used generally lies partly in the incompleteness of the method of calculation to determine dielectric constant and loss factor from the values of reflection or transmission coefficient experimentally obtained.

To find a precise and convenient method for this purpose, it seems desirable to determine theoretically the reflection and transmission coefficient of electromagnetic waves by multiple layer.

In this paper a theoretical formula will be derived for the reflection and transmission coefficient by multiple layer by solving Maxwell's equation in an orthodox way.

At the same time a convenient method will be reported for the determination of dielectric constant and loss factor from the values of reflection or transmission coefficient obtained by experiment.

Reflection and Transmission of Electromagnetic Wave by Multiple Layer. Behavior of Electromagnetic Wave in the Layer.

1. Fundamental Equations and Solutions.

—If an electromagnetic wave is propagated in an isotropic and uniform medium, the electric field and magnetic field vectors will satisfy the following Maxwell's equations,⁽²⁾

$$\frac{\epsilon'}{c} \frac{\partial \mathcal{E}}{\partial t} + \frac{4\pi\sigma}{c} \mathcal{E} = \text{rot } \mathcal{H} \quad (1a)$$

$$-\frac{1}{c} \frac{\partial \mathcal{H}}{\partial t} = \text{rot } \mathcal{E} \quad (1b)$$

$$\text{div } \mathcal{E} = 0 \quad (1c)$$

$$\text{div } \mathcal{H} = 0 \quad (1d)$$

where ϵ' denotes dielectric constant, σ conductivity, c the velocity of light and $\mathcal{E}$ and $\mathcal{H}$ are electric and magnetic field vectors, respectively.

The electromagnetic wave is assumed to be propagated along x -axis (from minus to plus) and to be linearly polarized. Electric and magnetic field vectors are assumed to lie on y -axis and z -axis, respectively. Then the solution of Eq. (1) is expressed as:⁽³⁾

$$\mathcal{E}_y = ae^{i\omega(t - \frac{yx}{c})} \quad (2a)$$

$$\mathcal{H}_z = a\mu e^{i\omega(t - \frac{yx}{c})} \quad (2b)$$

where

$$p^2 = \epsilon' - i \frac{4\pi\sigma}{\omega} \quad (3)$$

Here ω denotes circular frequency and a , a constant.

We rewrite Eq. (3) as follows:

$$p^2 = \epsilon' - i\epsilon'' \quad (3')$$

where

$$\epsilon'' = \frac{4\pi\sigma}{\omega} \quad (4)$$

If we write

$$p = n - ik \quad (5)$$

then n and k are expressed as

$$n^2 = \frac{1}{2} \{ \sqrt{\epsilon'^2 + \epsilon''^2} + \epsilon' \} \quad (6a)$$

$$k^2 = \frac{1}{2} \{ \sqrt{\epsilon'^2 + \epsilon''^2} - \epsilon' \} \quad (6b)$$

As stated above the electromagnetic wave is assumed to be propagated from $x = -\infty$ to $x =$

(1) Present address: Institute of Science and Technology, the University of Tokyo, Tokyo.

(2) The magnetic permeability of the medium μ is assumed to be 1.

(3) R. Becker "Theorie der Elektrizität" I, Leipzig and Berlin, 1933, p. 183.

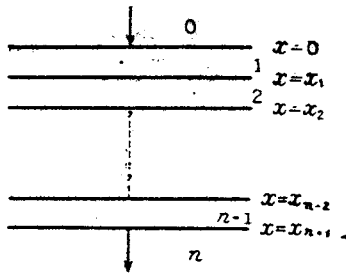


Fig. 1.

$+\infty$ A multiple layer consisting of $(n-1)$ sheets is placed with their boundary surfaces on $y-z$ planes as shown in Fig. 1. The origin of x -coordinate lies on the first boundary surface and the x -coordinate of the boundary surface between r th and $(r-1)$ th layers is noted x_r . Between $x=-\infty$ and $x=0$, there exists a semi-infinite medium, and another between $x=x_{n-1}$ and $x=+\infty$. They are numbered as 0 and n , respectively.

The electric and magnetic field vectors in $0, 1, \dots, r, \dots, (n-1), n$ media will be expressed by the following equations.

$$\mathcal{E}_y^{(0)} = a \{ e^{i\omega(t - \frac{p_0 x}{c})} + \mathcal{R}_0 e^{i\omega(t + \frac{p_0 x}{c})} \} \quad (7a)$$

$$\mathcal{H}_z^{(0)} = a p_0 \{ e^{i\omega(t - \frac{p_0 x}{c})} - \mathcal{R}_0 e^{i\omega(t + \frac{p_0 x}{c})} \} \quad (7b)$$

.....
.....

$$\mathcal{E}_y^{(r)} = a [\partial_r e^{i\omega(t - \frac{p_r(x-x_r)}{c})} + \mathcal{R}_r e^{i\omega(t + \frac{p_r(x-x_r)}{c})}] \quad (8a)$$

$$\mathcal{H}_z^{(r)} = a p_r [\partial_r e^{i\omega(t - \frac{p_r(x-x_r)}{c})} - \mathcal{R}_r e^{i\omega(t + \frac{p_r(x-x_r)}{c})}] \quad (8b)$$

$r = 1, 2, \dots, r, \dots, (n-2), (n-1).$

$$\mathcal{E}_y^{(n)} = a \partial_n e^{i\omega(t - \frac{p_n(x-x_{n-1})}{c})} \quad (9a)$$

$$\mathcal{H}_z^{(n)} = a p_n \partial_n e^{i\omega(t - \frac{p_n(x-x_{n-1})}{c})} \quad (9b)$$

$a\mathcal{R}_r$ and $a\partial_r$ denote the complex amplitude of the electric vector of reflected and penetrating waves at $x = x_r$, respectively.

2. Boundary Conditions.—The boundary conditions require that the electric and magnetic field vectors are continuous on the $x = x_r$ surfaces.

From the continuity of $\mathcal{E}_y$ on the surface $= 0$, we have

$$1 + \mathcal{R}_0 = \partial_1 e^{i\omega p_1 \frac{x_1}{c}} + \mathcal{R}_1 e^{-i\omega p_1 \frac{x_1}{c}} \quad (10_1)$$

and from the continuity of $\mathcal{H}_z$ on the surface $x = 0$, we have

$$p_0(1 - \mathcal{R}_0) = p_1 \{ \partial_1 e^{i\omega p_1 \frac{x_1}{c}} - \mathcal{R}_1 e^{-i\omega p_1 \frac{x_1}{c}} \}. \quad (10_2)$$

Similarly on the surface $x = x_1$, the boundary conditions require

$$\partial_1 + \mathcal{R}_1 = \partial_2 e^{i\omega p_2 \frac{(x_2-x_1)}{c}} + \mathcal{R}_2 e^{-i\omega p_2 \frac{(x_2-x_1)}{c}} \quad (10_3)$$

$$p_1(\partial_1 - \mathcal{R}_1) = p_2 \{ \partial_2 e^{i\omega p_2 \frac{(x_2-x_1)}{c}} - \mathcal{R}_2 e^{-i\omega p_2 \frac{(x_2-x_1)}{c}} \}. \quad (10_4)$$

In general, on the surface $x = x_r$, we have

$$\partial_r + \mathcal{R}_r = \partial_{r+1} e^{i\omega p_{r+1} \frac{(x_{r+1}-x_r)}{c}} + \mathcal{R}_{r+1} e^{-i\omega p_{r+1} \frac{(x_{r+1}-x_r)}{c}} \quad (10_{2r+1})$$

$$p_r(\partial_r - \mathcal{R}_r) = p_{r+1} \{ \partial_{r+1} e^{i\omega p_{r+1} \frac{(x_{r+1}-x_r)}{c}} - \mathcal{R}_{r+1} e^{-i\omega p_{r+1} \frac{(x_{r+1}-x_r)}{c}} \} \quad (10_{2r+2})$$

Finally from the boundary condition at $x = x_{n-1}$, the following equations are obtained.

$$\partial_{n-1} + \mathcal{R}_{n-1} = \partial_n \quad (10_{2n-1})$$

$$p_{n-1}(\partial_{n-1} - \mathcal{R}_{n-1}) = p_n \partial_n \quad (10_{2n})$$

We put $i\omega p_{r+1}(x_{r+1}-x_r)/c = a_{r+1}$, and rewrite above equations as follows:

$$\left. \begin{aligned} \mathcal{R}_0 - \partial_1 e^{+a_1} - \mathcal{R}_1 e^{-a_1} &= -1 \\ -p_0 \mathcal{R}_0 - p_1 \partial_1 e^{+a_1} + p_1 \mathcal{R}_1 e^{-a_1} &= -p_0 \\ \partial_1 + \mathcal{R}_1 - \partial_2 e^{+a_2} - \mathcal{R}_2 e^{-a_2} &= 0 \\ p_1 \partial_1 - p_1 \mathcal{R}_1 - p_2 \partial_2 e^{+a_2} + p_2 \mathcal{R}_2 e^{-a_2} &= 0 \\ \dots\dots\dots \\ \partial_{n-1} + \mathcal{R}_{n-1} - \partial_n &= 0 \\ p_{n-1} \partial_{n-1} - p_{n-1} \mathcal{R}_{n-1} - p_n \partial_n &= 0. \end{aligned} \right\} \quad (11)$$

We regard the equations (11) as a system of linear simultaneous equations of $2n$ unknown variables $\mathcal{R}_0, \partial_1, \mathcal{R}_1, \dots, \partial_{n+1}, \mathcal{R}_{n+1}$, and ∂_n . For the existence of non-trivial solution of Eqs. (11) it is necessary that the following determinant does not vanish:

by free wave method lie partly in the calculation of their values from the reflection or transmission coefficient experimentally obtained. In the following we shall report a convenient method for the determination of dielectric constant and loss factor from the reflection coefficient of a dielectric sheet placed on a metal plate. In the case where the refractive index is much greater than absorption coefficient, we can derive approximate formulae which enable us to compute these quantities from the experimental values of the reflection coefficient. In other cases when these approximate formulae do not hold, we may make tables which are convenient for the evaluation of these values.

1. Reflection of Electromagnetic Wave by a Dielectric Layer on a Metal.—The plane electromagnetic wave is considered to be linearly polarized and to be propagated from the air into a dielectric sheet on a metal at normal incidence as shown in Fig. 2. The complex reflection coefficient is to be expressed as follows:

$$\mathfrak{R} = \frac{\mathfrak{R}_{12} + \mathfrak{R}_{23} e^{-\frac{2i\omega pd}{c}}}{1 + \mathfrak{R}_{12}\mathfrak{R}_{23} e^{-\frac{2i\omega pd}{c}}} \quad (28)$$

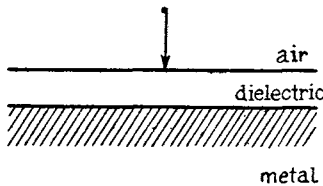


Fig. 2.

The equation (28) is essentially the same as the Eq. (22), but we have changed the subscripts in accordance with the convention adopted in other literatures.

Let ϵ' , and ϵ'' respectively be the dielectric constant and loss factor of the dielectric and p^2 be $\epsilon' - i\epsilon''$. We have then

$$\mathfrak{R}_{12} = -\frac{(p-1)}{(p+1)}; \quad \mathfrak{R}_{23} = -1$$

and therefore,

$$\mathfrak{R} = -\left[\frac{-\mathfrak{R}_{12} + e^{-\frac{2i\omega pd}{c}}}{1 + \mathfrak{R}_{12} e^{-\frac{2i\omega pd}{c}}} \right] \quad (29)$$

If we put

$$\mathfrak{R}_{12} = -R_{12}e^{-i\gamma}, \quad (30)$$

then

$$R_{12} = \sqrt{\frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}} \quad (31)$$

and

$$\tan \gamma = \frac{2k}{(n^2-1) + k^2} \quad (32)$$

The square of the absolute value of $\mathfrak{R}$ is expressed as follows:

$$\begin{aligned} R^2 &= \frac{\sinh^2\left(\frac{2\pi kd}{\lambda} + \frac{1}{2} \ln R_{12}\right) + \cos^2\left(\frac{2\pi nd}{\lambda} - \frac{\gamma}{2}\right)}{\sinh^2\left(\frac{2\pi kd}{\lambda} - \frac{1}{2} \ln R_{12}\right) + \cos^2\left(\frac{2\pi nd}{\lambda} + \frac{\gamma}{2}\right)} \\ &= \frac{R_{12}^2 + e^{-\frac{8\pi kd}{\lambda}} + 2R_{12}e^{-\frac{4\pi kd}{\lambda}} \cos\left(\frac{4\pi nd}{\lambda} - \gamma\right)}{1 + R_{12}^2 e^{-\frac{8\pi kd}{\lambda}} + 2R_{12}e^{-\frac{4\pi kd}{\lambda}} \cos\left(\frac{4\pi nd}{\lambda} + \gamma\right)} \quad (33) \end{aligned}$$

where λ denotes the wave length of the electromagnetic wave in the air. R^2 may be called reflection coefficient, and represents the ratio of the intensity of the reflected wave to that of the incident wave.

n is the refractive index and k is the absorption coefficient of the material composing the dielectric sheet of the thickness d . They are related to p , ϵ' , and ϵ'' through the Eqs. (5) (6a) and (6b).

If we determine the value of R^2 for various values of d , we can calculate n and k by Eq. (33). However, as R^2 is a transcendental function of n and k , it is difficult to obtain their values directly from the experimental values of R^2 . Therefore, we must either find approximate formulae appropriate to the calculation, or make tables useful to the computation.

2. The Case of $n \gg k$.—If $n \gg k$, approximate formulae can be obtained rather easily. In this case we have

$$\gamma \doteq 0 \quad (34)$$

$$R_{12} \doteq \frac{n-1}{n+1} \quad (35)$$

In Eq. (33), variable d appears in the form of nd or kd . Moreover nd appears only in the trigonometric functions and kd in the exponential functions.

According to the assumption $n \gg k$, the exponential functions in Eq. (33) change so slowly when compared to the trigonometric

functions that the former may be considered as constant in the small region of the variable d . Hence Eq. (33) may be rewritten as follows:

$$R^2 = \frac{a + b \cos\left(\frac{4\pi nd}{\lambda}\right)}{c + b \cos\left(\frac{4\pi nd}{\lambda}\right)} \quad (36)$$

where

$$\begin{aligned} a &= R_{12}^2 e^{-\frac{8\pi k d}{\lambda}} \\ b &= 2R_{12} e^{-\frac{4\pi k d}{\lambda}} \\ c &= 1 + R_{12}^2 e^{-\frac{8\pi k d}{\lambda}} \end{aligned}$$

a, b, c may be regarded as constant in the small region of variable d .

We denote the maximum and minimum values of R^2 as R_{12}^2 and R_m^2 , and the corresponding values of d as d_M and d_m , respectively. They may be obtained by ordinal method of differentiation, and we find

$$R_{12}^2 = \left(\frac{R_{12} + e^{-\frac{4\pi k d_M}{\lambda}}}{1 + R_{12} e^{-\frac{4\pi k d_M}{\lambda}}} \right)^2 \quad (37)$$

$$R_m^2 = \left(\frac{R_{12} - e^{-\frac{4\pi k d_m}{\lambda}}}{1 - R_{12} e^{-\frac{4\pi k d_m}{\lambda}}} \right)^2 \quad (38)$$

$$d_M = \frac{2N\lambda}{4n} \quad (39)$$

$$d_m = \frac{(2N+1)\lambda}{4n} \quad (40)$$

where $N=0, 1, 2, \dots$

As stated above, our problem is to determine n and k (or ϵ' and ϵ'') from the experimental curve of R^2 vs. d . For this purpose we first determine n from the value of d_M or d_m experimentally obtained by Eq. (39) or (40). Next we calculate R_{12} by Eq. (35) using the value of n thus obtained. Then we determine k from the values of R_M or R_m by Eq. (37) or (38), the values of n , R_{12} and d_M (or d_m). Eq. (37) or (38) is a linear equation of $\exp(-4\pi k d_M/\lambda)$ or $\exp(-4\pi k d_m/\lambda)$, so we can obtain these values easily, from which we can determine the value k , using the tables of exponential function.⁽⁵⁾ For higher approxi-

mation, we substitute the value of k into Eq. (31); and obtain the value of R_{12} . Using the value of R_{12} thus obtained, we can determine the value of k from Eq. (37) or (38) more exactly.

In the case when we can find many values of extrema though the value of k is very small we can determine the value of k from the decreasing rate of the extrema. Eq. (37) or (38) may be expanded with respect to $y = 4\pi k d/\lambda$, putting $e^{-y} = 1 - y + 1/2 y^2 \dots$, and as first order expansion, we have

$$R_M \doteq 1 - \frac{1 - R_{12}}{1 + R_{12}} y \quad (41)$$

$$R_m \doteq 1 - \frac{1 + R_{12}}{1 - R_{12}} y. \quad (42)$$

Differentiating with respect to $d/\lambda = z$, we have

$$\frac{dR_M}{dz} = -\frac{(1 - R_{12})}{(1 + R_{12})} 4\pi k \quad (43)$$

$$\frac{dR_m}{dz} = -\frac{(1 + R_{12})}{(1 - R_{12})} 4\pi k. \quad (44)$$

Thus from the curve R_M vs. d_M , or R_m vs. d_m , we can obtain the value of k .

3. The Case when the Assumption $n \gg k$ does not Hold.—In the case when $n \gg k$ does not hold, we can obtain the values of ϵ' and ϵ'' (or n and k) from the experimental values of R^2 according to the following method. We draw a curve which represents R^2 versus d/λ according to Eq. (33) for fixed values of ϵ' and ϵ'' (or n and k).

We draw another curve (which represents R^2 vs. d/λ according to Eq. (33)), for another fixed value of ϵ'' and the same value of ϵ' (or another fixed value of k and the same value of n). Thus we can obtain many curves representing R^2 vs. d/λ , a part of which is related to constant values of ϵ' and ϵ'' , and the other to the same value of ϵ' and the different values of ϵ'' . Then we have many curves of similar type which correspond to other fixed values of ϵ' . Thus we have many curves R^2 vs. d/λ corresponding to ϵ' and ϵ'' (or n and k) in the required region.

A curve R^2 vs. d/λ is characterized by two parameters ϵ' and ϵ'' . Maximum value of R^2 , R_{12}^2 or minimum value R^2 , R_m^2 are determined principally by ϵ'' , and the corresponding value of d , d_M and d_m by ϵ' .

From a curve, R^2 vs. d/λ , thus obtained, we mark R_{12}^2 , R_m^2 , d_M and d_m , and for a fixed value of ϵ' we draw curves R_{12}^2 vs. ϵ'' and

(5) K. Hayashi, "Kôto Kansû Hyô" (Tables of higher functions), 1st Ed., 1945; "Eu oyobi Sôkyokusen Kansû Hyô" (Tables of circular and hyperbolic functions), 1st Ed., 1945.

R_m^2 vs. ε'' . Similarly, for a fixed value of ε'' , we draw curves d_M vs. ε' and d_m vs. ε' .

To obtain the values of ε' and ε'' from the experimental values of reflection coefficients, we draw a curve R^2 vs. d/λ , and compare it with the curves calculated by the afore-described procedure. Thus we can obtain rough values of ε' and ε'' . Using the value of ε'' thus obtained, we can obtain ε' from the curve d_M/λ vs. ε' or d_m/λ vs. ε' by interpolation. (The value ε' thus obtained is almost a true value, for the curves d_M/λ vs. ε' or d_m/λ vs. ε' are insensitive to the value ε'' .) Similarly we can determine ε'' from the curve R_m^2 vs. ε'' or R_m^2 vs. ε'' , using rough value of ε' . (The curves R_m^2 vs. ε'' or R_m^2 vs. ε'' are insensitive to the value ε' .) The above procedure is essentially the same when we use n and k instead of ε' and ε'' .

Transmission Method

In the following a method will be reported, which consists in determining dielectric constant ε' and loss factor ε'' of a material from the relation of the transmission coefficient and thickness of dielectric sheet concerned.

1. The Formula of Transmission Coefficient.—The plane electromagnetic wave of unit amplitude is considered to be linearly polarized and to be propagated in the air. A dielectric sheet with plane boundary surface is placed as shown in Fig. 3.

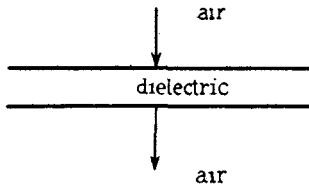


Fig. 3.

The direction of the propagation of incident wave is considered to be normal to the boundary surface. A part of the wave will be transmitted through the sheet characterized by dielectric constant ε' , loss factor ε'' and thickness d . The complex amplitude of the electric field vector of the transmitted wave is given by Eq. (25). If we change the notation ϑ_2 , and p_1 , to ϑ , and p , and considering

$$\vartheta_0 \vartheta_{12} = \frac{4p}{(1+p)^2}, \quad R_0 R_{12} = \left(\frac{p-1}{p+1} \right)^2$$

then we have

$$\vartheta = \frac{e^{-\frac{4\pi p d}{\lambda}} \times \frac{4p}{(1+p)^2}}{1 + \left(\frac{p-1}{p+1} \right)^2 e^{-\frac{4\pi p d}{\lambda}}} \quad (45)$$

If we write

$$\frac{p-1}{p+1} = -R_{12} e^{-\gamma}$$

then ϑ is expressed as follows, considering $p = n - ik$.

$$\vartheta = e^{-\frac{2\pi k d}{\lambda}} \times \frac{e^{-\frac{4\pi n d}{\lambda}} (1 - R_{12}^2 e^{-2\gamma})}{1 - R_{12}^2 e^{-2\gamma} \left(\frac{2\pi n d}{\lambda} + \gamma \right) \cdot e^{-\frac{4\pi k d}{\lambda}}}$$

The transmission coefficient of the sheet D^2 may be defined as $D^2 = |\vartheta|^2$, and expressed as:

$$\begin{aligned} D^2 &= e^{-\frac{4\pi k d}{\lambda}} \\ &\times \frac{(1 + R_{12}^4) - 2R_{12}^2 \cos 2\gamma}{1 + R_{12}^4 e^{-\frac{8\pi k d}{\lambda}} - 2R_{12}^2 e^{-\frac{4\pi k d}{\lambda}} \cos \left(\frac{4\pi n d}{\lambda} + 2\gamma \right)} \\ &= \frac{\sinh^2(-\ln R_{12}) + \sin^2 \gamma}{\sinh^2 \left(\frac{2\pi k d}{\lambda} - \ln R_{12} \right) + \sin^2 \left(\frac{2\pi n d}{\lambda} + \gamma \right)} \end{aligned} \quad (46)$$

2. Approximate Formulae.—(i) If $R_{12}^2 \ll 1$, we have

$$D^2 \doteq e^{-\frac{4\pi k d}{\lambda}} \quad (47)$$

In this case, the value of k can be obtained easily from the curve D^2 vs. d/λ experimentally obtained.

(ii) If $n \gg k$, we have the relations expressed with Eqs. (34) and (35). Eq. (46) is rewritten as

$$\begin{aligned} D^2 &\doteq e^{-4\pi k x} \\ &\times \frac{(1 - R_{12}^2)^2}{1 + R_{12}^4 e^{-8\pi k x} - 2R_{12}^2 e^{-4\pi k x} \times \cos 4\pi n x} \end{aligned} \quad (48)$$

where $x = d/\lambda$.

As stated in the case of reflection method, exponential function in Eq. (48) change very slowly when compared to trigonometric function according to the assumption that $n \gg k$, so that the former can be considered as a constant in a small region of variable x . Eq. (48) can be rewritten as follows, considering $\exp(-4\pi k x) = \alpha$, a constant, in this region.

$$D^2 = \frac{\alpha(1-R_{12}^2)^2}{1-2\alpha R_{12}^2 \cos 4\pi n x + R_{12}^4 \alpha^2} \quad (49)$$

The maximum and minimum value of D^2 and corresponding values of d , can at once be obtained. If we denote these values D_M^2 , D_m^2 , and the corresponding values of d , d_M and d_m , then we have

$$D_M = e^{-\frac{2\pi k d_M}{\lambda}} \times \frac{(1-R_{12}^2)}{(1-e^{-\frac{4\pi k d_M}{\lambda}} R_{12}^2)} \quad (50)$$

$$D_m = e^{-\frac{2\pi k d_m}{\lambda}} \times \frac{(1-R_{12}^2)}{(1+e^{-\frac{4\pi k d_m}{\lambda}} R_{12}^2)} \quad (51)$$

$$d_M = \frac{2N}{4n} \quad (52)$$

$$d_m = \frac{(2N+1)}{4n} \quad (53)$$

$N = 0, 1, 2, \dots$

To obtain the values of n and k (accordingly ϵ' and ϵ'') from the curve D^2 vs. d/λ which was experimentally obtained, we find at first the value of n from Eq. (52) or (53), then the value of k from Eq. (50) or (51), calculating the value of R_{12} from Eq. (35). Using these value of n and k thus obtained, more accurate value of k can be obtained from Eq. (50) or (51), calculating the value of R_{12} from Eq. (31).

(iii) If $k \ll 1$, the value of k may be obtained from the curves of extrema vs. x . Omitting the detailed calculations, we can finally express the derivatives of D_M and D_m with respect to x as follows:

$$\frac{dD_M}{dx} = -\left(1 + \frac{2R_{12}^2}{1-R_{12}^2}\right) \cdot 2\pi k \quad (54)$$

$$\frac{dD_m}{dx} = -\left(\frac{1-R_{12}^2}{1+R_{12}^2}\right) \frac{(1-R_{12}^2)}{(1+R_{12}^2)} \cdot 2\pi k \quad (55)$$

3. The Case when the Assumption $n \gg k$ is not valid.—In this case the values of ϵ' and ϵ'' can be obtained from the curve of D^2 vs. d/λ which was experimentally obtained by a similar method as described in the case of reflection method. That is, we draw many curves of D^2 vs. d/λ for the values of ϵ' and ϵ'' in the suitable region, and obtain the values of ϵ' and ϵ'' by interpolation.

Summary

The reflection and transmission coefficient of electromagnetic waves by multiple layer has been obtained theoretically.

A convenient method has been devised to determine dielectric constant and loss factor of a material in a form of a sheet placed on a metal, from the reflection coefficient.

A convenient method has also been developed to determine the dielectric constant and loss factor from experimental curve of transmission coefficient versus thickness of dielectric sheet concerned.

The author is grateful to Prof. San-ichiro Mizushima for his guidance, to Mr. Kenji Kuratani and to Mr. Kenji Nukazawa for their kind advices. His thanks are also due to the Ministry of Education for a grant in aid of this research.

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Determination of Dielectric Constant and Loss Factor by Free Wave Method. II. Measurement on Water and Some Insulators at $\lambda = 9.8$ cm.

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I. Measurement on Water by Reflection Method

• Several attempts have been made to determine the dielectric constant and loss factor of a substance by the measurement of the reflection coefficient of a dielectric sheet placed on a metallic plate.⁽²⁾ The experimental results cannot, however, be considered as sufficiently accurate, because of the incomplete method of calculating dielectric constant and loss factor from reflection coefficient and of the considerable experimental error which seems to arise mainly from the imperfect and unsteady source and the uneven metallic plate used as a reflector.

The former difficulty was already removed by one of us, as reported in the previous paper.⁽³⁾ As to the latter, we have tried to remove it by constructing a steady and powerful source of wave and by using a mercury sheet as the reflector.

With an apparatus constructed in this way we have measured the dielectric constant and loss factor of water at the wave length of 9.8 cm. As will be reported in the following, water shows anomalous dispersion and absorption at this wave length.

The apparatus is shown schematically in Fig. 1. The 9.8 cm. wave generated with split-anode magnetron A was emitted vertically into the free space from a horn B through a wave guide G. A wooden vessel V with a rectangular surface of 60×60 cm.² was placed horizontally under B. This area was just sufficient to remove the edge effect. A crystal detector C consisting of silicon crystal and nickel wire was so adjusted that the deflection of microammeter attached to it was proportional to the energy of the wave. C was moved vertically between B and V, and the energy distribution of the standing wave was determined.

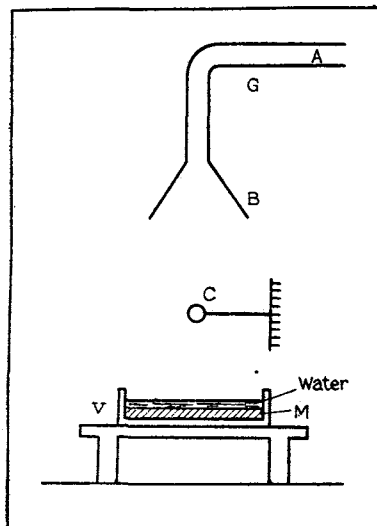


Fig. 1.

The measurement was carried out as follows. The vessel V is first filled with mercury M only. The incident wave with an amplitude E_0 is reflected by M to form a standing wave between B and M. The maximum and minimum values of the energy of the standing wave would be proportional to $4E_0^2$ and zero, respectively, when there would be no reflection other than that from the surface of the mercury. We could show that this was actually the case in our experiment.

Next, we place on the mercury a water layer whose thickness can be calculated accurately from the volume of water and the area of the vessel. The reflected and incident waves now form an imperfect standing wave, and the maximum and minimum values of its intensity will become proportional to $E_0^2(1+R)^2$ and $E_0^2(1-R)^2$, respectively. In other words, the ratio of the extreme values will be $(1-R)^2/(1+R)^2$. This ratio can be determined experimentally by moving C vertically and reading the microammeter deflections. The value of R can at once be calculated from this ratio.

(1) Now at Research Institute of Applied Electricity (the University of Hokkaido).

(2) See e.g. G. Béz, *Physik. Z.*, **40**, 394 (1939).

(3) M. Yasumi, this Bulletin, **24**, 53 (1951).

Such a measurement is made at different thickness d of the water layer and finally a curve of R^2 vs. d is obtained.

We can also determine the wave length in air from the positions of C corresponding to the extreme values of microammeter reading. The wave length thus determined was 9.8 cm. in agreement with the value obtained by the Lecher wire method.

The procedure of calculating dielectric constant ϵ' and loss factor ϵ'' (or refractive index n and absorption coefficient k) was reported in a previous paper.⁽³⁾ The part necessary for the following discussion will be briefly repeated here.

The reflection coefficient of water layer of thickness d placed on mercury is expressed as

$$R^2 = \frac{\sinh^2\left(\frac{2\pi kd}{\lambda} + \frac{1}{2} \ln R_{12}\right) + \cos^2\left(\frac{2\pi nd}{\lambda} - \frac{\gamma}{2}\right)}{\sinh^2\left(\frac{2\pi kd}{\lambda} - \frac{1}{2} \ln R_{12}\right) + \cos^2\left(\frac{2\pi nd}{\lambda} + \frac{\gamma}{2}\right)} \quad (1)$$

where

$$R_{12}^2 = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (2)$$

$$\tan \gamma = \frac{2k}{(n^2 - 1) + k^2}. \quad (3)$$

For $n \gg k$, the maximum and minimum values R_M^2 , R_m^2 of R^2 are calculated approximately as follows:

$$R_M^2 = \frac{R_{12} + e^{-\frac{4\pi kd_M}{\lambda}}}{1 + R_{12} e^{-\frac{4\pi kd_M}{\lambda}}} \quad (4)$$

$$R_m^2 = \frac{R_{12} - e^{-\frac{4\pi kd_m}{\lambda}}}{1 - R_{12} e^{-\frac{4\pi kd_m}{\lambda}}} \quad (5)$$

$$R_{12} = \frac{n-1}{n+1} \quad (6)$$

$$d_M = \frac{2N\lambda}{4n} \quad (7)$$

$$d_m = \frac{(2N+1)\lambda}{4n} \quad (8)$$

$$(N = 0, 1, 2, \dots)$$

where d_M and d_m are the values of d corresponding to R_M^2 and R_m^2 , respectively.

In the present experiment, n and k were obtained from the curve R^2 vs. d in the following way. We found first an approximate value of n , using Eq. (7) or (8), and calculated

approximate value of R_{12} , substituting the value of n into Eq. (6). An approximate value of k could be obtained from Eq. (4) or (5), using the said value of R_{12} , and d_M or d_m . We drew a curve of R^2 vs. d , putting the values of n and k obtained above into Eq. (1) and compared it with the experimental curve. The calculated curve was slightly different from the experimental one, and we changed the values of n and k slightly until the former curve became almost identical with the latter. Thus the more exact values of n and k could be obtained.

The values of reflection coefficient R^2 of water at 5.5°C. obtained at various thicknesses d of the layers are shown in Table 1. The values of n and k which are obtained by above-described procedure are shown in Table 2 which includes also those of the absorption index $\kappa (=k/n)$ and the real (ϵ') and imaginary (ϵ'') parts of the complex dielectric constant.

Table 1

The Reflection Coefficient R^2 of the Water Layer of the Thickness d (mm.) Measured at 5.5°C.

d , mm.	R^2	d , mm.	R^2
0.00	1.00	9.61	0.638
2.20	0.776	10.96	0.762
2.74	0.090	12.31	0.678
3.02	0.242	13.66	0.540
3.83	0.727	14.01	0.554
5.18	0.873	14.28	0.568
6.53	0.789	14.57	0.650
7.88	0.429	15.39	0.678
8.80	0.471		

Table 2

Dielectric Data for Water

t , °C.	5.5	$\kappa (=k/n)$	0.120
λ , cm.	9.8	ϵ'	73.8
n	8.65	ϵ''	18.1
k	1.04		

The value of static dielectric constant of water at this temperature amounts to 86.1⁽⁴⁾, which is much greater than the value of $\epsilon' = 73.8$ found in this experiment. Therefore water shows anomalous dispersion at this wave length. This is in conformity with the value of absorption index ($\kappa = 0.120$) found by us. The detailed discussions on relaxation time, etc. will, however, be postponed until we obtain more data at different wave lengths.

(4) Calculated from the equation given by Drake, Pierce and Dow (*Phys. Rev.*, **35**, 613 (1930)).
 $\epsilon' = 78.59[1 - 0.00461(t-25) + 0.000155(t-25)^2]$
 See also, Wymann, *Phys. Rev.*, **35**, 623 (1930).

Measurement on Some Insulators by Transmission Method

The previous paper described the procedure of obtaining the dielectric constant and the loss factor of an insulating material from the transmission coefficient and the thickness of the sheet.⁽³⁾ In the following we shall report some experimental data of transmission coefficient and the values of dielectric constant and loss factor obtained therefrom.

The apparatus is shown schematically in Fig. 2. As in the reflection experiment a linearly polarized wave of the wave-length of 9.8 cm. was generated from a split-anode magnetron A and was emitted vertical into the free space from a horn B through a wave guide G. A large aluminium plate P was placed at an angle of 45° to the floor to avoid the reflection of the wave from it. The fact that the reading of the microammeter connected to the crystal detector C remained constant in the middle part of the space between the horn and the aluminium plate showed that there was actually no reflection from the floor. As in the reflection experiment the detector system was so adjusted as to make the microammeter reading proportional to the intensity of the wave.

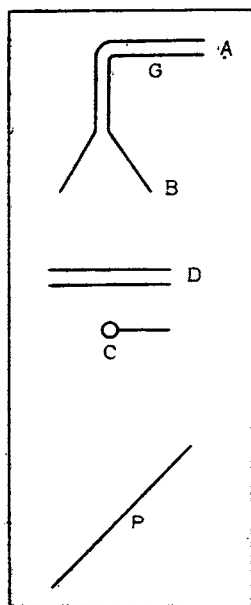


Fig. 2.

We now place a dielectric sheet D to be measured between the horn and the detector, and record the microammeter reading I_d proportional to the energy of the transmitted wave. Then we remove the sheet and again

record the microammeter reading I_0 proportional to the energy of the incident wave. The transmission coefficient of the sheet is simply given by

$$D^2 = I_d/I_0. \quad (9)$$

In this measurement we have, however, to show that in the former case the microammeter reading indicates only the energy of the transmitted wave. This was shown by the fact that the microammeter showed no deflection when an aluminium plate of the same size as the sample (70×70 cm.²) was placed upon the sample.

The transmission experiment was made on the sheets of ebonite, bakelite, methacryl resin, and polystyrene of various thicknesses d . The results are shown in Table 3.

Table 3
The Transmission Coefficient D^2 of Several
Substances of the Thickness d (mm.)
Measured at the Wave-length of 9.8 cm.

Ebonite 15°C.	Bakelite 15°C.	Methacryl resin 15°C.	Polystyrene 5°C.
d D^2	d D^2	d D^2	d D^2
5 0.92	3 0.87	6 0.79	2 1.00
12 0.79	8 0.62	12 0.68	3.5 0.99
15 0.80	13 0.59	25 0.90	5 0.98
20 0.85	15 0.60	31 0.94	7 0.93
25 0.92	18 0.72		8.5 0.88
32 0.98	23 0.83		
35 0.96	28 0.82		

From these values of the transmission coefficient obtained at different thicknesses we can calculate refractive indices n , absorption coefficients k , dielectric constants ϵ' , and loss angles δ according to the procedure reported in the previous paper.⁽³⁾ In Table 4 are shown the results of the calculation except that for polystyrene for which we have too few data to calculate these quantities.

Table 4
Dielectric Data for Ebonite, Bakelite and
Methacryl Resin (15°C.)

	Ebonite	Bakelite	Methacryl resin
n	1.60	1.92	1.65
$\kappa = k/n$	0.005	0.035	0.015
ϵ'	2.6	3.7	2.7
$\tan \delta$	0.01	0.07	0.05

For these samples the condition $n \gg k$ holds and we can also use the approximate formulae derived by one of us.⁽³⁾ Repeating them briefly,

$$D_M^2 = \frac{e^{-\frac{4\pi k d_M}{\lambda}} (1 - R_{12}^2)^2}{(1 - R_{12}^2 e^{-\frac{4\pi k d_M}{\lambda}})^2} \quad (10)$$

$$D_m^2 = \frac{e^{-\frac{4\pi k d_m}{\lambda}} (1 - R_{12}^2)^2}{(1 + R_{12}^2 e^{-\frac{4\pi k d_m}{\lambda}})^2} \quad (11)$$

$$R_{12} = \frac{n-1}{n+1} \quad (6)$$

$$d_M = \frac{2N\lambda}{4n} \quad (7)$$

$$d_m = \frac{(2N+1)\lambda}{4n} \quad (8)$$

$$N = 0, 1, 2, 3, \dots$$

we have D_M^2 and D_m^2 are the maximum and the minimum values of D^2 , d_M and d_m the corresponding values of thickness d , and λ is wave length. Using Eq. (7) or Eq. (8), we first obtain the value of n which we put into Eq. (6) and then calculate the value of k from Eq. (10) for Eq. (11).

Summary

The reflection coefficient of water layer placed on mercury has been measured at a wave length 9.8 cm. and at 5.5°C. From the curve of reflection coefficient *vs.* thickness of the water layer, dielectric constant and loss factor (or refractive index and absorption coefficient) have been calculated according to the procedure described previously.

Water has shown anomalous dispersion and absorption at this wave length.

The dielectric constant and loss factor have been measured for ebonite, bakelite and methacryl resin at the same wave length, by the transmission method.

In conclusion we wish to thank Mr. Isao Ichishima and Mr. Kenji Kuratani for their kind advices, and to Mr. Yoichiro Mashiko who prepared the samples used in this experiment. We are indebted to the Ministry of Education for a research grant.

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Energy of Hydrogen Bond in Tetragonal Pentaerythritol

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Introduction

There appeared already numerous papers dealing with the energy of hydrogen bond. In most of these papers, it is estimated from experimental data of substances in pure liquid or solution state. Generally, in the pure liquid or solution state, the molecular arrangement is not known so accurately that the net contribution of the hydrogen bond cannot be sorted out exactly. On the other hand, the energy of association of some carboxylic acids determined from the temperature variation of equilibrium constant for the hydrogen bond dimerization in the gaseous state⁽¹⁾ would be of unambiguous significance for the derivation

of the hydrogen bond energy, since the molecular structure of these dimers have already been determined by the electron diffraction method.⁽²⁾ In the same sense, the energy data of a crystalline substance, of which the structure is known by the x-ray analysis, will be also useful for this purpose. The only one example of such investigation hitherto carried out is the case of the hydrogen bond energy for ice.^{(3),(4)} Now that the crystal structure of pentaerythritol is completely determined independently by one of the present authors and

(1) (a) Davies, *Ann. Report Chem. Soc.*, (1947); (b) F. W. Johnson and L. U. Nash; *J. Am. Chem. Soc.*, **72**, 547 (1950).

(2) (a) J. Karle, L. O. Brockway, *J. Am. Chem. Soc.*, **66**, 574 (1944); (b) V. Schomaker, J. U. O'Gorman, *J. Am. Chem. Soc.*, **69**, 2638 (1947).

(3) Unfortunately, the unit cell of ice is not determined uniquely.

(4) (a) Bernal and Fowler, *J. Chem. Phys.*, **1**, 515 (1933); (b) T. Ogura, *Busseiron* (in Japanese), No. 12, 1. (1948); (c) A. W. Searcy, *J. Chem. Phys.*, **17**, 210 (1949).

by Cox and his co-workers,⁽⁵⁾ this substance may be suitable for the determination of strength of hydrogen bond in the crystalline state. Thus, we attempted to determine the heat of sublimation of this material and compare the results with the calculated values of the lattice energy.

Experimental

The sample used in the present investigation is the product of Kahlbaum Company. It was recrystallized from distilled water and was purified by fractional sublimation under high vacuum (below 1×10^{-5} mm. Hg) at about 130°. By the method of differential thermal analysis, the melting point of the extremely purified sample finally employed for the experiment was determined to be 265.5°⁽⁶⁾. The vapor pressures were measured by the effusion method, of which we have already described in a previous paper.⁽⁷⁾ The obtained numerical values are summarized in Table 1 and the vapor pressure equation derived from these experimental data is given at the bottom. Some thermodynamical data calculated from it are shown in Table 2.

Table 1

Vapor Pressures of Pentaerythritol

$t^{\circ}\text{C}$	$P_{\text{mm. Hg}} \times 10^3$	(log $P_{\text{mm. Hg}} + 3$) _{obs.}	(log $P_{\text{mm. Hg}} + 3$) _{calc.}
123.8	1.70	0.230	0.235
126.1	2.25	0.350	0.345
129.8	3.15	0.498	0.496
132.2	3.93	0.594	0.599
134.5	4.96	0.696	0.697
136.9	6.19	0.792	0.791

$$\log P_{\text{mm. Hg}} = 14.525 - 6861.1/T$$

Table 2

$\Delta H_s = 31.4 \pm 0.2$ kcal./mole
$\Delta S_s = 53.3 \pm 0.6$ e. u./mole
$\Delta G_{298.1} = 15.5 \pm 0.4$ kcal./mole
ΔH_s : Heat of sublimation
ΔS_s : Entropy of sublimation
ΔG : Free energy of sublimation

Calculation of Lattice Energy

(a) **van der Waals Energy.**—In a series of papers,⁽⁸⁾ we have calculated the lattice

energies of more or less complicated crystals and showed empirically that the application of the Slater-Kirkwood formula for the van der Waals interaction may be used within the error of about 10 % of the observed values. In these calculations, the contributions of the atoms or atomic groups, into which the molecule is splitted, are summed up. The general agreement between the calculated and the observed values to about 10 % may be looked upon as suggesting that the higher order interactions such as Margenau's force are roughly compensated by the repulsive forces.^(8a)

In the present case of pentaerythritol, the molecule is splitted into three kinds of force centers; that is, the central C atom, CH₂ and OH groups. According to the Slater-Kirkwood theory the interaction energy between two molecules is given in the form of the following equation:

$$V = -\frac{3}{2} \frac{e\hbar}{m^{1/2}} \sum_{ij} \frac{\alpha_i \alpha_j}{(\alpha_i/n_i)^{1/2} + (\alpha_j/n_j)^{1/2}} \frac{1}{R_{ij}^6} \quad (1)$$

where e is the elementary charge, m mass of electron, $\hbar = h/2\pi$, n the number of electrons in the outermost electronic shell, α polarizability of an atom or an atomic group, R_{ij} distance between the centers of force, suffix i or j denotes one or the other of the considered pair of the centers.

The molecular arrangement in the crystal with numbers assigned to molecules for convenience is illustrated in Fig. 1. The lattice constants adopted in the calculation are respectively $a = 6.074 \text{ \AA}$. and $c = 8.877 \text{ \AA}$. at 130°.⁽⁹⁾ The polarizabilities of atomic groups are estimated as follows. To obtain the polarizability of CH₂ group, we could make use of either the difference of molecular refractions corresponding to the increase of a CH₂ group in the homologous series of normal hydrocarbons and of normal alcohols or the similar quantities deduced from the symmetrically branched hydrocarbon series.⁽¹⁰⁾

For the former two series, there are sufficient data of refractive indices for wave lengths of H_α, H_β, H_γ, and D-line, while the data for the latter exist only for the wave length of D-line. Using these values, it is possible to calculate the mean molecular refraction of CH₂ group at infinite wave length, ($M_{\lambda=\infty}$) by application

(5) (a) F. J. Llewellyn, E. G. Cox, T. H. Goodwin, *J. Chem. Soc.*, 883, 1937; (b) I. Nitta, T. Watanabe, *Nature*, 140, 365 (1937); *Sci. Papers. Inst. Phys. Chem. Research*, 34, 1669 (1938).

(6) Ebert, 260.5°; Mark, 252.5°; Seifert, 252°; Schleede, 257°.

(7) J. Nitta, S. Seki, M. Momotani and K. Sato, *J. Chem. Soc. Japan*, 71, 378 (1950).

(8) (a) I. Nitta, S. Seki, *J. Chem. Soc. Japan*, 64, 475 (1945); (b) S. Seki, H. Ohihara, *Sci. Papers. Osaka Univ.*, 1, 1 (1949); (c) I. Nitta, S. Seki, M. Momotani, *J. Chem. Soc. Japan*, 71, 430 (1950).

(9) These lattice constants are calculated from the experimental data of thermal expansion coefficient determined by x-ray method in this laboratory (unpublished).

(10) We have utilized the refractive indices of C(CH₃)₄, (CH₃)₃CC(CH₃)₂, (CH₃)₂CC(CH₃)₂, (CH₃)₂CC(CH₃)₂, and of C(C₂H₅)₄.

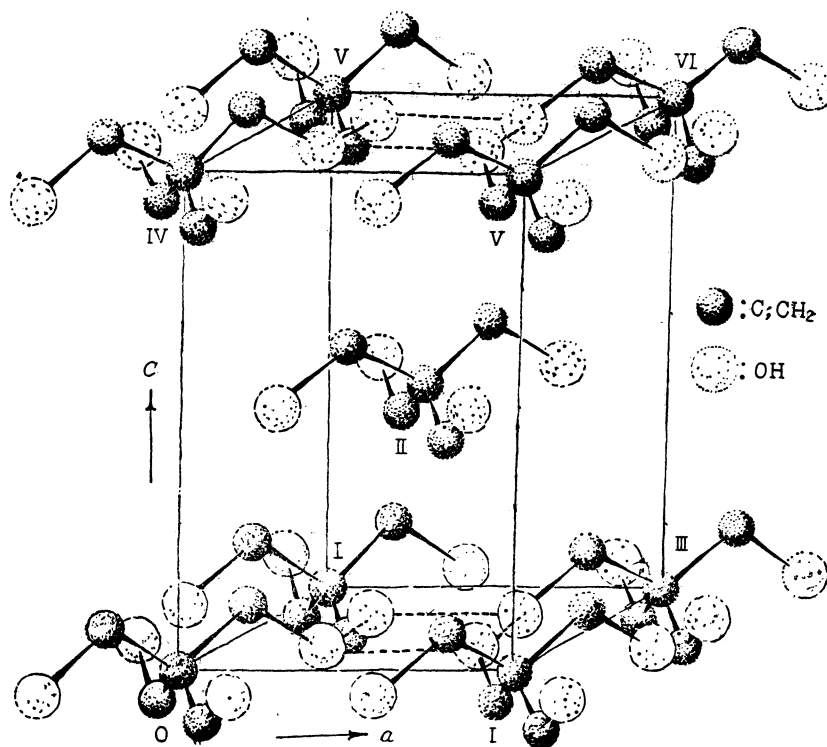


Fig. 1.—Crystal structure of tetragonal pentaerythritol (dotted lines show the hydrogen bonds).

of the Cauchy dispersion formula. In Table 3, there are given mean molecular refraction of a CH_2 group from these three sources.

Table 3

Mean Molecular Refraction of CH_2 Group					
	M_γ	M_β	M_D	M_a	$M_{\lambda=\infty}$
From normal alcohols	4.72	4.68	4.64	4.61	4.51
From normal paraffines	4.76	4.68	4.64	4.61	4.51
From branched(*) paraffines	—	—	4.45	—	4.32

* Egloff, "Physical Constants of Hydrocarbon", (1939).

In Table 3 it can be seen that the values derived from the upper two series are in very good agreement with each other, while those from the third is considerably smaller. The $M_{\lambda=\infty}$ value for the last one is estimated by assuming the same relative decrement with wave length as the former. We used the value of 4.32 for calculation, since the situation of CH_2 group in pentaerythritol may rather be approximated to that of the branched chain hydrocarbon series. The molecular refractions

of a OH group and the central carbon atom are deduced from the data of normal alcohols and of branched paraffines. From these values of molecular refraction at infinite wave length, we obtain the polarizabilities of the three atomic groups, which are tabulated in Table 4.⁽¹¹⁾

Table 4

Molecular Refraction ⁽¹¹⁾ and Polarizabilities			
	M_D	$M_{\lambda=\infty}$	$\alpha \times 10^{24}$ cc.
CH_2 group	4.45	4.32	1.709
OH group	2.61	2.48	0.981
Central carbon	3.04	2.98	0.928

Inserting these polarizabilities and atomic parameters into the formula (1) and multiplying by $N_A/2$ (N_A ; the Avogadro number), we obtain the results shown in Table 5.

(11) The refractive index of this crystal measured by Dr. Kiriya in this laboratory are $n_o=1.553$ and $n_e=1.515$ for ordinary and extra-ordinary rays, respectively (D-line). Inserting these values in the Lorentz-Lorenz formula, we can obtain the values of $M_o=31.27$ and $M_e=29.27$. On the other hand, assuming the additivity of atomic refraction, we have obtained from the data listed in Table 4 the value of molecular refraction; $M_D=31.28$ which is in better agreement with the M_o value given above.

Table 5
Lattice Energy Contributions of Different Atomic Groups and the
Numbers of Summation Taken in Calculation

Molecule	Distances from molecule 0	van der Waals interactions between different atomic groups						Total
		C~O	C~CH ₂	C~OH	CH ₂ ~CH ₂	CH ₂ ~OH	OH~OH	
I	6.073 Å.	4.5	70.0	94.4	269.9	702.2	1332.7	2473.7
II	6.178 Å.	4.0	58.4	48.6	254.3	352.1	71.2	788.6
III	8.590 Å.	0.5	7.8	10.0	24.5	65.8	85.4	194.0
IV	8.881 Å.	0.9	6.3	3.0	20.8	14.2	3.3	48.5
V	10.770 Å.	—	0.8	0.5	3.3	3.4	0.9	8.9
(part of summation)		53.8	797.4	816.4	3280.0	5944.4	6252.8	17144.8
(part of integration)		6	35	23	205	115	95	477
Total van der Waals energy								17.622 kcal./mole
Numbers of pairs taken for summation		26	94	94	376	376	376	1334

In this calculation, van der Waals interactions between the molecule 0 and the first neighbors (molecules I and II), the second neighbors (molecules III and IV) and the third one (molecule V) are summed up one by one, and for the remaining part of these interactions, summation is replaced by integration, assuming the uniform distribution of the centers of attractive forces. As shown evidently in Table 5, the contribution of OH groups to the van der Waals energy is most predominant. It is also shown that the part due to integration does not exceed more than 3 %, indicating the approximation by integration is sufficient for the present purpose.

(b) **Electrostatic Energy.**—In the calculation of electrostatic interaction between free molecules, the dipole model is usually employed. However, for the molecular interaction in the crystalline state, the point charge model would be more adequate than the dipole model, for the intermolecular distance is much smaller here. In the present work, we used the point charge model, putting an effective charge $+\epsilon$ on the nuclear position of the carbon atom in CH₂ group, $-(\epsilon+\epsilon')$ on the oxygen atom and $-\epsilon'$ on the hydrogen atom in OH group. Exact estimation of such formal charges is of course difficult. In the present case, following the usual method, the charge ϵ is deduced from the bond moment 0.8 D for C—O by dividing this value by the corresponding bond distance 1.46 Å. This comes out to be 0.551×10^{-10} e.s.u., which corresponds to 11.5 % ionic character of this bond. The value of ϵ' can be estimated in the same way. However, the cyclic formation of hydrogen bonds will cause further elongation of the bond length as well as the increase of charge distribution of O—H bond. Taking this circumstances into account, we may use

for trial three bond moments of 1.66 D, (bond moment of the free OH group in aliphatic alcohols), 1.79 D and 1.93 D, on the assumption of the normal bond length of 0.96 Å. These three values correspond respectively to the ionic character of 36 %, 39 % and 42 %. The formal charges derived from these values are $\epsilon' = 1.726, 1.870$ and 2.015×10^{-10} e.s.u. respectively. However, for the reason mentioned above, the latter two values will be preferable. The electrostatic potential V_{ei} is expressed by the following equation:

$$V_{ei} = \sum_{ij} \frac{\epsilon_i \epsilon_j}{R_{ij}} \quad (2)$$

where ϵ_i is the formal charge of the i -th atom, ϵ_j that of the j -th atom and R_{ij} is the distance between these point charges. We have used this equation only for the first and the second neighbors and the remaining part has been calculated approximately in the following manner.

We can rewrite equation (2) as follows:

$$V_{ei} = \sum_R \sum_{ij} \frac{\epsilon_i \epsilon_j}{|\vec{R} - \vec{r}_i + \vec{p}_j|} = \sum_R \sum_{ij} \frac{\epsilon_i \epsilon_j}{|\vec{R} + \vec{\sigma}_{ij}|}, \quad (3)$$

$$\vec{\sigma}_{ij} = \vec{p}_j - \vec{r}_i$$

where $\vec{r}_i$ is the radius vector of the i -th point charge from the center of the molecule 0 (see Fig. 1) and $\vec{p}_j$ is that of the j -th point charge from the molecular center which is situated at $\vec{R}$ from the center of the molecule 0. For the contribution of the molecules of the third neighbors and of the molecules lying farther than these, the interaction energies become

$$\Delta E = \sum_R' \sum_{ij} \frac{\epsilon_i \epsilon_j}{|\vec{R} + \vec{\sigma}_{ij}|} \quad (4)$$

where $\sum'_k$ implies the summations excluding the first and the second neighbors. Using the relation $R \gg \sigma$ this can be expanded by the Taylor theorem. In terms of components of these vectors ΔE becomes,

$$\begin{aligned} \Delta E &= \sum'_X \sum'_Y \sum'_Z \sum'_{ij} \frac{1}{4!} \left(x_{ij} \frac{\partial}{\partial X} + y_{ij} \frac{\partial}{\partial Y} \right. \\ &\quad \left. + z_{ij} \frac{\partial}{\partial Z} \right)^4 \frac{\epsilon_i \epsilon_j}{(X^2 + Y^2 + Z^2)^{1/2}} \\ &= \sum'_X \sum'_Y \sum'_Z \{ 3(X^4 + Y^4) + 8Z^4 + 6X^2 Y^2 \\ &\quad - 24Z^2(X^2 + Y^2) \} / (X^2 + Y^2 + Z^2)^{3/2} \\ &\quad \times \frac{3}{16!} \sum' (r_{xi}^2 + r_{yi}^2 - 2r_{zi}^2) (p_{xj}^2 + p_{yj}^2 \\ &\quad + p_{zj}^2) \epsilon_i \epsilon_j \quad (5) \end{aligned}$$

where X, Y, Z ; x_{ij}, y_{ij}, z_{ij} ; r_{xi}, r_{yi}, r_{zi} and p_{xj}, p_{yj}, p_{zj} are the three cartesian components of the vectors $\vec{R}, \vec{\sigma}_{ij}$ and $\vec{p}_j$. Cutting off the higher term than the sixth, it is found that the terms involving the first, the second, the third and the fifth derivatives vanish on account of the symmetry properties.

The results calculated by equations (2) and (5), multiplied by $N_A/2$, are tabulated in Table 6.

Table 6
Electrostatic Energies of First and Second Neighbors

Sort of molecule	Number of molecule	Energies per one pair		
		A	B	C
I	4	-3.28	-3.79	-4.35
II	8	-0.72	-0.79	-0.87
III	4	+1.84	+2.08	+2.33
IV	2	+0.25	+0.24	+0.23

Electrostatic Energy Contributions of Different Parts

	A	B	C
First neighbors (molecules I and II)	-18.88	-21.48	-24.36
Second neighbors (molecules III and IV)	+ 7.86	+ 8.80	+ 9.78
Outer part	+ 0.05	+ 0.07	+ 0.08**
Total	-10.79	-12.61	-14.50

Case A, B and C correspond to the 36%, 39% and 42% ionic character of OH bond. Unit is kcal./mole.

* Calculated by Eq. (2). ** Calc. by Eq. (5).

It is seen that the electrostatic forces of the second neighbors and of the outer part are as a whole contributing repulsively. This is evident from the symmetry and arrangement of the molecules in the crystal.

Discussion of Results

Adding the van der Waals energy to the electrostatic one, we obtain three values for the total energy; 28.59, 30.33, and 32.12 kcal./mole respectively, corresponding to the three degrees of the ionic characters 36%, 39% and 42% of the OH-bond. These values are in general agreement with the experimental value: 31.4 ± 0.2 kcal./mole. By the reason mentioned in the preceding section the latter two of the calculated values may be more reasonable. Evidently, to calculate the interaction energy more exactly, we must take into account the repulsive energy, the energy due to the induction effects, the higher order van der Waals energy and the resonance energy. However, as described at the beginning of the third section, we have seen in many examples that the van der Waals energies calculated by the Slater-Kirkwood formula come out nearly equal to, or somewhat larger than, the experimental values. These facts seem to show empirically that the repulsive energy is nearly cancelled by the higher order van der Waals energies. It may be supposed also that the contribution of the induction effects will be small. In the above calculation, the increment of formal charge of the OH bond may be said to take this effect partly into account in a certain sense. As to the so-called resonance energy of the hydrogen bond, it is estimated from the deuterium and other effects that its contribution for the present bond length of hydrogen bond is very small as compared with the electrostatic contribution. Hence, it may be neglected without introducing any serious error.

For the estimation of the energy of hydrogen bond, it should be remarked that the definition of the energy of hydrogen bond is rather ambiguous and depending on the methods of determination. For example, in the case of dimerization of carboxylic acids, the energy of hydrogen bond is determined from the temperature dependence of equilibrium constant by the application of the van't Hoff isochore. Therefore, the energy obtained in this way involves that of reorganization of the dissociated molecules and does not correspond exactly to the hydrogen bond energy in the state of dimeric association.

Furthermore, it is uncertain whether we should take into consideration the interaction energy only of the atoms directly concerned with hydrogen bonding, or, in addition to it, the energy due to the remaining atoms. It is actually known that the effect of hydrogen bond upon the state of the remaining atoms

will modify the interaction energy.

For the estimation of the magnitude of hydrogen bond energy in this crystal, neglecting the energy of reorganization, there may be considered, for the present, following three cases. Of these the simplest may be such energy defined as interaction energies only between OH groups which are directly linked together by the hydrogen bond. From Tables 5 and 6, this is found to be 5.1 or 5.7 kcal./mole one hydrogen bond, according to whether we adopt the case B or C. The second estimation is as follows. The molecules in this crystal form distinct layers, in each of which they are linked together by the hydrogen bonds (Fig. 1). Thus, the work necessary to separate all the molecules of such a layer may be a second definition of the hydrogen bond energy. Following this definition, it comes out to be about 4.5 or 4.8 kcal./mole. Thirdly, it can be seen in Tables 5 and 6 that, although the intermolecular distances of molecules I and II from the molecule 0 are nearly equal, both the van der Waals and electrostatic energies are considerably different (Table 7). This difference may be looked upon as due to the effect of hydrogen bonding, for the molecule I is hydrogen-bonded with molecule 0, while the molecule II is not. From this point of view, we obtain as the approximated hydrogen bond energy the value of 4.68 or 5.16 kcal./mole.

Table 7

Difference of Interaction Energy
between Molecule I and II

Mole- cule	van der Waals energy	Electrostatic energy		Total	
		B	C	B	C
I	-2.47	-3.79	-4.35	-6.26	-6.82
II	-0.79	-0.79	-0.87	-1.58	-1.66
Difference	-1.68	-3.00	-3.48	-4.68	-5.16

Comparing the energy of hydrogen bond with the total lattice energy, it is found that in any case the contribution of hydrogen bonding amounts to approximately two-thirds of the total energy.⁽¹²⁾ It can be seen also in Table 7, as an instance, that, although the electrostatic contribution makes larger part of the whole energy, the van der Waals energy is not at all negligible.

(12) At 187.7°, the tetragonal pentaerythritol transforms into the cubic modification. This phase transition is intimately related to the breaking of the hydrogen bond. I. Nitta, S. Seki, M. Momotani, *Proc. Japan Acad.*, **26** (1950) (9) 26; I. Nitta, S. Seki, H. Momotani, K. Suzuki S. Nakagawa, *Ibid.* **26** (1950) (10) 11; I. Nitta, T. Watanabé, S. Seki, M. Momotani, *Ibid.* **26** (1950) (10) 19.

To show such a situation by another example, we calculated in the same way as above, the hydrogen bond energy of formic acid dimer. Moelwyn-Hughes⁽¹³⁾ has already calculated the electrostatic part of this energy, adopting the dipole model and neglecting the contribution of the van der Waals energy. His results are 8.6 and 13.1 kcal./mole corresponding to the O—H...O distances of 2.85 and 2.55 Å., respectively. On the other hand, Davies⁽¹⁴⁾ has calculated the electrostatic contribution of this energy using the point charge model, and the induction energy by the use of the dipole model. The sum of these energies amounts to 13.4 kcal./mole for the hydrogen bond distance of 2.67 Å. These results seem, at first sight, to give good agreements with the experimental value of 14.13 kcal./mole.^(1b) However, they are both not satisfactory in such regards that the former used the dipole model and hydrogen bonds distance which do not correspond to the actual case, and both authors do not take into account the contribution of the van der Waals energy. Thus, we recalculated the electrostatic energy due to the point charge model, and the van der Waals energy, using the numerical values of the polarisabilities of atomic groups and the ionic character of each bond shown in Table 8. In this case, the revised molecular configuration recently determined by Brockway and others^(2a) is used. The obtained results are summarized in Table 9.

Table 8

Atom or atomic group	$\alpha \times 10^{24}$	Bond	Bond moment	Ionic character		
				A	B	C
O	0.630	C=O	2.50D	42%	44%	46%
OH	0.981	C—O	0.8 D	12%	14%	16%
CH	1.350	O—H	1.66D	36%	39%	42%
		C—H	0.4 D	7%	7%	7%

Case A is corresponding to the observed dipole moment.

Table 9

van der Waals energy {	1.36
(O—H...O)	
<i>ibid.</i> (excluding O—H...O)	1.37
Electrostatic energy A, 12.15; B, 13.77; C, 15.17	
Total	14.88 16.50 17.89 kcal./mole

It is shown that in this molecule the contribution of van der Waals energy is not so

(13) Moelwyn-Hughes, *J. Chem. Soc.*, **1938**, 1243.

(14) Davies, *Trans. Faraday Soc.*, **36**, 383 (1940).

much as in the case of pentaerythritol, and still it amounts to about 15% of the whole.

Comparing this result with the experimental value, the model A is apparently in best agreement. However, as already pointed out, it should be taken into account that the experimental value must contain the energy of reorganization of the dissociated monomer molecules. It is recognized that in the monomer state the *cis*-form is more stable by ca. 7 kcal./mole than the *trans*-form.⁽⁹⁾ As the shape of a single molecule in the dimer association state is a midform *cis* and *trans*, that it will be less stable by a few kcal./mole than the *cis*-form.⁽¹⁵⁾ If we assume that almost all

dissociated monomer molecules take the *cis*-form at the temperature of experiment, we must compare the calculated value with the experimental one with an addition of a few kcal./mole for such energy of reorganization. Thus, it is seen that again the case B or C is rather in better agreement with the observed value.

After all, the energy of hydrogen bond for this substance may be estimated to be about 8 kcal./mole, which is somewhat larger than that of pentaerythritol.

This work was carried out by the help of the research grant of Ministry of Education.

(15) We cannot estimate this energy difference exactly, because of the change of molecular structure and inter-atomic distances on dissociation of the dimer into monomer.

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A Note on the Schulz's Osmotic Pressure Equation

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Introduction

It is well known that there exist two types of osmotic pressure expressions, one presented by Wo. Ostwald:

$$\pi/c = RT/M + Bc^{n-1} \quad (1)$$

and the other presented by Schulz:

$$\pi/c = RT/M(1 - cs). \quad (2)$$

The notation of these equations is similar to what is usually employed. Recently, many theoretical treatments for high polymer solutions have been accomplished by Flory,^{(1),(2)} Huggins^{(3),(4)} and others, and osmotic pressure was represented by power series expansion in concentrations in all their reports as follows:

$$\pi/c = RT/M + A_2c + A_3c^2 + \dots \quad (3)$$

These are regarded as an interpretation of Ostwald type. Concerning the Schulz's equation

(SE), however, there has not been any theoretical explanation in spite of its empirical use.

This paper presents an explanation of the SE, which may offer some empirical knowledge for the following points.

(1) For the purpose of computing molecular weight of polymer more accurately, it is necessary to obtain the precise form of the π/c vs. c curve. Although recent theories demand upward curve, straight lines were obtained from many experimental data, showing that the accuracy of osmotic measurements cannot predict the higher terms in Eq. (3) at low concentrations. On the other hand, the SE leads to opposite curvature at very low concentrations. Thus it is required to examine the degree of approximation of the SE and to obtain the condition for its application.

(2) In order to investigate the state of polymer molecules in solution, it may be useful to inquire the source of parameters in osmotic pressure equations. The parameters in the equations derived by Flory, Huggins, and others have no clear physical meaning. Although s in the SE is also merely a simple parameter, he gave a physical meaning on it, that is, the "specific

(1) P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).

(2) P. J. Flory, *Ibid.*, **13**, 463 (1945).

(3) M. L. Huggins, *Ibid.*, **9**, 440 (1941).

(4) M. L. Huggins, *J. Phys. Chem.*, **46**, 151 (1942).

covolume" of solute. It is necessary to examine whether s calculated by Eq. (2) represents the true value for the above physical meaning.

Formal Transformation of the Schulz's Equation

First of all, on the view-point discussed above, we try to equate the right-hand side of the SE with that of the Huggins, which is expressed as

$$\pi/c = RT/M + RT\left(\frac{1}{2} - \mu\right)c/V_1\rho_2^2, \quad (4)$$

where V_1 is the molal volume of solvent, ρ_2 , the density of polymer, and μ a constant for any given system.

Obeying the Flory's expression $c = \rho_2 v_2$ (v_2 is the volume fraction of polymer), and $M/V_1\rho_2 = x$, Eq. (4) is reduced to

$$A = 1 + x\left(\frac{1}{2} - \mu\right)v_2, \quad (5)$$

where A is the so-called "osmotic pressure coefficient" ($A = \pi/RTc/M$). Substituting $cs = s'v_2$, the SE is reduced to

$$A = 1/(1 - s'v_2). \quad (6)$$

From Eqs. (5) and (6)

$$1/s' = 1/x\left(\frac{1}{2} - \mu\right) + v_2 \quad (7)$$

is obtained. It must be noted that s' corresponds to the Flory's "swelling factor," which is defined as the ratio of the volume effectively occupied by a polymer molecule in solvent to that in its unswollen state.⁽²⁾ While the SE was presented as an approximation, Eq. (5) was derived theoretically, showing that x and μ are predominant factors for osmotic pressure. So if Eq. (7) is derived in any other way, it may be said that the SE is interpreted theoretically, s in the SE being provided with a certain physical meaning.

Before discussing this subject, it is necessary to confirm the agreement of Eq. (7) with experimental results. We quote the Brown and Ferry's data,⁽⁵⁾ one of the most reliable results. And $1/s'$ values are plotted against v_2 in Figs. 1 and 2. These plots are on a line with gradient 1/1 within probable experimental error, satisfying Eq. (7). This fact is merely a reiteration of the previously noted agreement

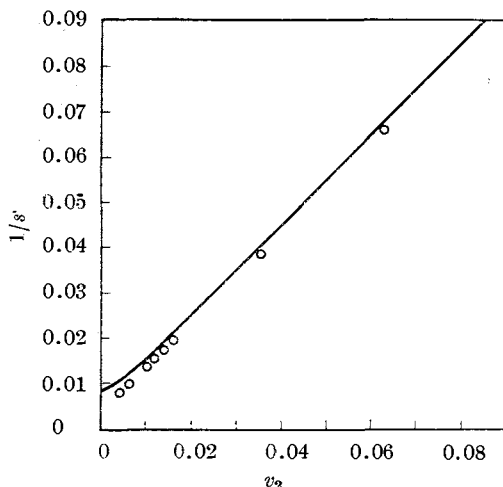


Fig. 1.—Comparison between the theoretical $1/s'$ vs. v_2 curve and the experimental plots (PVAc—methyl-ethyl ketone at 25°C.)

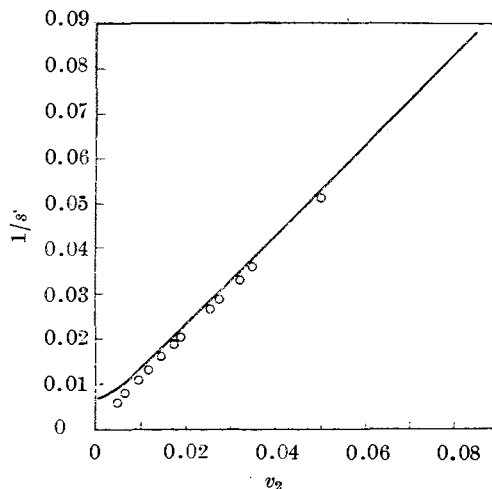


Fig. 2.—Comparison between the theoretical $1/s'$ vs. v_2 curve and the experimental plots (PVAc—1,2,3-trichloropropane at 15°C.)

of Eqs. (2) and (4) with experimental results, but we can confirm that Eq. (7) is to be allowed in this case.

Theoretical Treatment

As discussed above, since Eq. (7) has been introduced by combining the SE with the theoretical Eq. (4), the independent derivation of Eq. (7) will bring in the theoretical basis of the SE and the condition under which its approximation may be permitted.

It seems an appropriate assumption that very dilute solution consists of two regions, one completely unoccupied by solute, and the other possessing an average "concentration"

(5) G. Brown and J. D. Ferry, *J. Chem. Phys.*, **17**, 1107 (1949).

of solute determined by the statistical configurations of the polymer chain. It must be noted, however, that the state of affairs in the commonly used "dilute solution" differs from that in very dilute solution. In the former case, the intermolecular interaction cannot be neglected but in the latter case it may be neglected. Here, we are concerned with the former case.

We are going to turn our attention to one polymer molecule and consider the influence of its environment on it. The actual domain pervaded by a polymer chain cannot be defined sharply. It may be assumed that each molecule is distributed within an effective volume of sphere of radius R_e . Thus the swelling factor s' employed previously is considered to be the value for this effective volume. The s' vs. v_2 relation will be introduced from the condition of the equilibrium between inside and outside of this sphere.

The Flory's treatment⁽⁶⁾ of configurations of polymer chain may be acceptable by some modification for the region occupied by a polymer molecule, although his intramolecular statistic treatment as a swelling phenomenon does not indicate the total interferences within the random coiled molecule as the result of neglecting "short range interference." The free energy in the region occupied by a polymer molecule is given by

$$\Delta F/kT = n \ln v_1 + \mu x v_1 + 3(\alpha^2 - 1)/2 - 3 \ln \alpha \quad (8)$$

(from Eq. (22) in the Flory's report⁽⁶⁾), where n is the number of solvent molecules, v_1 , the volume fraction of solvent in this region, x , the number of the "lattice segments," that is, the ratio of the volume of a polymer molecule to the volume of the assumed cell, α , the factor by which linear dimension of the distribution of segments becomes larger than that of the "random flight" configurations owing to long range interference, and μ is a parameter introduced from the van Laar's expression; $\Delta H/kT = \mu x v_1$. This definition of μ is related to μ_1 employed usually in the thermodynamic treatment of polymer solutions as $\mu = \mu_1/x_s$ (where x_s is the number of the lattice cells in a solvent molecule).

Adopting the above equivalent sphere of radius R_e ,

$$n = (4\pi R_e^3/3 - xV)/x_s V, \quad (9)$$

where V is the volume of the lattice cell, and

R_e is calculated from Eq. (13) in the Flory's report⁽⁶⁾ ($R_e = 0.52 \alpha l z^{1/2}$, where l is the length of each segment for the "equivalent chain" and z is the number of the segments in a molecule.)

Applying the relations $lz = l'x$, $l' = V^{1/3}$, and $c = l/l'$, to the above expression for R_e , Eq. (9) gives

$$\alpha = \{2c^{3/2}x_s(n+x/x_s)/x_s^{5/2}\}^{1/3}. \quad (10)$$

Substituting this expression for α and $nx_s/(nx_s + x)$ for v_1 in Eq. (8) and differentiating with respect to n , there is obtained for the partial molal free energy

$$\ln a_s = \Delta \bar{F}_{1s}/kT = \ln(1 - v_{2s}) + v_{2s} + \mu_s v_{2s} + A v_{2s}^{1/3} - B v_{2s}, \quad (11)$$

where a_s is the activity of solvent, and v_{2s} the volume fraction of polymer, subscript s showing the equivalent sphere ($A = 2^{2/3} c x_s/x_s^{4/3}$, and $B = x_s/x$).

Next, the activity of solvent in the environment region must be investigated. For the range of 0.01 to 0.10 volume fraction, we assume that the Huggins' expression for the activity of solvent in high polymer solutions is applicable to that in the environment region.⁽⁸⁾ Therefore,

$$\ln a_e = \Delta \bar{F}_{1e}/kT = \ln(1 - v_{2e}) + (1 - 1/x)v_{2e} + \mu_e v_{2e}^2, \quad (12)$$

where subscript e illustrates the environment region.

Thus the activity of solvent in the environment region is replaced to the mean value in the whole region of the system. This approximation may be permitted as far as we deal with the equilibrium between one solute molecule and its environment in the vast region involving other polymer molecules. Namely, the activity of solvent in the environment can be put approximately equal to that in the whole region on a statistic average, considering the intermolecular interaction.

For the condition of the equilibrium between the above two regions, $\ln a_s = \ln a_e$ is obtained. Hence from Eqs. (11) and (12),

$$\begin{aligned} \ln(1 - v_{2s}) + v_{2s} + \mu_s v_{2s}^2 + A v_{2s}^{1/3} - B v_{2s} \\ = \ln(1 - v_{2e}) + (1 - 1/x)v_{2e} + \mu_e v_{2e}^2. \end{aligned} \quad (13)$$

(7) This formula is analogous to the Flory's (Eq. (7) in *J. Chem. Phys.*, **18**, 108 (1950)) obtained for the swelling of network structure, except the coefficient B is two times larger than that of the Flory's.

(8) In very dilute solution ($s'v_2 \ll 1$), the activity of the region completely unoccupied by solute can be calculated and the result is $\ln a_e = \ln(1 - 8s'v_2)/8s'z$.

Since v_{2s} obviously equals to $1/s'$, the $1/s'$ vs. v_2 relationship has been derived here ($v_{2s} \div v_2$). Because Eq. (13) cannot be solved readily, numerical values of both sides of it are calculated by substituting suitable values for v_{2s} and v_{2e} respectively. Then equating the numerical values of these two sides, $1/s'$ vs. v_2 relation is obtained numerically.

In the above calculation constants A , B , μ_s and μ_e , must be estimated:

(1) A . The exact values of c cannot be deduced from theory, but are anticipated in the range from 0.1 to 1.0. We can select the proper dimension of the lattice cell freely and assume that $x_s = 1$, and $x = M/\rho_2 V_1$. Thus A is calculated for the proper values of c such as to illustrate the case that might arise in practice. ($A = 2^{2/3} c x_s / x^{1/3}$)

(2) B is calculated readily. ($B = x_s / x$)

(3) μ_e is obtained by usual manner from the osmotic data.

(4) μ_s may not equal numerically to μ_1 in the Flory's report. While μ_1 is applied to the interaction of an individual polymer molecule with its immediate environments, μ_s is indicative of the total polymer-solvent interaction within the region occupied by a polymer molecule. In order to eliminate the deviation of the Flory's treatment from the true thermodynamical value, it may be appropriate that the Huggins' expression for the partial molal free energy of dilution⁽⁹⁾ ($\bar{F}_1 = kT[\ln(1-v_2) + (1-1/x)v_2 + \mu v_2^2]$) should be applicable to this spherical region, instead of that attained from the Flory's procedure ($\Delta\bar{F}_1 = kT[\ln(1-v_2) + v_2 + \mu_1 v_2^2]$), resulting that $\mu_1 = \alpha/RT$ is transferred to $\mu = 1/\beta + \alpha/RT$ without any alteration of the expression of the activity of solvent. This procedure is not yet satisfactory because circumstances in the above spherical region differ from those in polymer solutions. μ_s is supposed to be a little larger than the Huggins' μ , owing to the restriction⁽¹⁰⁾ imposed on the possible number of configurations in the above spherical region.

Flory and co-workers used the μ -value determined on a polymer solution for the μ -value of the gel swollen in the same liquid

in the treatments^{(11),(12)} of the swelling of gels. In this point, as pointed out by Doty and co-workers,⁽¹³⁾ lies an important source of inaccuracy in the Flory's procedure. The difference between μ -values determined by swelling and osmotic pressure is calculated by Doty and co-workers to be about 0.06 unit for a cross-linked polymer (polystyrene) in various solvents. Although we can assume the above spherical region as if it were an extremely loose gel, the distinction between the spherical region and its environment is obscure. The difference between μ_s and μ_e , is supposed to be very small in our case. Thus we estimate this difference to be approximately 0.01 unit. Further quantitative discussion may be difficult owing to the complication of the above restriction to configurations and the weakness of the theoretical basis of μ itself.

Now employing these values of A , B , μ_e and μ_s , examples of the numerical calculation and the graphical method for the purpose of solving Eq. (13) are shown in Table 1 and Fig. 3 respectively, and the theoretical curve thus obtained is illustrated in Figs. 1 and 2, compared with the previously inserted experimental plots. A good coincidence between the theoretical curve and the experimental plots is observed.

Table 1

An Example of the Numerical Calculation of Eq. (13)

(methylethyl ketone solution of P. V. Ac.⁽⁵⁾)
($M = 300,000$).

(Right-hand side) $x = 2800$, $c = 1$, $A = 4.0 \times 10^{-5}$,
 $B = 3.57 \times 10^{-4}$, $\mu_s = 0.44$

v_{2e}	$\ln(1-v_{2e})$ $-v_{2e} \times 10^4$	$A v_{2e}^{1/3}$ $\times 10^4$	$-B v_{2e}$ $\times 10^4$	$\mu_s v_{2e}^2$ $\times 10^4$	$\ln a_e$ $\times 10^4$
0.01	-0.5039	0.0862	-0.0357	0.44	-0.0134
0.03	-4.5948	0.1243	-0.1072	3.96	-0.6183
0.05	-12.9364	0.1474	-0.1786	11.00	-1.9676
0.07	-25.7127	0.1648	-0.2500	21.56	-4.2379
0.09	-43.1127	0.1792	-0.3214	28.16	-7.6149

(left-hand side) $\mu_e = 0.43$, $x = 2800$

v_{2e}	$\ln(1-v_{2e})$ $\times 10^4$	$(1-1/x)v_{2e}$ $\times 10^4$	$\mu_e v_{2e}^2$ $\times 10^4$	$\ln a_e$ $\times 10^4$
0.01	-100.5039	99.9643	0.43	-0.1096
0.03	-304.5948	299.8929	3.87	-0.8367
0.05	-512.9364	499.8214	10.75	-2.3676
0.07	-725.7127	699.7500	21.07	-4.8927
0.09	-943.1127	899.6781	34.83	-8.6042

(9) In our case, v_2/x term in the Huggins' expression vanishes when the entropy of dilution is combined with the entropy of elastic deformation of the molecule.

(10) This restriction is caused by the fact that the spherical region consists of a sequence of segments. Namely in this region the number of configurations is constrained owing to the expectancy for the occurrence of a segment in a cell immediately adjacent to a cell known to be occupied, while in the treatments of polymer solutions the effect of this expectancy is averaged as a whole in some manners considering the discontinuous nature of the solutions.

(11) P. J. Flory and J. J. Behner, *J. Chem. Phys.*, **11**, 521 (1943).

(12) H. F. Boyer, *J. Chem. Phys.*, **13**, 363 (1945).

(13) P. Doty, M. Brownstein and W. Schlener, *J. Phys. Coll. Chem.*, **53**, 213 (1949).

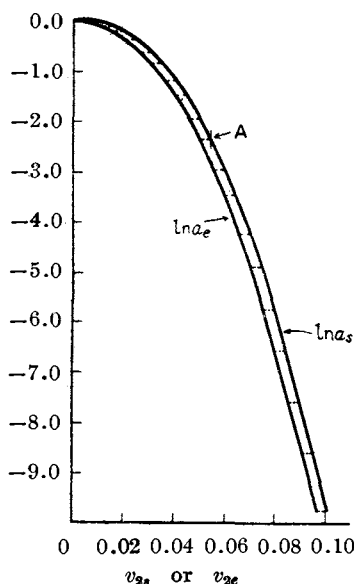


Fig. 3.—An example of the graphical method of Eq. (13). A: Volume fraction of polymer in the spherical region which is in equilibrium with a 0.05 by volume solution of polymer.

Now, expanding the logarithmic terms in Eq. (13) in series and neglecting terms beyond the first two,

$$-(1/2 - \mu_s)v_{2s}^2 + v_{2s}/x + Av_{2s}^{1/3} \\ = -(1/2 - \mu_e)v_{2e}^2 - v_{2e}/x \quad (14)$$

is obtained. If the relation

$$Av_{2s}^{1/3} + \Delta\mu v_{2s}^2 = 2v_{2s}/x, \quad (15)$$

where $\Delta\mu = \mu_s - \mu_e$, is satisfied, then follows

$$v_{2s} = v_{2e} + 1/x(1/2 - \mu_e). \quad (16)$$

Eq. (16) coincides entirely with Eq. (7). Therefore, Eq. (15) is the necessary condition to satisfy Eq. (7) and for the SE to afford a theoretical basis.

The trial substitution of the above numerical values for A , x , $\Delta\mu$ and v_{2s} in Eq. (15) shows that Eq. (15) affords a legitimate approximation as illustrated in Table 2. In spite of the considerable large deviation from Eq. (15) in the range of moderately concentrated solutions, i.e., over 0.07 volume fraction, a good agreement with experimental results is obtained as illustrated in Figs. 1 and 2, probably owing to the fact that the higher terms neglected in the derivation of Eq. (14) is more effective to cover the above deviation as concentration increases. In the above calculation we assume

that $c = 1$, from the viewpoint that each segment for the "equivalent chain" is supposed to correspond to one monomer unit of polyvinyl acetate, whose volume roughly equals to the molecular volume of the solvents. However, it must be noted that the deviation from Eq. (15) due to the c -values is rather small as illustrated in Table 2.

Table 2

The Test of the Validity of Eq. (15) for Various Values of c (Methylethyl ketone and 1,2,3-trichloropropane solutions of P. V. Ac.)⁽¹⁴⁾

x	v_{2s}	$\Delta\mu v_{2s}^2 + Av_{2s}^{1/3} \times 10^4$			$2v_{2s}/x \times 10^4$
		$c=0.25$	$c=0.5$	$c=1.0$	
2,800	0.01	0.033	0.056	0.096	0.071
	0.03	0.121	0.152	0.214	0.213
	0.05	0.286	0.322	0.397	0.355
	0.07	0.532	0.573	0.655	0.497
	0.09	0.855	0.900	0.989	0.639
2,400	0.01	0.030	0.051	0.091	0.083
	0.03	0.119	0.149	0.207	0.250
	0.05	0.285	0.319	0.388	0.417
	0.07	0.529	0.568	0.645	0.583
	0.09	0.852	0.894	0.978	0.750

Meanwhile, Schulz found the following relation from experiments

$$\pi = ks^{-\nu}, \quad (17)$$

where k and ν are constants characteristic to the polymer-solvent system. The theoretical basis of Eq. (17) may be interpreted as follows: it is obvious from the above assumption that the activity of solvent in the whole region may be approximated to that within the spherical region. Thus it results that the activity of solvent in polymer solutions is the function of v_{2s} ($=1/s\rho_2$) only (see Eq. (11)). Hence

$$\pi = -\Delta\bar{F}_1/V_1 = -RT \ln a_s/V_1 \\ = -RT \{ \ln(1 - v_{2s}) + v_{2s} + \mu_s v_{2s}^2 \\ + Av_{2s}^{1/3} - Bv_{2s} \} / V_1. \quad (18)$$

Substituting the numerical values calculated from the Staudinger's experimental data⁽¹⁴⁾ on polyvinyl acetate-acetone system for A , B and μ_s in Eq. (18), the numerical calculation is carried out. The $\log \pi$ vs. $\log s$ relations thus obtained are illustrated in Fig. 4, compared with the experimental plots. The calculated

(14) H. Staudinger and H. Warth, *J. prakt. Chem.*, **155**, 261 (1940).

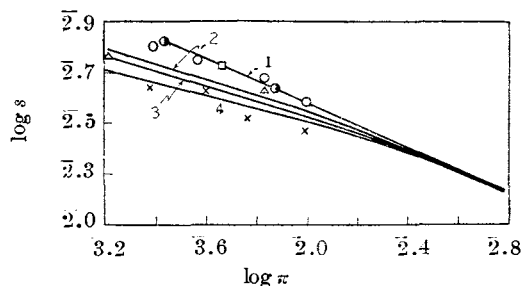


Fig. 4.—Comparison between the theoretical $\log \pi$ vs. $\log s$ curves and the experimental plots. Curve 1, Pro. No. 2 ($x=3350$); curve 2, Pro. No. 3R ($x=2250$); curve 3, Pro. No. 4R ($x=1600$); curve 4, Pro. No. 3 ($x=1870$); □, Pro. No. 2; ○, Pro. No. 3; ●, Pro. No. 3R; △, Pro. No. 4R; ×, Pro. No. 5.

plots are approximately on straight lines and the experimental plots are also not so far from them.⁽¹⁵⁾ Thus it is proved not only that Eq. (18) can be approximated to Eq. (17), but also that the theoretical values of k and ν agree with those values determined by the experiments. Because swelling pressure is assumed to be an expression of the activity of solvent within the spherical region, it is appropriate that k and ν are applicable to the swelling pressure of the same system.

Conditions for the Establishment of the Schulz's Equation

As discussed above, the influence of both c and $\Delta\mu$ on Eq. (15) are not predominant enough to be considered significant. Now the test of the validity of Eq. (15) for various values of x and v_2 is illustrated in Table 3. Eq. (15) holds its validity over the considerable wide range of x . However, it must be noted that Eq. (15) affords a satisfactory approxima-

tion only in a limited range of concentration corresponding to x . Considering the influence

Table 3

The Test of the Validity of Eq. (15) for Various Value of x and v_2 , ($c=1$, $\Delta\mu=0.01$)

	$x=100(A=3.42 \times 10^{-3})$		$x=1000(A=1.59 \times 10^{-4})$		$x=10000(A=1.34 \times 10^{-5})$	
v_2	$\frac{\Delta\mu v_2^2}{A v_2^{1/3}} + \frac{2v_2}{x \times 10^4}$	$\frac{2v_2}{x \times 10^4}$	$\frac{\Delta\mu v_2^2}{A v_2^{1/3}} + \frac{2v_2}{x \times 10^4}$	$\frac{2v_2}{x \times 10^4}$	$\frac{\Delta\mu v_2^2}{A v_2^{1/3}} + \frac{2v_2}{x \times 10^4}$	$\frac{2v_2}{x \times 10^4}$
0.01	7.38	2.0	0.352	0.2	0.012	0.02
0.03	10.72	6.0	0.533	0.6	0.092	0.06
0.05	12.85	10.0	0.835	1.0	0.253	0.10
0.07	14.53	14.0	1.144	1.4	0.493	0.14
0.09	16.14	18.0	1.521	1.8	0.813	0.18

of the higher terms neglected in Eq. (14) and the uncertainty of $\Delta\mu$ on Eq. (15), we roughly estimate the range of concentration, to which the SE might be applicable, as follows; $v_2=0.04 \sim 0.08$ for $x=100$, $v_2=0.01 \sim 0.07$ for $x=1,000$ and $v_2=0.01 \sim 0.05$ for $x=10,000$.

Conclusion

(1) We have given a theoretical basis to s in the Schulz's equation (2).

(2) Since the deficiency of this approximate treatment lies in the uncertainty of $\Delta\mu$, a comprehensive investigation including both the experimental and theoretical study of the above "restriction imposed on possible configurations" is necessary for the refinement of our theory.

(3) The above treatment does not concern with extremely dilute solution ($sv_2 \ll 1$).

I should like to express my appreciation to the director K. Makishima for his encouragement and support to this work.

(15) When x is extremely small, Eq. (17) fails its validity.

Energy and Entropy Changes Accompanying the Molecular Association of δ -Valerolactam in Its Carbon Tetrachloride Solution

By Masamichi TSUBOI

(Received December 4, 1950)

Introduction

Recently the present writer made measurements of the infra-red absorption intensities of the $3.11\ \mu$ and $3.24\ \mu$ bands of δ -valerolactam in its carbon tetrachloride solutions at various concentrations and temperatures. The results of these experiments are of interest in connection with the problem concerning the molecular association of cyclic amides, since they show decidedly that δ -valerolactam molecules form on association exclusively ring dimers, the two bands being due to one and the same ring dimer structure. Furthermore, from the data obtained, calculations were made of the changes of energy and entropy accompanying the ring dimer formation. Some details of these experiments and their results are presented in this paper.

Experimental

The samples examined are carbon tetrachloride solutions of δ -valerolactam

$$\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ | \quad | \\ \text{CH}_2 \quad \text{CH}_2 \\ | \quad | \\ \text{CO}-\text{NH} \end{array}$$

purified by vacuum distillation.

As containers of the solutions, specially-made silica glass cells of different lengths (from 0.1 to

10 cm.) were used. (See Fig. 1.) Each cell has windows of plane-parallel silica glass plates (W), set by welding at both ends of its horizontal tube (H), parallel to each other, and an electric heating device is attached to the cell so that its content can be kept at desired temperatures.

The spectrometer with quartz prism here used is the same one which the writer used in his previous work.⁽¹⁾

δ -Valerolactam in carbon tetrachloride solutions exhibits, as reported in a previous paper,⁽¹⁾ three N-H bands, at $2.92\ \mu$ (due to free molecule), $3.11\ \mu$ (due to associated molecule) and $3.24\ \mu$ (also due to associated molecule). In the present experiments, measurements of the absorption intensities of these N-H bands were made with the object of determining the concentrations with respect to the free and associated molecules in the solutions of various concentrations (with respect to δ -valerolactam) at different temperatures.

Unfortunately, accurate absorption intensity measurements of the $2.92\ \mu$ band were not possible, owing to the interference of the absorptions in the neighborhood of $2.9\ \mu$ by the quartz prism used. Accordingly, measurements were made only of the other two bands at $3.11\ \mu$ and $3.24\ \mu$.

Results and Interpretations

(1) From the measurements of transmittance (I/I_0) of the solutions for rays of $3.11\ \mu$ and

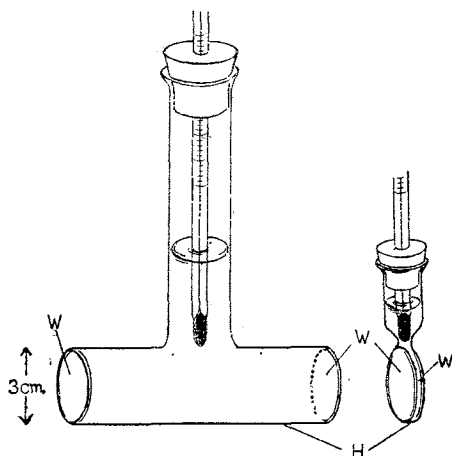


Fig. 1.

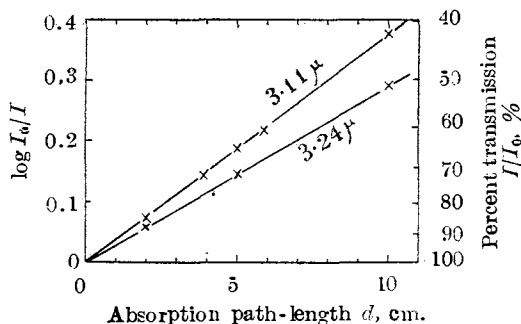


Fig. 2.—Observed relation between $\log I_0/I$ and d : concentration, $0.00165\ \text{mol/l.}$; temperature, 30.1°C.

(1) M. Tsuboi, This Bulletin, **22**, 215 (1949).

3.24 μ of various path-lengths (d), it was found that the observed relations between I/I_0 and d accord with the Lambert's law, deviations from it due to errors in observation being within a few per cent of $\log I_0/I$. Some examples of the relations obtained are shown in Figs. 2 and 3.

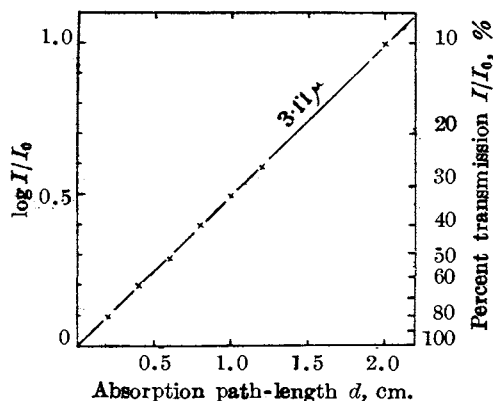


Fig. 3.—Observed relation between $\log I_0/I$ and d : concentration, 0.00997 mol/l; temperature, 30.1°C.

Based on the relations stated above, the value of $\frac{1}{d} \log \frac{I_0}{I}$ (denoted hereafter as x) for each solution is conveniently used in this paper to represent the absorption intensity of each band, for this value is independent of the path-length and is proportional to the concentration of the associated molecules to which the absorption band is assigned.

(2) In Table 1 are given the results of exploratory observations made as to how the

Table 1

Temp. °C.	Concn. mol/l.	x obsd. for the 3.11 μ ray	x obsd. for the 3.24 μ ray	$\frac{x_{3.24\mu}}{x_{3.11\mu}}$
30.1	0.03338	1.98	1.60	0.81
30.1	0.00997	0.498	0.395	0.79
30.1	0.00507	0.202	0.154	0.76
60.7	0.00487	0.100	0.077	0.77
30.1	0.00399	0.148	0.116	0.79
30.1	0.00165	0.0377	0.0291	0.77

values of x of the solutions for the 3.11 μ and 3.24 μ rays vary with the temperatures (t) and concentrations (c) with respect to δ -valerolactam. A notable fact seen in the table is that, while the values of both x for the 3.11 μ ray ($x_{3.11\mu}$) and x for the 3.24 μ ray ($x_{3.24\mu}$) vary with t and c , the ratios $x_{3.11\mu}/x_{3.24\mu}$ for any given t and c remain constant. This fact indicates that the two bands are due to one and

the same kind of associated molecule and that the determination of one of the x 's is sufficient for determination of the concentration of that molecule.

(3) In the third column of Table 2 are given

Table 2

Temp. °C.	Concn. mol/l.	x for 3.11 μ ray (obsd.)	x for 3.11 μ ray (calcd.)
30.1	0.03338	1.98	2.01
	0.02158	1.24	1.22
	0.01362	0.700	0.709
	0.01320	0.682	0.681
	0.00997	0.498	0.483
	0.00905	0.441	0.429
	0.00757	0.355	0.343
	0.00555	0.231	0.220
	0.00507	0.202	0.203
	0.00399	0.148	0.147
45.3	0.00296	0.0922	0.0975
	0.00165	0.0377	0.0415
	0.01295	0.528	0.538
	0.00497	0.147	0.143
60.7	0.03204	1.47	1.42
	0.01270	0.381	0.392
	0.00487	0.100	0.097
	0.00159	0.0129	0.0143

the values of x for the 3.11 μ ray, as observed with the solutions of various concentrations (with respect to δ -valerolactam) and temperatures. It is to be shown below that these results can be explained on the assumption, in accordance with the indication given in (2), that there is only one kind of associated molecule in the solutions, i. e., $(C_5H_9NO)_2$, to which the 3.11 μ band is attributable, and that this dimer coexists with monomer C_5H_9NO in equilibrium, $2C_5H_9NO \rightleftharpoons (C_5H_9NO)_2$.

On the assumption as stated above, the monomer $\rightleftharpoons$ dimer equilibrium constant K now at issue must be expressed as

$$K = \frac{x/\kappa}{(c - 2x/\kappa)^2},$$

where κ is the molecular absorption coefficient for the 3.11 μ ray and c the concentration with respect to δ -valerolactam. While, the observed relations between c and x seen from Table 2 accord well with the relations obtained from the above equation, if appropriate values are given to K and κ . Thus, the values of x observed at 30.1° (given in the third column of Table 2) show close agreement with those calculated by putting $K=206$, $\kappa=158$ in the equation (given in the fourth column), differences between them being less than several per

cent of the values of α , with one exception.⁽²⁾ The values of α observed at 60.7° also agree well with those calculated from the equation by putting $K=45$, $\kappa=159$. Furthermore, it is to be noticed that the values of κ given above for 30.1° and for 60.7° are practically equal to each other. This is just as it should be, since in the temperature range now in concern the molecular absorption coefficient for the ray of 3000 cm^{-1} or thereabout in frequency must be independent of temperatures.⁽³⁾

The value of K at 45.3° is 90, as calculated from the observed values of α and the assumed value of κ (=159).

In Table 3 the values of K for three different

Table 3

Temperature, °C.	K	ΔF , kcal/mol	ΔS , E. U.	ΔE , kcal/mol
30.1	206	-3.21		
45.3	90	-2.84	-23.5	-10.3
60.7	45	-2.52		

temperatures are given, with, in parallel column, the values of free energy change (ΔF) on association, which were calculated from the corresponding values of K (by the formula $\Delta F = -RT \ln K$). When the logarithms of these values of K are plotted against $1/T$, the points obtained fall on a single straight line (as shown in Fig. 4). From the inclination and the in-

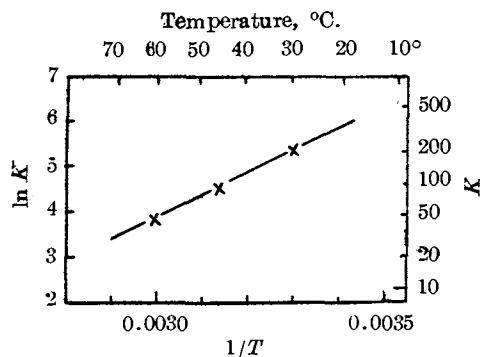
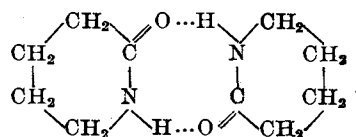


Fig. 4.

tercept of this straight line, the values of energy change (ΔE) and the entropy change (ΔS) accompanying the dimer formation in the solution are obtained as $\Delta E = -10.3 \pm 1.0$ kcal/mol and $\Delta S = -23.5 \pm 2.5$ E. U. The ΔE value

here obtained is about twice as much as the value known for ordinary single hydrogen bond.

All the facts stated above, in combination, show decisively that δ -valerolactam molecules form on association only one type of dimer—the ring dimer with the inter-monomer double hydrogen bonds of the structure:



and that both of the two N-H association bands (at 3.11μ and 3.24μ) are attributable to this single structure.

The conclusion reached here does not agree with the view advanced by some previous writers, as Darmon and Sutherland,⁽⁴⁾ who tend to attribute the two N-H association bands exhibited by cyclic amides to two different types of associated molecules.

Appendix.—In Fig. 5 is shown graphically the relation between association degree of δ -valerolactam molecules and the concentration and temperature of the solution, as obtained from the values of ΔE and ΔS .

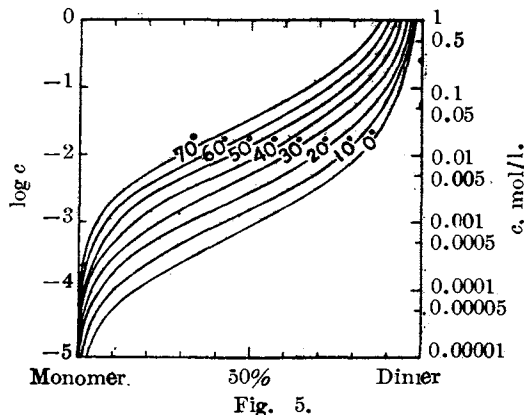


Fig. 5.

The writer wishes to express his sincere thanks to Professor San-ichiro Mizushima and Dr. Takehiko Shimanouchi for their kind guidance throughout this work. The cost of this research has been partly defrayed from Grant in Aid for Scientific Research from the Ministry of Education.

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(2) In the exceptional case where $c=0.00165$ mol/l., the difference between the calculated and observed values of α is about 10% of it. This is probably attributable to the error in determining such a small concentration.

(3) R. C. Tolman, "Statistical Mechanics with Applications to Physics and Chemistry", 1927, p. 775.

(4) S. E. Darmon and G. B. B. M. Sutherland, *Nature*, 164, 440 (1949).

Mechanisms of Agglomeration of Red Cells by High Polymer Compounds⁽¹⁾

By Kiyoshi INOKUCHI

(Received December 9, 1950)

Introduction

It is well-known that erythrocytes agglomerate each other under various conditions. This erythrocyte agglomeration is divided into two types, *i.e.*, specific and non-specific ones, the former being observed in the immunological reaction while the latter practically in all other cases. The increase in sedimentation rate of erythrocytes, which often becomes the object of clinical examination for various diseases, is considered to be due to the agglomeration of erythrocyte. Recently, the mechanism of immunological (specific) agglomeration has been elucidated by the physicochemical studies carried out by Pauling⁽²⁾ and his collaborators. The present author's paper deals with the results of experiment performed with the purpose of elucidating the mechanism of the non-specific agglomeration caused by the addition of several substances of known structure. First of all the action of high molecular substances has been investigated expecting that this series of substances has different mode of action from that of the low molecular.

In 1921 Fahraeus⁽³⁾ reported that gum arabic and other macromolecular substances produced pseudoagglutination. Later, this work has been argued by many workers and Meyer⁽⁴⁾ and his associates in 1945 proposed the view that probably all highly asymmetrical molecules of large size will cause an increase in the sedimentation rate when added to normal blood. The reasons for this phenomenon, however, are not definitely known. In order to elucidate the mechanism of this phenomenon, the following experiments were carried out.

Experimental

The quantitative expression of the degree of

agglomeration was made by sedimentation experiment. To 0.5 ml. of packed red cells which have been washed with isotonic saline were added 1.5 ml. of colloid saline solution of pH about 7, and after sufficient agitation, the sedimentation rate was measured by the Westergren method. As has been reported a period of constant rate of falling was observed to follow an induction period. As the sedimentation rate in the constant rate period can be reproduced with sufficient accuracy and characterizes the sedimentation system under investigation, this value will be employed for further discussion. With the assumption that the sedimentation obeys a modified Stokes' law, the relation between the size of agglomerate and sedimentation rate may be expressed by the following equation

$$r = C \sqrt{\eta v}$$

where C is a constant determined by sedimentation system, r , the mean radius of agglomerate, η , the relative viscosity of medium, v , the sedimentation rate in constant rate period.

The present author observed the agglomeration effect of various polymers upon the human red cells which had been washed with saline. This observation is compared with the results carried out by many investigators in the presence of plasma. These polymers are classified for the convenience sake into several groups and their agglomerating effects are shown in Table 1. It can be seen in this table that plasma does not play any important role in this phenomenon, except the case of globulin. Moreover it may be deduced from this table that among the negative colloids, fibrous ones generally show this effect, while spherical ones exert but little action at best. It has been observed that the agglomeration brought about by negative colloids is reversible and the agglomerate forms rouleaux structure, while the positive polymers which exert far stronger agglomerating action than the negative ones, cause an irreversible agglomeration and the agglomerate forms random clumping, but not rouleaux structure. In order to clarify, first of all, the mechanism of the agglomeration by

(1) This work was reported at the meeting for general discussion of colloid chemistry under the auspices of Chemical Society of Japan, Kyōto, Nov., 1950. The earlier part of this work was carried out at the Faculty of Science of the University of Kyūshū.

(2) L. Pauling, *J. Amer. Med. Assoc.*, **62**, 2643 (1940).

(3) R. Fahraeus, *Acta Med. Scand.*, **3**, 55 (1921).

(4) K. Meyer, E. Hahnel and R. R. Feiner, *Proc. Soc. Exptl. Biol. Med.*, **58**, 36 (1945).

Table 1

Water soluble polymers	Agglomeration effect on red cells	
	in whole blood	washed with saline
Negative colloid		
(1) Fibrous colloid		
(a) Electrolytic colloid		
Na-alginate	+(5)	+
Na-glycolcellulose	+	+
Na-desoxyribonucleate	+(4)	+
Pectin	+(6)	+
Gelatin	+(7)	+
Potassium salt of polyvinyl alcohol sulfuric ester	+	+
Gum arabic	+(3)	
Fibrinogen	+(8)	
Na-hyaluronate	+(4)	
Type-III pneumococcus polysaccharide	+(9)	
(b) Non-electrolytic colloid		
Glycolcellulose	+	+
Mannan	+	+
Polyvinyl alcohol	+(10)	+
Dextran(10)	+(11)	+
(2) Spherical colloid		
(a) Electrolytic colloid (Globular protein)		
Ovalbumin	-	-
Serum albumin	-(5)	-
Serum globulin	+(5)	-
Hemoglobin	-	-
(b) Non-electrolytic colloid		
Glycogen	±(6)	±
Positive colloid		
Poly N-trimethyl glucosamine (Macramine)		+++
Clupeine sulfate		+++

these substances, sodium alginate was mainly used as a representative of these polymers.

Decrease in Concentration of Alginate in Bulk.—The decrease in the concentration of alginate was measured, which was expected to occur by the addition of erythrocytes if the adsorption of alginate by erythrocytes would take place. The decrease in concentration,

however, was so small that it barely exceeds the limit of experimental error.

Electric Charge of Erythrocytes by the Addition of Alginate.—The change of the electric charge on the erythrocytes by the addition of alginate was also measured using a flat microelectrophoretic cell. As shown in Fig. 1, the electric charge on erythrocytes increases

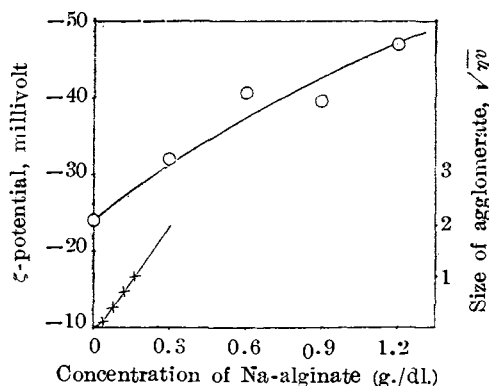


Fig. 1.—Charge of red cell and size of red cell agglomerate versus alginate concentration: circles show ζ -potential and crosses, the size of agglomerate, temp., 16°C; pH, 7.3.

proportionally with the amount of alginate. This result clearly shows some change have taken place on erythrocyte surface.

Adsorbability of Erythrocytes on Alginate Film.—Thin film of alginic acid made on the glass by treating Na-alginate film with hydrochloric acid, was immersed in an isotonic saline suspension of erythrocyte for a few minutes and then washed with isotonic saline solution. Some number of erythrocytes thus were found remaining on the film without having removed by washing. The adsorbabilities of cells on the films of several metallic alginates which are insoluble in water were observed in the same manner. As shown in Table 2, it was found that the adhering abilities of erythrocyte on alginate films are different according to the kind of metal ion of alginate,

Table 2

Numbers of erythrocytes adhered to the various metallic alginate films (Relative number)

H-alginate...	340, 320	Zn-alginate...	38, 89, 48
Ca- "	10, 5, 12	Ba- "	35, 37, 43
Cu- "	84, 87, 78	Mn- "	43, 32, 36

These metallic alginate films were prepared by treating the Na-alginate films in various metallic solution.

- (5) Maynard B. Chenoweth, *Ann. Surg.*, **127**, 1173 (1948).
- (6) Ch. Wunderly, *Experimentia*, **1**, 332 (1945).
- (7) Koop, *Surgical Clinics of North America*, Philadelphia number, 1313 (1944).
- (8) J. Gray and E. B. Mitchell, *Proc. Soc. Exptl. Biol. Med.*, **51**, 403 (1942).
- (9) W. J. Nungester and Klein, *Proc. Soc. Exptl. Biol. Med.*, **36**, 315 (1937).
- (10) cf. F. P. Turner et al., *Surg. Gyn. Obst.*, **5**, 673 (1949).
- (11) A. Grönwall and B. Ingelman, *Acta physiol. Scand.*, **9**, 188 (1945).
- (12) Ch. Wunderly, *Viertel jähreschr. Naturforsch. Ges. Zürich*, **89**, 170 (1944).

namely Ca-alginate film almost failed to show the ability to adhere erythrocytes on it, while they adsorb considerably on the film of alginic acid.

The Effect of Some Change Occurred on Erythrocyte Surface.—With the purpose of finding the effect of some change occurred on the erythrocyte surface, the amino radical, considered to be the positive center of erythrocyte, was attempted to be blocked up. Fraenkel⁽¹²⁾ reported that the amino radical of serum albumin was attacked by formaldehyde. The effect of alginate upon erythrocytes, treated with formaldehyde, was thus observed. The results are shown in Fig. 2. It shows that the

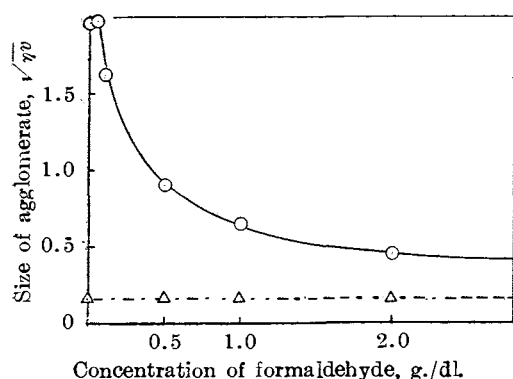
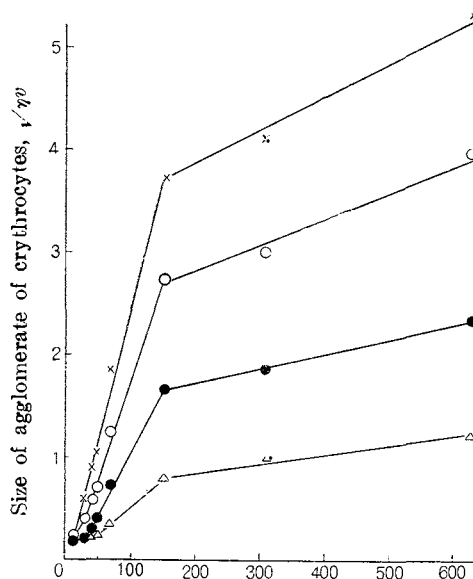


Fig. 2.—Effect of formaldehyde upon the red cell agglomeration by alginate (circles). Triangles show the only effect of formaldehyde on red cells in the absence of alginate, temp., 16.5°C.; Na-alginate, 0.1%; pH, 6.6.

agglomerating action of alginate decreases with the concentration of formaldehyde used. Moreover, Klotz⁽¹³⁾ has shown that some organic anions, *i.e.*, methyl orange and dinitrophenol, picric, and cinnamic ions combine with the amino radicals of serum albumin. The effect of these anions upon erythrocyte agglomeration by alginate was observed. It was shown that the coexistence of 0.1 mol/dl. of these four anions prevents completely the agglomeration by alginate. Salicylic, benzoic, and sulfanilic ions, which have been considered to give similar action to the afore-stated substances, also show the inhibiting effect on erythrocyte agglomeration by alginate.

Effect of Degree of Polymerisation of Alginate⁽¹⁴⁾ on the Agglomeration.—As



Degree of polymerisation of Na-alginate

Fig. 3.—Size of agglomerate of red cell versus degree of polymerisation of alginate added, x 0.16%, O 0.12%, ● 0.08%, Δ 0.04%.

shown in Fig. 3, it has been observed that the agglomerating action of alginate increases remarkably with increase in the degree of its polymerisation as well as its concentration. The effect of the former factor is the greatest in certain range of the degree of polymerisation.

Discussion

Possible mechanism of Agglomeration of Erythrocytes by Na-alginate.—From the afore-stated results that the electric charge of cells increases with the increase in concentration of alginate added, and that erythrocytes are capable to adsorb on the alginic acid film, it may be considered that alginate molecule is adsorbed on erythrocyte surface.

It was observed by the author that diacetyl alginate, prepared by the acetylation of OH radicals of Na-alginate, aggregates to practically the same extent as the original alginate. Furthermore as shown in Table 2, it was found that the adhering abilities of erythrocyte on alginate films are different according to the kind of metal ion of alginate. These facts show that the dissociated radical of alginate, *i.e.*, carboxyl one, is the centre of its adsorption on erythrocytes. On the other hand, the attempts to block up the amino groups on cell surface have brought the preventing effect of agglomeration of cells. This shows that the centre

(12) Fraenkel-Conrat and Olcott, *J. Biol. Chem.*, **174**, 827 (1948).

(13) Klotz and Curme, *J. Amer. Chem. Soc.*, **70**, 397 (1948).

(14) Polymer homologues of alginate was prepared by the method reported by the author in *Memoirs of the Faculty of Science, Kyushu University*, Ser. C, **1**, 115 (1950).

of adsorption on erythrocyte are considered to be the amino groups on its surface, presumably that of lysine, arginine, histidine, etc. From these facts, it may be concluded that alginate molecule is adsorbed on erythrocyte surface by the electrostatic force. Although alginate is a macromolecule having carboxyl radicals on each unit, simultaneous-fitting of all the carboxyl radicals of alginate in the positive centres on the cell probably cannot occur due to the steric hinderance. It is more likely that alginate molecule combines with red cell with a small portion of the radicals and that the remaining portion of them is left unreacted. It is probable that the unreacted radicals then combine with the second cell, thus alginate molecule holding the cells together. Such a view is supported by the experimental fact, as mentioned above, that the agglomerate of erythrocytes increases in size with the increase in the degree of polymerisation of alginate added. The increase in the degree of polymerisation causes the increased molecular extension in solution, which in turn facilitates the molecule to act as link joining cells together.

Other substances shown in the group of negative electrolytic fibrous colloid in Table 1 are generally considered to provide the similar properties, as alginate with respect to this effect. Besides, it was also reported that with pectin,⁽⁶⁾ sodium desoxyribonucleate,⁽⁴⁾ and sodium hyaluronate⁽⁴⁾ their agglomerating effects increase with the polymerisation degree as seen in sodium alginate. The above indicated mechanism is, therefore, the common one for negative fibrous electrolytes.

Non-electrolytic Fibrous Colloids.—As shown in Table 1, glycolcellulose, mannan, dextran, and polyvinyl alcohol have been known to possess the action to agglutinate red cell. These substances are similar in structure to the fibrous electrolytes, except only that the hydrophilic radicals are OH group which is not dissociated. The dependence of agglomeration upon the polymerisation degree was also reported for this series of substances.^{(4) (9)} Moreover, it has been found by the present author that these substances show their agglomerating action neither in the presence of formaldehyde, nor of some organic anions such as cinnamic, salicylic, etc. These facts also support the view that the same mechanism as that of alginate is also available for these substances. However, the force contributing to the adsorption of the colloids upon cells probably is a nature of hydrogen bond, acting between OH groups of colloids and the amino radicals on red cell surface.

Reason for the Lack of Agglomeration

Effect of Globular Protein.—As shown in Table 1, the native globular proteins, for instance, ovalbumin, serum albumin, serum globulin, hemoglobin, cause no agglomeration of red cell. The question arises why these proteins lack this action in spite of the presence of dissociated radicals in their molecules. As to this problem, at least two possible reasons may be considered, *i.e.*, the lack of adsorption of these proteins on cell surface or too small molecular extension of these proteins. Pauling⁽¹⁵⁾ reported that erythrocytes previously treated with bisdiazotarsanilic benzidine forms agglomerate and this is due to the formation of $-NN-\langle \text{ } \rangle-\langle \text{ } \rangle-NN-$ bridge between the cells. Obviously, the length of the bridge between the protein molecules is much larger than that of bisdiazobenzidine. Moreover, according to the present author's experiment, the partially degraded alginate, which is estimated to have smaller order of molecular extension in comparison with that of serum albumin, shows the agglomerating action. In view of these experimental facts, the lack of agglutination effect cannot be considered to be due to their too small molecular extension. Thus, we prefer another possibility that this negative result is due to the lack of the adsorption of the protein on cells. Now we face to the problem why globular protein cannot attach to the cell surface, while fibrous colloids can do. Red cells, in this case, possess negative charge as a whole, which causes the repulsive force against negative colloids. Therefore we must consider a necessary condition for the combination of these colloids with cell surface in spite of the repulsion between them. The author proposes the following view concerning this point. In order that negative colloid can couple with the weakly positive radicals situated among strongly charged negative groups on cell surface, it is necessary that the negative group in the polymer molecule has a mobility in solution strong enough to be capable of attaching themselves to the positive centres surrounded by negative ones on the surface of cells. This view is easily understood by the fact that the low molecular organic anions are capable of combining with the amino group of negatively charged protein. A fibrous molecule is considered to have a favorable property to satisfy the necessary condition mentioned above, since each part of the molecule seems to possess a sufficient flexibility in solution. In addition to this property, fibrous molecule easily holds cells together on account of the large molecular extension in solution.

(15) D. Presman, D. H. Campbell and L. Pauling, *J. Immunol.*, **44**, 101 (1942).

Globular protein, however, does not satisfy this necessary condition, because each part of the protein molecule is closely packed in space by virtue of hydrogen bonds. The negative radicals of the protein, which are fixed each other in space and accordingly unfavorable to change their mutual positions in solution, thus cannot appreciably attach to the positive centres on cells surrounded by strongly charged negative ones due to steric hinderance. Owing to such properties of the molecular shape of the polymers, a fibrous molecule exerts agglomeration effect on erythrocytes, while a spherical one does not show it.

It is very interesting to note that a considerable agglomeration occurs when globulin is added to whole blood, which is in accord with the results obtained by Gray and others, while it does not occur in the absence of plasma as shown in Table 1. Many interesting problems concerning globulin remains unexplained, waiting for further research.

Agglomerating action of Glycogen.—Generally speaking, the agglomerating effect of this substance upon cells is very small, but in higher concentration the agglomeration occurs to some extent. The molecular extension of glycogen in solution is considerably small as seen from the knowledge of viscosity. Moreover, the mobility of each part of the molecule in solution is considered to be neither so poor as that of globular protein, nor so rich as of fibrous colloid. In view of these properties of glycogen, the experimental result obtained can be explained.

Some Suggestions to Clinical Problems.—In general, the rate of erythrocytes sedimentation in pathological state has been considered to be dependent on the nature and concentration of the protein components of the plasma. However, some experimental evidences, suggesting that erythrocytes sedimentation rate may likewise be profoundly influenced by non-protein substances, were reported by several workers.⁽⁴⁾ If it might be assumed that certain polymers

of fibrous shape appear in blood in the course of diseases and they were responsible for the increased sedimentation rate in the pathological state, the mechanism of this clinical phenomenon may also be explained by the same mode proposed above.

Summary

The mechanisms of agglomeration of erythrocytes caused by hydrophilic negative polymers were investigated and the following views were proposed.

(1) Among the negative colloids, fibrous colloids show the erythrocyte agglomeration, while spherical ones do not cause it.

(2) Agglomeration by the negative colloids is caused by two actions, *i.e.*, adsorption of these polymers upon cells and their action to join cells together. Those substances which lack either or both of these actions fail to cause the agglomeration.

(3) Fibrous structure of macromolecule favors these actions on account of the large extension of molecule and adequate flexibility of each part of the molecule in solution.

(4) The dissociated or dipole radicals of the negative polymers and amino groups of the protein of cell surface are considered to be the centres of adsorption respectively.

The author expresses his hearty thanks to Prof. Dr. J. Sameshima and Dr. T. Tachibana of the University of Tokyo and Prof. T. Sasaki of the University of Kyushu for their kind guidance in the course of this study. The author also wishes to express his gratitude to Prof. Dr. T. Tomoda and Prof. Dr. S. Hojo of the University of Kyushu who granted the chance to make this work possible.

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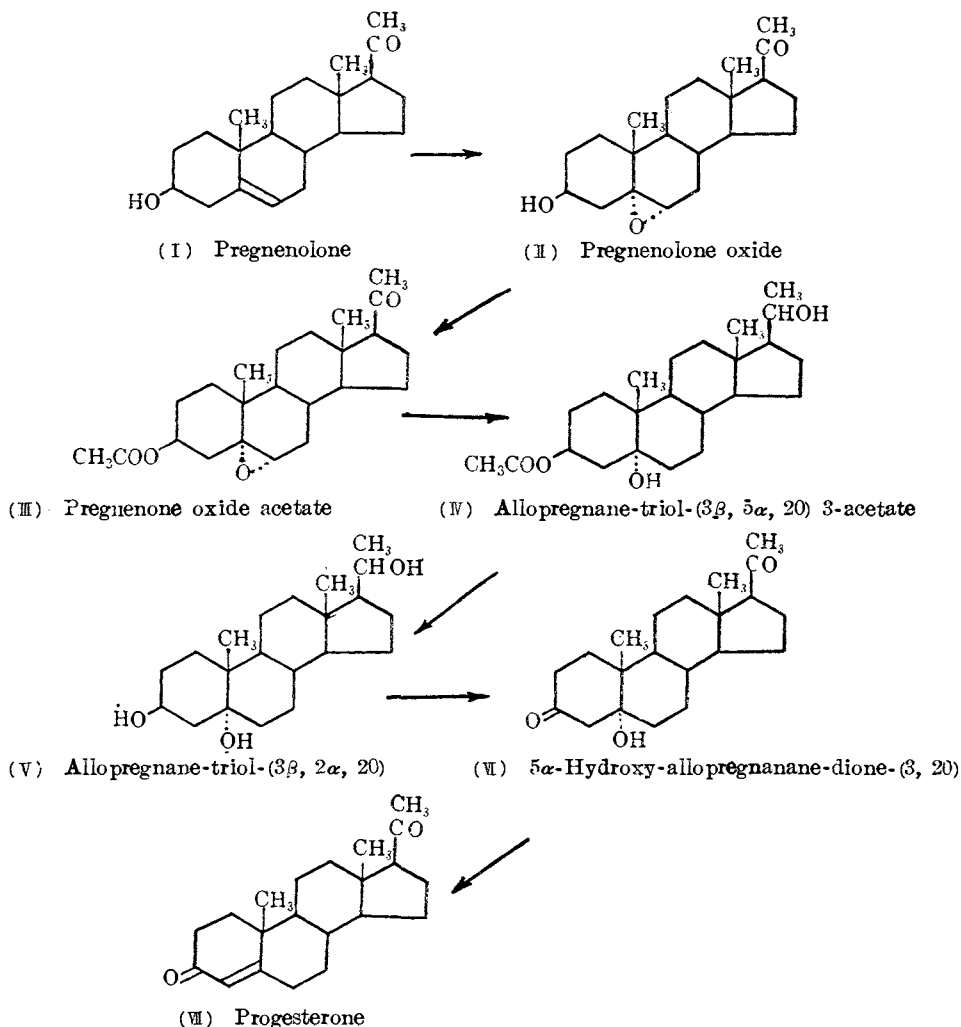
A New Synthesis of Progesterone⁽¹⁾

By Yoshiyuki URUSHIBARA, Misao CHUMAN and Shunyo WADA

(Received December 9, 1950)

The principle used in this synthesis originates in the reduction of cholesterol oxides⁽²⁾ and is the same as used in the new synthesis of testosterone,⁽³⁾ consisting essentially of catalytic reduction of a 3β -hydroxy-5,6 α -epoxy-steroid to a 3β ,5 α -dihydroxy-compound followed by oxidation to a 5α -hydroxy-3-ketone and dehydration to a Δ^4 -3-ketone. The 5,6 α -oxido steroid gives always a 5α -hydroxy-

compound on catalytic reduction, and this change can be taken as an evidence for an α -oxido structure. With an oxide possessing a carbonyl group a little complication may possibly arise, because at the same time the carbonyl group may be reduced or either epimeric alcoholic group. In the case of the synthesis of testosterone, α -dehydroisoandrosterone oxide acetate gave fortunately the



(1) Japanese Patent applied for on July 1st, 1948, and entered as No. 184914 on October 20th, 1950.

(2) Y. Urushibara and M. Chuman, This Bulletin, **22**,

70 (1949).

(3) Y. Urushibara and M. Chuman, This Bulletin, **22**, 1 (1949).

desired androstane-triol-(3 β , 5 α , 17 β)⁽⁴⁾ 3-acetate on catalytic reduction, as reported. Later experiments, however, yielded sometimes mixtures of epimeric triols.⁽⁵⁾ The synthesis of progesterone starts from pregnenolone (I), and reduction of the carbonyl group at carbon atom 20 might cause a similar problem. But, such a complication, if any, can be eliminated in this case, because the carbon atom in question is oxidized again to a carbonyl group in the final product, progesterone.

The present synthesis cannot claim a method swifter or simpler than any of the known starting from pregnenolone, if the number of the steps of reactions involved be considered, but it proved notwithstanding a new method worth studying, because it afforded a proof for the α -oxido configuration of the pregnenolone oxide (II) and gave a satisfactory over-all yield.

Pregnenolone oxide (II) was prepared by the action of perbenzoic acid on pregnenolone (I) (65 mg.), and recrystallized from ethyl acetate. It melts at 185–187°, and is soluble in ethyl acetate, ethanol, methanol, and acetone, difficultly soluble in ether, and insoluble in petroleum ether. Yield about 90% of the theory (60 mg.).

Pregnenolone oxide acetate (III) was obtained by acetylation of the above oxide (II) (140 mg.) with acetic anhydride and pyridine, and recrystallized from acetone. It melts at 165–

166°. Yield about 90% (130 mg.). M. Ehrenstein and M. T. Decker⁽⁶⁾ treated pregnenolone acetate with potassium permanganate and obtained an oxide melting at 163–165°. Although a direct identification is lacking, the present authors believe that they obtained the same substance.

The above acetate (III) (50 mg.) was dissolved in glacial acetic acid and shaken with hydrogen and platinum oxide. About two mols of hydrogen were absorbed. The reduction product (IV) was then hydrolyzed with methanolic potassium hydroxide, and the hydrolyzate, perhaps an epimeric mixture of allopregnane-triols-(3 β , 5 α , 20) (V), was oxidized without purification with chromic acid in glacial acetic acid. The oxidation product was recrystallized from a mixture of ethanol and ethyl acetate. 5 α -Hydroxy-allopregnane-dione-(3,20) (VI) thus obtained forms small plates melting at 264–266° and difficultly soluble in most organic solvents. Yield about 80% (35 mg.).

Dehydration of the above 5 α -hydroxy-allopregnane-dione (VI) (20 mg.) with dry hydrogen chloride in chloroform gave progesterone (VII) in prisms melting at 125° after recrystallization from methanol. Yield about 80% (15 mg.). The substance showed a perfect physiological activity characteristic of progesterone.

The authors thank for the Scientific Research Encouragement Grant from the Ministry of Education.

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(4) The triol 3-acetate gave finally testosterone through succeeding processes and was designated as 17 α in conformity with the configuration of testosterone assigned at that time. Later it has been known that the configuration of testosterone was corrected to 17 β , and in consequence the triol is undoubtedly the androstane-triol-(3 β , 5 α , 17 β).

(5) Compare L. Ruzicka and A. C. Muhr, *Chem. Abst.*, **38**, 6294 (1944).

(6) *J. Org. Chem.*, **5**, 544 (1940).

Plastic Deformation of the Regenerated Cellulose Fibers. I. Dichroic Study of the Deformation of Freshly Prepared Fibers

By Saburo OKAJIMA and Yasuji KOBAYASHI

(Received December 14, 1950)

I. Introduction

The authors studied quantitatively the dichroic behaviors of the natural and artificial fibers and found that dichroism can reasonably show their inner structures.⁽¹⁾ The deformation process of the regenerated fiber was also studied by using this phenomenon and it was concluded that the results confirm Kratky's second theory⁽²⁾ in the early stage of stretching in the case of the freshly prepared and swollen state. But this conclusion was made by neglecting the volume change of the fiber during stretching, and P. H. Hermans⁽³⁾ has recently pointed out the importance of this volume effect. So we also repeated the study taking this effect into consideration and found that the previous conclusion must be changed a little, so it is reported here especially about the case of the freshly prepared and not yet dried fibers. That of the reswollen sample will be given in the following papers.

II. Experiment

(1) **Sample.**—Isotropic model filaments of regenerated cellulose were prepared by the cuprammonium process as already described⁽⁴⁾ in the study of the refractive indices. One or two days were necessary to prepare a sufficient amount of the sample, but the degradation of cellulose did not occur if the spinning solution was kept from air (oxygen) and light during spinning. For this purpose the whole apparatus were placed in a closed box controlled at a definite temperature and the surface of the spinning solution was covered with a thin layer of oil. The conditions of preparation and some properties of the fibers are summarized in Table I. Their cross sections are almost completely circular.

(2) **Measurement of the Dichroic Constant D .**—The samples are stretched in water and dyed

Table 1

Sample No.	Spinning solution			Fiber		
	Cellulose (%)	Cu (%)	NH ₃ (%)	DP	Swelling deg.	v_L
14	13.4	4.9	10.1	380	4.5	2.00
6a	11.8	5.5	21.5	380	7.1	1.91
15	9.3	3.1	6.1	370	4.6	1.93
K	4	1.7	4	300	13.6	1.97
20	3	1.5	8	580	14.5	1.95

without drying, in a methanol solution of congo red (0.10-0.05%) for half an hour at room temperature, excepting No. 6a, which was dyed after drying in an aqueous dye solution after the old method⁽⁴⁾ and then $D = K_{\parallel}/K_{\perp}$ was measured; $K_{\parallel}$ and $K_{\perp}$ are the absorption coefficients of the dyed fiber for the plane polarized D-line oscillating in the directions parallel and perpendicular to the fiber axis. D is the dichroic constant of Preston,⁽⁵⁾ exhibiting the inner structure of the fiber.

For this measurement a new microphotometer has been constructed according to the principle of the Leipho-microphotometer (Leitz) used in the previous study. The new photometer has the same accuracy as that of the previous one.

III. Experimental Results

(1) $v_{1w} \sim v_{2w}$.—An isotropic specimen of the original length l_{0w} was stretched to l_{1w} and kept for one to two days at that length, and then it was released and the residual length l_{2w} was read with a calipers after it had relaxed to the equilibrium state. During these operations the specimens were kept always in the water of the room temperature. Then the total (v_{1w}) and the residual (v_{2w}) stretching degrees are calculated as follows:

$$v_{1w} = l_{1w}/l_{0w} \quad \text{and} \quad v_{2w} = l_{2w}/l_{0w}.$$

The relation between v_{1w} and v_{2w} is very characteristic as shown by a typical example in Fig. 1; in the early stage of stretching

(1) S. Okajima and others, *J. Soc. Chem. Ind. Japan*, **49**, 38, 128 (1946); *J. Soc. Textile and Cellulose Ind. Japan*, **3**, 89, 94 (1947); **4**, 21 64 (1948).

(2) O. Kratky, *Kolloid-Z.*, **84** (1938).

(3) P. H. Hermans, J. J. Hermans, D. Vermaas and A. Weidinger, *J. Polymer Science*, **3**, 1 (1948).

(4) S. Okajima and others, *J. Soc. Chem. Ind. Japan*, **43**, 355 (1940); etc.

(5) J. M. Preston, "Modern Textile Microscopy," Emmott and Co., London, 1933.

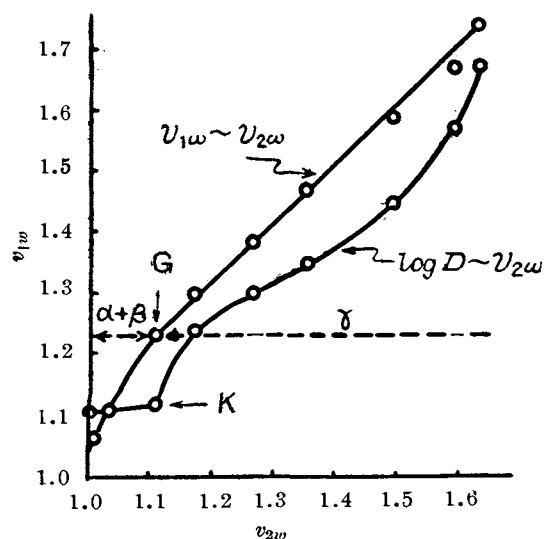


Fig. 1.—No. 15.

($\alpha + \beta$ -range) the larger part of v_{1w} is recovered but when v_{1w} goes beyond this range v_{2w} grows in the linear proportion to v_{1w} (γ -range). This transition point from $\alpha + \beta$ -range, G, can be recognized clearly.

$\alpha + \beta$ -range is generally about 10% as shown by the above example although there exist some fluctuations.

(2) Volume Change during Stretching.—

The diameters of the specimen, b_{0w} , b_{1w} and b_{2w} , corresponding to the lengths l_{0w} , l_{1w} and l_{2w} respectively, were measured microscopically and the corresponding volume ratios were calculated as below:

$$R_{1w} = b_{1w}^2 \cdot l_{1w} / b_{0w}^2 \cdot l_{0w} = V_{1w} / V_{0w}$$

and

$$R_{2w} = b_{2w}^2 \cdot l_{2w} / b_{0w}^2 \cdot l_{0w} = V_{2w} / V_{0w},$$

and similarly the ratio R_{2d} from the corresponding dry volume V_{2d} and V_{0d}

$$R_{2d} = b_{2d}^2 \cdot l_{2d} / V_{0d} = V_{2d} / V_{0d}.$$

The swelling degrees before and after stretching q_0 and q_2 were given by

$$q_0 = V_{0w} / V_{0d} \quad \text{and} \quad q_2 = V_{2w} / V_{0d},$$

where V_{0d} is the air-dried volume of the isotropic fiber.

In the above notation the suffixes 0 and 1 mean the states before and after stretching respectively and 2 especially the equilibrium state after relaxing. The suffixes w and d denote the wet and air-dried states respectively.

The volume change also corresponds to its $v_{1w} \sim v_{2w}$ curve as shown in Fig. 2. R_{1w} increases slightly (4~10%) till $v_{1w} = 1.1$ (α -range) and decreases slowly to the original

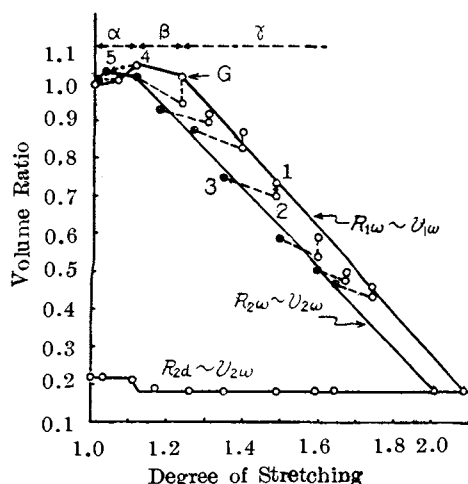


Fig. 2.—No. 15.

value (β -range) and then suddenly and linearly decreases with the increase of v_{1w} till breaking (γ -range). When the fiber is kept at a certain length (l_{1w}) in the γ -range for two days at room temperature, its diameter and the volume decrease slowly, though they increase again when the fiber is released and allowed to shrink freely. In the α - and β -ranges the volume does not change while being kept at l_{1w} but decreases slightly after releasing. These changes are shown in the figure by the two representatives 1→2→3 and 4→5.

Such multiphase deformation is also seen in the change of $R_{2d} \sim v_{2w}$ i. e., it remains unchanged in the $\alpha + \beta$ -range ($v_{2w} = 1.0 \sim 1.1$ or $v_{1w} = 1.0 \sim 1.23$) but decreases at G and again is kept constant thereafter (γ -range). Therefore q_2/q_0 is not always equal to R_{2w} .

In Fig. 2 the points R_{1w} or R_{2w} are not always on the smooth lines but small fluctuations can be seen, which are thought to be due principally to the slight fluctuations among the specimens of the same sample. If we trace R_{1w} of the same specimen every time we stretch it a little same remarkable phenomena can be seen as Fig. 3 shows:

(i) The β -range extends to 1.2~1.3 of v_{1w} .

(ii) The curves of No. 15 of lower swelling degree is zig-zag and it is clearly beyond the scope of the experimental error, and it may be supposed that the deformation did not happen uniformly in the exact sense, while this tendency is slight in the case of the highly swollen fiber as No. K.

No. 15, No. K

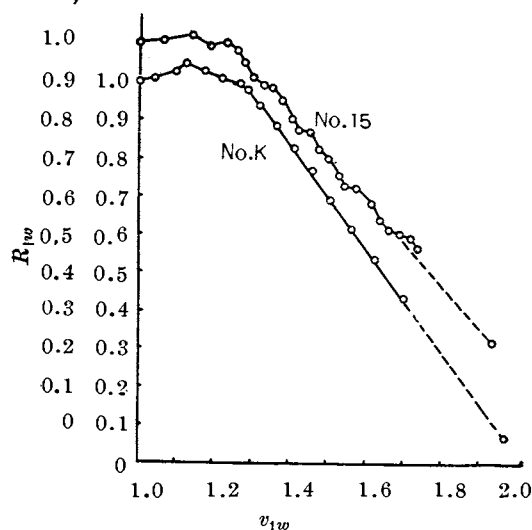


Fig. 3.

(iii) Extrapolating the lines further, beyond the breaking points and reading the values of v_{1w} at $R_{2a} = V_{2a}/V_{0w}$ they are 1.9~2.0 and nearly constant, and correspondingly v_{2w} obtained by extrapolating R_{2w} -line are 1.8~1.9. This means that the stretching follows the expelling of the intermicellar free water and if the stretching can be continued without breaking, the complete dehydration of the free water occurs when the fiber is stretched by nearly 100%. As this is very suggestive the values of these v_{1w} are specially denoted by v_L and shown in the last column of Table 1. We shall return to this point later.

(3) $D \sim v_{2w}$.—As $\log D/I$ is equal to 20 according to our calculation⁽¹⁾ $\log D$ is plotted against v_{2w} in the present study. Then it is convenient to know also the relation $I \sim v_{2w}$ directly from the same curve; I is the intrinsic double refraction of the fiber and measured as reported previously.⁽⁵⁾

As an example, No. 15 is shown in Fig. 1; there appears a kinck point K on the $\log D$ -curve, which corresponds completely to the point G on the $v_{1w} \sim v_{2w}$ curve already described and in the $\alpha + \beta$ -range the increase of D is very slight. Fig. 4 shows other examples, which have similar discontinuities and their curves are slightly sigmoid. In the case of No. 6a the values of I determined by the retardation method are also given in the figure by the mark +. They were determined by mounting the air-dried specimens into tri-cresylphosphate, so the values gained are the total double refractions, and the curve of I does not coincide completely with that of $\log D$, but runs parallel.

IV. Comparison of the Data with the Theoretically Calculated Curves

In the previous study the above discontinuity was missed due to too small points of observation in the first stage of deformation, and $n_{||}$ and $n_{\perp}$ ⁽⁶⁾ are plotted against v_{2w} which was corrected only in the slight intrinsic anisotropy of the original samples. The same treatment applied to the present data leads to the same conclusion as before (Fig. 5), where the curves 1 and 2 are calculated ones on the

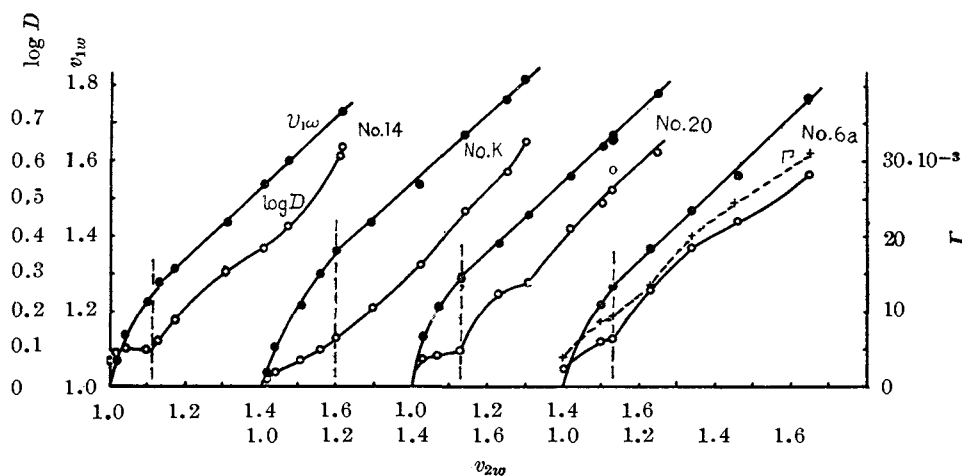


Fig. 4.

(5) S. Okajima and Y. Kobayashi, *J. Soc. Chem. Ind. Japan*, **46**, 941 (1941).

(6) The refractive indices of fiber for the plane-polarized D-line, oscillating parallel and perpendicular to the fiber axis.

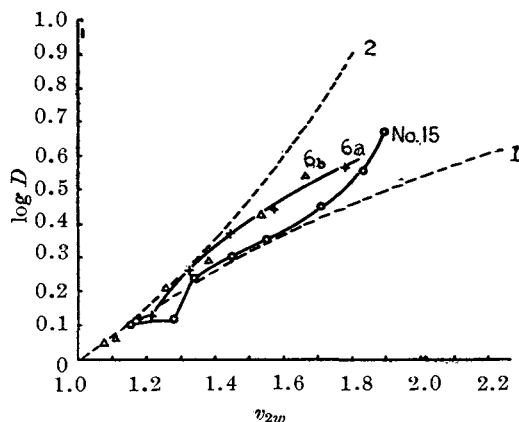


Fig. 5.

assumptions of the first and second theories of Kratky respectively. The point corresponding to the knick point also deviates clearly in this treatment, which has been overlooked carelessly.

Now such discontinuity showing a multiphase deformation was found out in the present stage of our knowledge the authors must be satisfied with discussing the deformation in the last stage only. And in this case stretching degree must be corrected not only from the smallest intrinsic anisotropy of the original sample but also from the volume decrease due to stretching.

As to the theoretical relation assuming the volume change during the stretching, an affined deformation has been described by J. J. Hermans⁽⁷⁾ and discussed experimentally by P. H. Hermans and others;⁽⁸⁾ it will be discussed later also in this paper. The Kratky's theories also assume the constancy of the fiber volume, so in order to compare with the observed data it is necessary to extend the theories to the case where the volume is changed.

(1) **The First Theory of Kratky.**—It is assumed in the original paper of Kratky that micells are thin rods and a cube is considered in the fiber, each of which contains a micell in it and whose diagonal coincides with the direction of the micell as shown in Fig. 6.

Now stretching the isotropic filament by v -fold

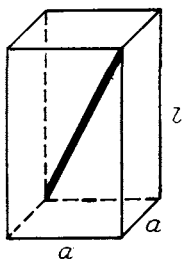


Fig. 6.

this cube also deforms and the length l is stretched to lv and a_0 shrinks to a_2 , when the volume also shrinks to V_2 from V_0 , then the volume of each cube changes as follows:

$$\text{Before stretching: } V_0 = a_0^3 \cdot l \quad (1)$$

$$\text{After stretching: } V_2 = a_2^3 \cdot lv \quad (2)$$

$$\text{From Fig. 6, } \tan \theta_0 = \sqrt{2} a_0 / l \quad (3)$$

$$\tan \theta = \sqrt{2} a_2 / vl \quad (4)$$

The initial intensity of the micells in the isotropic fiber, J_0 , is constant and independent of the micellar inclination θ_0 relative to the fiber axis but it changes to J by stretching as shown in the next relation.

$$J \sin \theta d\theta = J_0 \cdot q_0 / q_2 \cdot \sin \theta_0 d\theta_0 \quad (5)$$

From (1), (2), (3) and (4)

$$\tan \theta = \{(V_0/V_2)^{1/3} \cdot v\}^{-3/2} \tan \theta_0 \quad (6)$$

Now from (5) and (6) the desired relation is obtained.

$$J = q_0/q J_0 v a^3 / (v a^3 \sin^2 \theta + \cos^2 \theta)^{3/2} \quad (7)$$

where

$$v a = v(V_0/V)^{1/3} = v \cdot R_2^{-1/3} \quad (8)$$

The refractive indices and D can be calculated from (7) and (8) as already carried out using the original relation of Kratky, but from the formula (7) it can be easily seen that the new relations $n_{\parallel}$, $n_{\perp} \sim v a$ or $D \sim v a$ coincide with the relations $n_{\parallel}$, $n_{\perp} \sim v$ or $D \sim v$ respectively, so even when the volume changes during stretching, the experimental data can be compared with the already calculated relations by using $v a$ instead of v .

For calculation of $v a$, $v_{2w} \cdot R_{2w}^{-1/3}$ is generally used excepting a few cases, where $v_{2w} \cdot (q_0/q_2)^{1/3}$ is used. These two values are not always equal to each other as pointed out in the paragraph III--(2), but the differences are very slight. $R_{2w}^{-1/3}$ requires only the wet volumes and they are obtained more accurately.

In Fig. 7 the knick point K is placed on the theoretical curve and each value of $v a$ is corrected being multiplied by $v_k/(v a)$ at the knick point) where v_k is the theoretical abscissa of the point K on the calculated curve. Moreover, the origins of the curves are shifted one by one upward in the order of the decreasing degree of swelling for the sake of avoiding confusion. Then some interesting facts are seen:

(i) The curves nearly correspond to the

(7) J. J. Hermans, *J. Colloid Science*, **1**, 235 (1946); *Trans. Faraday Soc.*, **43**, 591 (1947).

(8) P. H. Hermans and D. Vermaas, *Trans. Faraday Soc.*, **42**, 155 (1946).

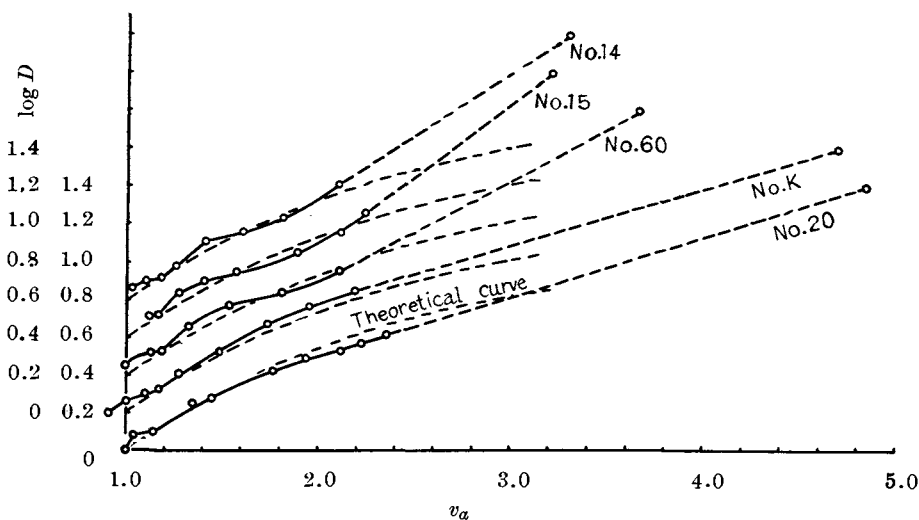


Fig. 7.

theoretical one, but on precise observation the coincidence is not perfect, and the curves are more or less sigmoid. This tendency is more remarkable when the cellulose concentrations of the spinning solutions are larger and the swelling degrees of the filaments are lower (see Table 1). We may consider therefore that the filaments spun from the solutions of the higher concentration have denser structures and their particles (aggregates or parts of molecules) rotate predominantly rather than flow, but in the middle stage of deformation they flow rather easily. This may be due to the change of the relative easiness of the two types of the motion, rotation and flowing, which is caused by the change of the inner structure, depending upon the dehydration, and packing and orientation degrees of the particles. Those three factors, dehydration, orientation and packing, may act dependently to each other. The fibers spun from the dilute solutions are thought to be less dense and flow governs predominantly. Even in this case the curves deviate upward from the theoretical one in the last stage of deformation.

(ii) The authors defined v_L in the paragraph III-(2)-(iii). This is the imaginative degree of stretching, where accompanied with orientation, the free water in the fiber may be expelled completely. So now we suppose that the orientation may also be complete at this point and plot its $\log D = 1.415$ (complete orientation) against the corrected v_L according to the same principle as above. Then those points, marked by $\circ$, can be recognized to be on the extrapolating curve of each sample as shown in Fig. 7. This illustrates that there is an intimate relation between orientation and

dehydration due to stretching. But when and how this characteristic of deformation is given during the fiber is regenerated is an interesting problem to be studied further.

(2) **The Affined Deformation Theory of J. J. Hermans.**—A new theory of deformation is proposed for the case of the rubberlike polymers, assuming the constancy of volume. This is given as follows:

$$\beta_{\parallel} - \beta_{\perp} = k(v^2 - v^{-1}),$$

where $\beta_{\parallel} - \beta_{\perp}$ is the orientation of the network, k a constant and v the stretching degree relative to the isotropic state. When the volume changes during stretching this is modified to

$$\beta_{\parallel} - \beta_{\perp} = k(q_2/q_0)^{2/3} \cdot (v_a^2 - v_a^{-1})$$

by J. J. Hermans. So for our present case

$$\log D = k'(V_{2w}/V_{0w})^{2/3}(v_a^2 - v_a^{-1})$$

If this theory is right, $\log D$ must be linearly proportional to $(V_{2w}/V_{0w})^{2/3}(v_a^2 - v_a^{-1})$ and its inclination must be independent of the degree of swelling. And actually plotting our data a linear relationship can be considered nearly applicable on the whole as in Fig. 8. Of course this happens in the γ -range and all the points in the $\alpha + \beta$ -range deviate upwards from the line. But precise observation shows that the relations of the samples No. 14, 15 and 6a are slightly sigmoid and there is the same trend as pointed out in Fig. 7, while in the cases of the highly swollen fibers, No. 20 and K, they are exactly linear also in this case.

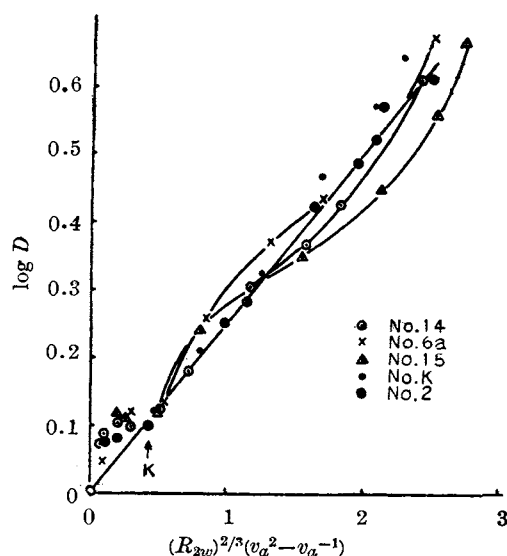


Fig. 8.

V. Conclusion

The results can be concluded as follows:

- (1) When a freshly spun fiber is stretched its volume increases slightly at first together

with a very slight orientation. When the fiber is further stretched beyond this range, the orientation becomes very remarkable and, at the same time, the volume decreases due to dehydration which proceeds in proportion to the stretching degree.

- (2) In the γ -range the deformation may generally be considered to proceed nearly according to the first theory of Kratky in the case of the highly swollen fiber. The curve $\log D \sim v_a$ of the sample of low swelling degree is sigmoid around the theoretical one and this tendency is more remarkable as the swelling becomes lower.

- (3) As to the affined deformation theory the same trend can be seen. It holds good nearly completely in the case of the fiber of higher swelling degree.

Thus the deformation mechanism of the cellulose seems to be very complicated to be expressed by a single mechanism on the whole range. It requires more abundant and more direct experimental data as well as the precise theory.

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Plastic Deformation of the Regenerated Cellulose Fibers. II. Deformation of Freshly Prepared Fibers from the Standpoint of Refractive Indices

By Saburo OKAJIMA and Shigeru HAYAMA

(Received December 14, 1950)

I. Introduction

In the report already presented by one of the authors⁽¹⁾ about the same problem, the refractive indices $n_{\parallel}$ and $n_{\perp}$ were plotted against the stretching degree v_{210} , in the swollen state, for the author believed that the orientation degree of the regenerated fiber remained unchanged even when it was air-dried or reswollen, as its dichroic constant had been found unchanged by these treatments.⁽²⁾ It was concluded from the result that the defor-

mation conformed to the second theory of Kratky⁽³⁾ till $v_{210} = 1.4$, but to the first theory⁽⁴⁾ thereafter. In this conclusion the volume change during stretching was neglected, so taking this factor into consideration, the authors studied the problem from the standpoint of dichroism and some different conclusions were obtained in the previous paper.

Now to ascertain this result from other points of view the same study was repeated again by tracing the change of the refractive indices during stretching.

(1) S. Okajima, *J. Soc. Chem. Ind. Japan*, **49**, 167 (1946).

(2) S. Okajima, T. Nakayama and F. Adachi, *J. Soc. Chem. Ind. Japan*, **49**, 128 (1946).

(3) O. Kratky, *Kolloid-Z.*, **84**, 149 (1933).

(4) O. Kratky, *Kolloid-Z.*, **64**, 213 (1933).

II. Experiment

(1) **Sample.**—Two samples were used. They were prepared by the cuprammonium method already described in a previous report,⁽⁵⁾ but in the present study the more viscous solution of cellulose was used. The conditions of preparation were summarized in Table I; the sample No. 20 was the same as that used in the previous paper.

Table I

Sample No.	S-1	S-20
Spinning solution		
Cellulose (%)	13.6	3
Cu (%)	5.9	1.5
NH ₃ (%)	18.7	8
Spinning temp. (°C.)	25	20
DP	270	580
Swelling degree, q_0 ⁽⁶⁾	6.53	13.9

(2) **Stretching.**—The swollen isotropic fiber of 30~95 cm. (l_{0w}) was stretched slowly in water to l_{1w} and the length was kept unchanged overnight. After that tension was released for one day, the residual length, l_{2w} was measured. During the operation the fiber was kept always in water; the temperature were 22.5° and 14° in the cases of S-1 and S-20 respectively. The stretched fibers were air-dried and their refractive indices were measured.

(3) **Intrinsic Double Refraction.**—The specimens were dried under vacuum at 60° and $n_{||}$ and $n_{\perp}$ were measured by the Becke's method. The immersion liquids were prepared by mixing appropriate amounts of two or three among monochlorobenzol, *o*-dichlorobenzol, iodbenzol and tricresylphosphate. Observed data were corrected on the standard base of $n_{iso} = 1.5356$, as it has already been precisely reported.⁽⁷⁾ The intrinsic double refraction Γ is given by $n_{||} - n_{\perp}$.

In the above notations $n_{||}$ and $n_{\perp}$ are the refractive indices of fiber for the plane-polarized D-line, oscillating parallel and perpendicular to the fiber axis, while n_{iso} is that of the isotropic one.

(4) **Swelling Degree.**—The volumes of the fiber swollen in water during stretching, V_{0w} , V_{1w} , V_{2w} and the volumes after drying V_{0d} , V_{2d} , were measured microscopically as described previously. From these results the swelling degrees, q_0 and q_2 were calculated. The detail of the method has been given in the preceding paper. The suffixes w and d mean the wet and dry states. 0 and 1 the states before and immediately after stretching and 2 the residual one.

III. Experimental Results

(1) **S-1.**—Fig. 1 shows the relation $R_{2w} \sim$

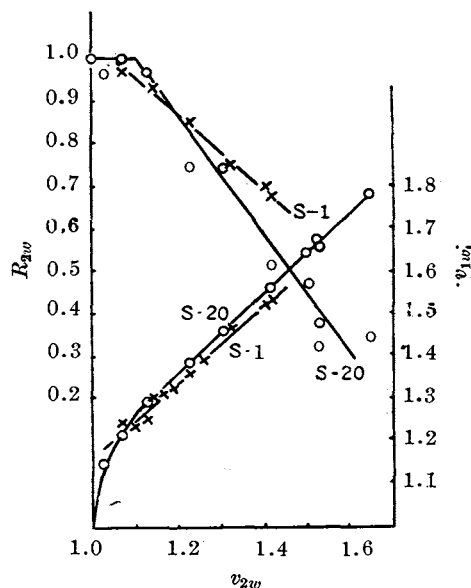


Fig. 1.

v_{2w} and $v_{1w} \sim v_{2w}$. The knick point G can not be observed clearly in this case. Correcting the effect of the small intrinsic double refraction of the original sample and plotting Γ against v_{2w} , a similar curve (1) is obtained to that shown in the previous paper (Fig. 2).

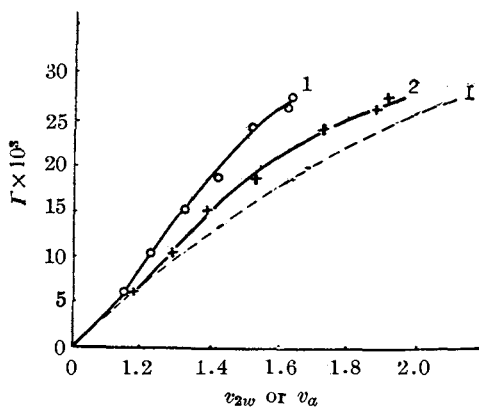


Fig. 2.—S-1.

But when the correction of the volume decrease is added further to the above v_{2w} and it is denoted as v_a the curve (2) is obtained. Both curves are qualitatively similar and it may be concluded that comparing with the theoretical curve (I), they deviate upward at the beginning but afterwards go parallel to the theoretical curve, which has already been calculated⁽⁸⁾ on

(5) S. Okajima and other. *J. Soc. Chem. Ind. Japan*, **43**, 355 (1940); etc.

(6) About the notations used in this report, see the preceding paper.

(7) S. Okajima and Y. Kobayashi, *J. Soc. Chem. Ind. Japan*, **46**, 941 (1943).

(8) S. Okajima, *J. Soc. Chem. Ind. Japan*, **40**, 793, 795 (1937).

the assumption of Kratky's first theory.

(2) S-20.—In this case too similar phenomena can be seen. (Figs. 1 and 3). A knick

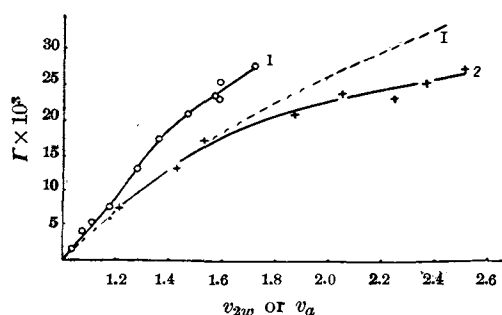


Fig. 3.—S-20.

point G is clearly seen in this case. The relation $\Gamma \sim v_{2v}$ is also the same as that of S-1 but corrected curve against v_a satisfies the theory from the first and deviates for $v_a > 1.6$.

The swelling degrees of S-1 and S-20 are 6.56 and 13.9 respectively. The deformation curve of the former, which is prepared from the solution of the higher cellulose concentration and has a smaller swelling degree, deviates remarkably upward from the theoretical curve, while the latter prepared from the solution of the more dilute cellulose concentration and highly swollen satisfies the theory. This tendency coincides with that gained dichroically in the preceding study.

IV. Comparison with the Data by P. H. Hermans and Others

P. H. Hermans, J. J. Hermans, D. Vermaas and A. Weidinger⁽⁹⁾ studied the orientation of the viscose and the regenerated fibers using x-ray and retardation methods and obtained very interesting results, among which the case of the regenerated fibers is very akin to our study, so their data are picked up in Table 2 in order to compare them with ours. The notations are changed according to the present authors' rule.

In Table 2 Γ is calculated as $f_0 \cdot \Gamma_\infty$, where f_0 is the orientation factor and Γ_∞ is the intrinsic double refraction at the complete orientation and 0.043 according to Hermans. v_a is also corrected in such a way that the first point of each curve comes on the theoretical one.

Table 2

Cellulose conc., %	q_0	q_{2v}	v	v_a	q_2/q_0	$\Gamma \times 10^3$
(i) Freshly regenerated fiber.						
F ₃ 4.0	8.1	7.85	1.04	1.04	0.97	1.5
	7.7	7.35	1.19	1.20	0.96	5.6
	7.6	6.3	1.45	1.545	0.83	15.3
F ₅ 6.0	5.95	5.8	1.03	1.04	0.98	1.5
	5.95	5.4	1.20	1.24	0.91	8.0
	5.95	4.7	1.49	1.60	0.79	18.9
	5.95	3.5	1.79	2.09	0.59	29.5
F ₉ 10.5	4.7	4.7	1.05	1.04	1.00	1.7
	4.7	4.3	1.24	1.26	0.92	10.5
	4.5	3.16	1.56	1.73	0.70	23.4
	4.75	3.16	1.65	1.86	0.665	25.8
(ii) Reswollen fiber						
R ₃ 4.0	2.34	2.45	1.25	1.06	1.05	2.4
	2.09	2.26	1.39	1.17	1.08	7.1
	2.10	2.18	1.62	1.38	1.04	12.0
	2.15	2.02	1.99	1.76	0.94	17.6
R ₅ 6.0	2.34	2.73	1.22	1.03	1.15	1.2
	2.30	2.84	1.41	1.17	1.23	4.1
	2.36	2.95	1.64	1.35	1.25	10.1
	2.20	2.52	1.92	1.65	1.14	18.1
R ₉ 15.5	2.31	2.60	1.23	1.05	1.13	1.9
	2.29	2.75	1.43	1.19	1.20	6.45
	2.33	2.35	1.73	1.585	1.00	18.9
	2.31	2.26	1.96	1.83	0.98	24.1

According to these data the volume of the fiber decreases from the first in the freshly regenerated one, but a remarkable increase can be seen in the case of the reswollen fiber. Our data also confirm this, and even the freshly prepared sample also showed a slight increase of the volume as described in Part I.

The relation between Γ and v_a is shown in Fig. 4; all the samples have the similar behaviors and they satisfy the first theory on

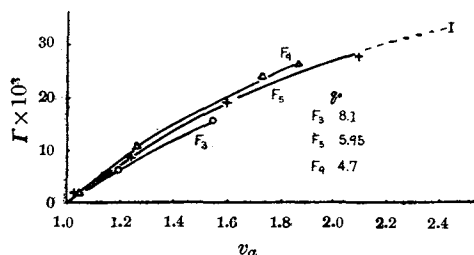


Fig. 4.

the whole. But on precise observation, the curves of F₉ and F₃ deviate up and down respectively from the theoretical curve (1), although F₅ coincides with it completely. At the swelling degrees of F₃, F₅ and F₉ are 8.1,

(9) P. H. Hermans, J. J. Hermans, D. Vermaas and A. Weidinger, *J. polymer Science*, **3**, 1 (1948).

5.95 and 4.7 respectively, it may be said that the higher the swelling degree of the fiber is, the more effective the orientation is. This tendency is the same as already pointed out repeatedly by the authors.

As to the case of the reswollen fiber it will be treated fully in the following papers.

V. Comparison with the Affined Deformation Theory

Affined deformation formula proposed for the rubber-like polymers has been extended by J. J. Hermans⁽¹⁰⁾ as below for the case where the volume is changed during the deformation

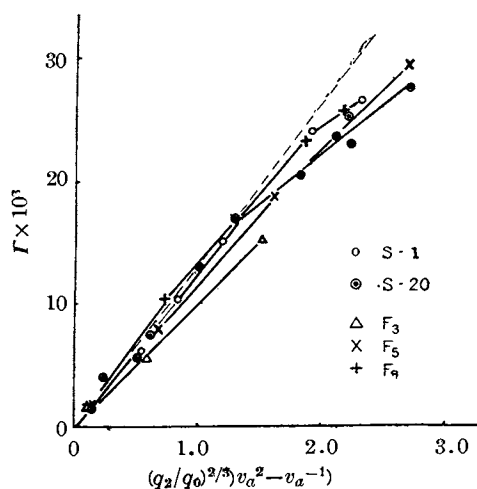


Fig. 5.

(10) J. J. Hermans, *Trans. Faraday Soc.*, **43**, 591 (1947).

$$\Gamma = k(q_2/q_0)^{2/3}(v_a^2 - v_a^{-1}).$$

This has also been discussed by our dichroic data and its approximate conformity has been recognized in the preceding paper.

In Fig. 5 our values of Γ and Hermans' data in Table 2 are plotted against $(q_2/q_0)^{2/3}(v_a^2 - v_a^{-1})$. The broken line in the figure is a theoretical relation which is required by the line shown in Fig. 8 in Part I. Of course the inclination of this line is calculated from that of the log D -line by using the relation.

$$\log D = 20 \Gamma.$$

Now all the points are on each line for the smaller degree of stretching and the inclinations of the lines are nearly coincide with that of the theoretical one, excepting the cases F_3 and F_5 . But for the abscissa larger than 1.3 the points deviate downward. So the conformity between the experiment and theory is limited within a narrow range and can not be said to be perfect.

VI. Conclusion

The results obtained by using the double refraction are similar to that already described in the first report.

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Synthesis of Some Organic Compounds by Electric Discharge. I-V.

By KIICHIRO SUGINO and EIICHI INOUE

(Received December 26, 1950)

Introduction

Most of the studies on the organic reactions in the electric discharge have been very qualitative in nature. For example, even the synthesis of simple organic compounds by non-disruptive electric discharge has not yet been succeeded from both the practical and

the theoretical point of view. The reason for this is that the variables to obtain a desired compound are not systematically examined and also that the identification of the reaction product is not made accurately.

During these five years, the authors have found some interesting reactions occurring in silent discharge, which had not yet been reported

in the literature. These reactions are summarized as follows.

(1) Formation of phenol from benzene and air.

(2) Formation of benzyl alcohol, benzaldehyde, benzoic acid and cresols from toluene and air.

(3) Formation of cyclohexanol and cyclohexanone from cyclohexane and air.

(4) Formation of aniline and other basic compounds from benzene and ammonia.

The authors have then undertaken the present study in order to establish a new practical method of the synthesis of these compounds. The study also seeks to establish the fundamental chemistry of these synthetic reactions in the discharge and at the same time to present some mechanisms and theory of these reactions.

Synthesis of Phenol from Benzene.⁽¹⁾ (II, III)

When a mixture of benzene and air was discharged in an ozonizer under suitable conditions, phenol was obtained in yields as high as 30% of the total reaction product. The apparatus was a simple one as is shown in Fig. 1.

Air was bubbled into benzene reservoir at a

definite temperature in order to obtain a mixture of benzene and air of constant composition. The content of benzene gas in air could be varied by changing the temperature of the reservoir and the rate of flow of air. The mixed gas was then flowed into the operated ozonizer at constant velocity. The exit gas was passed through 2*N* sodium hydroxide solution and then cooled through a trap to 5° to condense almost of the unconverted benzene together with the reaction product which was not absorbed in the alkali solution. A part of the unconverted benzene and gaseous reaction products, if existed, were allowed to exhaust. During the reaction, solid brown deposit was formed on the glass wall of the ozonizer. This deposit, after the reaction, was dissolved by washing the wall with an alkali solution and the latter was added to the above sodium hydroxide solution in which the phenolic substances formed was contained.

Separation of phenol and other acidic reaction products from the sodium hydroxide solution was carried out according to the following scheme.

Phenolic substances thus obtained boiled at 76-78° at 11 mm.Hg and was thought to consist of pure phenol. It was purified by repeating the distillation. The final product

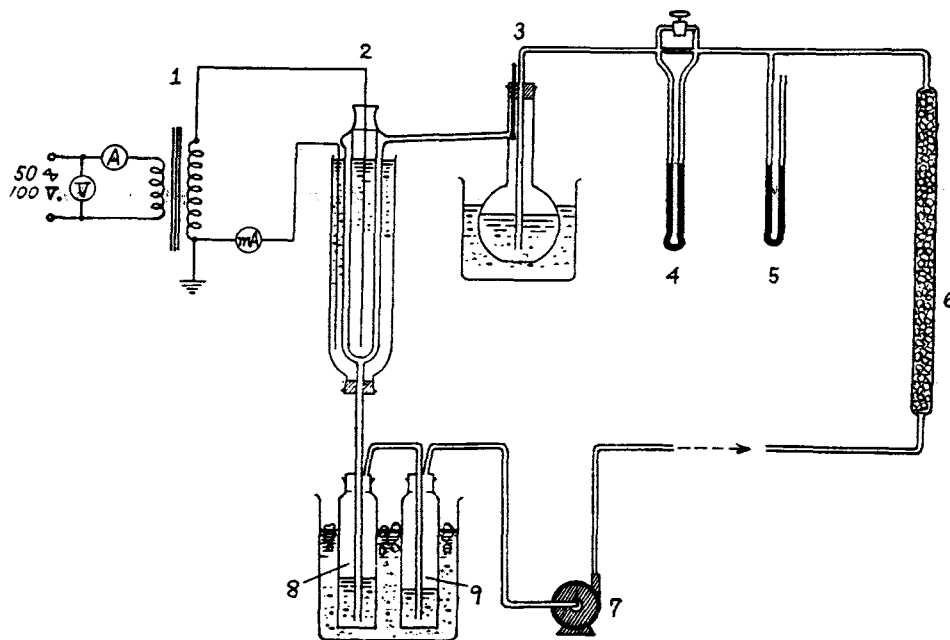
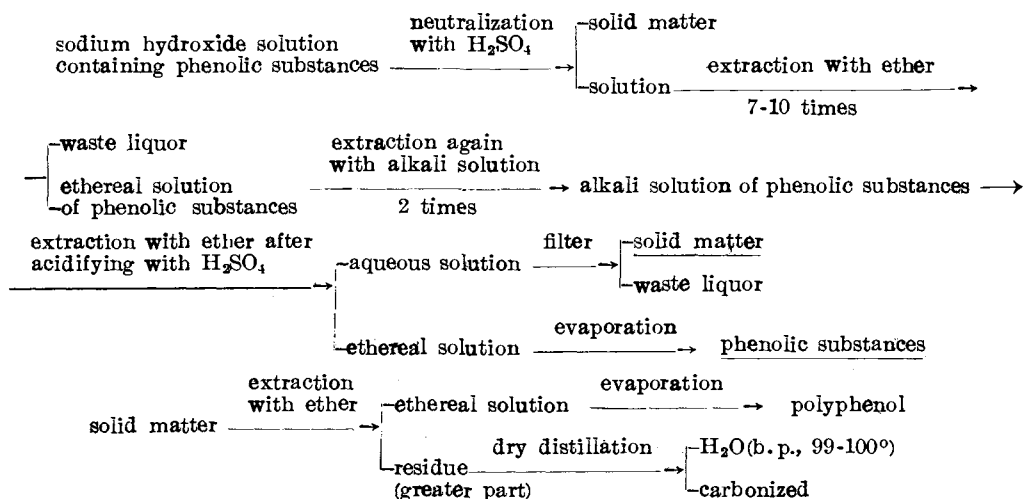


Fig. 1.—1, Transformer; 2, discharge tube; 3, benzene reservoir; 4, flowmeter; 5, manometer; 6, CaCl_2 tube; 7, blower; 8, NaOH solution; 9, trap.

(1) A part of the research was already published in

Japanese in *Jour. Chem. Soc. Japan*, 71, 518 (1950).



boiled at 177-178° at atmospheric pressure and crystallized at room temperature.

Conditions of experiments and results obtained are shown in Table 1.

Table 1

	Run 1	Run 2	Run 3
Electrical factor			
Cycle	50	50	50
Volt (secondary), kV.	15	15	15
Current (%), mA.	1.25	1.25	1.25
Temp. of ozonizer, °C.	50	50	50
Composition of gas used, Vol. %			
C ₆ H ₆	5.0	6.5	7.5
Air	95.0	93.5	92.5
Temp. of gas, °C.	30	20	20
Gas pressure, mm.	750	750	750
Rate of flow, L/hr.	120	120	30
Time, hr.	56	17	15.5
C ₆ H ₆ used, kg.	1.0	0.5	0.13
Reaction products			
Phenol, g.	2.5	1.3	1.2
Other products, g.	6.0	3.0	3.7
Conversion efficiency, % (grams of liquid and solid reaction products/grams of C ₆ H ₆ used) × 100	0.85	0.86	3.8
% of phenol in total reaction product	30	30	25

Magnitude of the tube: all glass (pyrex)
ozonizer. Effective length, 22 cm.; space gap,
0.25 cm.; diameter, 4 cm.

Formation of gaseous decomposition products of benzene has not been able to recognize exactly.

As is clear from the table, under the conditions described above, 0.85-3.8% of benzene used could be converted to phenol and other

reaction products by running it with air one time in the ozonizer (effective length, 22 cm.). The quantity of phenol in the reaction product was reached to about 30% and the electrical energy consumed was about 150-250 kwhr./1 kg. phenol.

In these experiments, solid brown deposit was always formed on the glass wall and it is the main reason for the decrease of the conversion of benzene to phenol. Later, it was found that when the glass wall of the discharge tube was covered with liquid layer of benzene, the formation of solid deposit was reduced to to a very small quantity and the reaction product consisted mainly of phenol. In this case, the mixed gas of benzene and air, before flowing into the ozonizer, was cooled by the methods shown in Fig. 2, so a part of benzene was condensed and it was run down on the glass wall of the ozonizer, where the silent

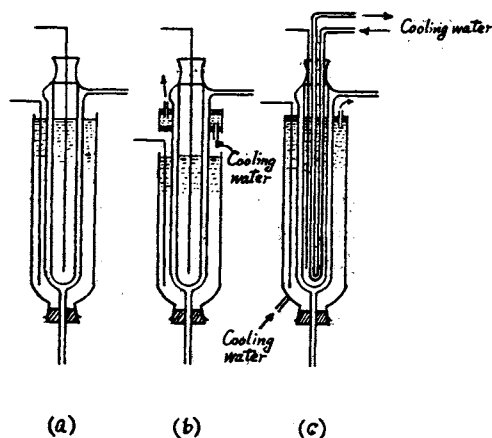


Fig. 2.—(a), air cooling; (b) and (c), water cooling.

discharge occurred. Other procedures were almost the same as the case described above. Results obtained are shown in Table 2.

In this case, the electrical energy consumed was about the same as in the case of Table 1.

Table 2

	Run 1	Run 2	Run 3
(same as Table 1)			
Discharge tube			
Electrical factor			
Cycle	50	50	50
Volt (secondary), kV.	15	15	15
Current (%), mA.	1.3	1.3	1.3
Rate of flow of air, l./hr.	25	50	50
Temp. of gas, °C.	45	64	60
Gas pressure, mm.	755	765	755
Temp. of ozonizer, °C.	58	58	20
Method of cooling of the mixed gas	Fig. 2, (a)	Fig. 2, (b)	Fig. 3, (c)
Rate of running of liquid C_6H_6 , cc./hr. }	120	550	550
Time, hr.	60	30	32
C_6H_6 used, kg.	6.3	14.5	15.5
Reaction product			
Phenol, g.	3.8	1.7	1.6
Other products, g.	2.0	0.7	0.4
Conversion efficiency (same as Table 1), % }	0.1	0.017	0.013
% of phenol in total reaction product }	66	71	80

Table 3

	Run 1	Run 2	Run 3	Run 4
Magnitude of the tube (all glass (pyrex) ozonizer)				
Effective length, cm.	24	25	50	70
Space gas, cm.	0.25	0.25	0.25	0.25
Diameter (outer), cm.	4.0	3.5	3.5	3.5
Electrical factor				
Cycle	50	50	50	50
Volt (secondary), kV.	15	15	15	15
Primary kw.hr.	1.32	1.36	2.24	2.85
Temp. of ozonizer, °C.	40	40	40	40
Composition of gas used, Vol. %				
$C_6H_5CH_3$	1.8	2.1	2.1	2.2
Air	98.2	97.9	97.9	97.8
Temp. of gas, °C.	17	18	18	18
Gas pressure, mm.	765	725	725	725
Rate of flow, l./hr.	60	60	60	60
Time, hr.	110	80	80	62
$C_6H_5CH_3$ used, g.	510	420	418	332
Total reaction product, g. }	17.9	14.1	27.1	28.5
Conversion efficiency, %				
(grams of total reaction product/grams of $C_6H_5CH_3$ used) $\times 100$ }	3.5	3.4	6.5	8.6

The Oxidation of Toluene. (IV)

By using the same silent discharge apparatus described in Fig. 1, results were obtained which are summarized in Table 3. In this case, the variation of the conversion efficiency due to the effective length of the ozonizer was examined.

Analysis of the Reaction Product:—The reaction product was caught in the trap containing 5 *N* sodium hydroxide solution and some toluene which was cooled to 4–5°.

The total product was separated into the neutral part (dissolved in unconverted toluene) and the acidic part (dissolved in 5 *N* sodium hydroxide solution). The neutral part, after driving off the unconverted toluene by distillation, was subjected to fractional distillation under reduced pressure. It was thus separated into four fractions which had the properties shown in Table 4 and were identified as benzaldehyde (Fraction 1) and benzylalcohol (Fraction 2) respectively. Recovery of acidic compounds from the alkali solution was carried out as usual and the crude product thus obtained was also subjected to fractional distillation under reduced pressure into four fractions. Fraction 2 and 3 had the properties noted in Table 4 and were identified as *o*-cresol and benzoic acid respectively.

Table 4

Neutral Part		Acidic Part	
Fraction (B. p., °C.)	Properties	Fraction (B. p., °C.)	Properties
1. (50–55) _s	B. p., 179–181°C. $n_D^{20} = 1.545$ benzalphenyl-hydrazone M. p., 156°C.	1. (20–35) _{ss}	odor like to CH_3COOH
2. (70–75) _s	B. p., 200–205°C. $n_D^{23} = 1.540$	2. (60–65) _s	B. p., 187–191°C. $n_D^{20} = 1.543$ color reaction with $FeCl_3$ +
3. (100–120) _s	$n_D^{20} = 1.567$	3. (100–110) _s	M. p., 121°C. sublime
4. Residue		4. Residue	

Table 5

	Run 1	Run 2	Run 3	Run 4
(1) Benzyl alcohol, g.	5.2	3.7	7.2	8.7
(2) Benzaldehyde, g.	3.3	1.8	3.7	6.7
(3) Benzoic acid, g.	0.3	0.5	0.7	0.8
(4) <i>o</i> -Cresol, g.	4.8	4.0	6.8	4.0
(1) + (2) + (3) + (4) / Total reaction product $\times 100$, % }	76	71	68	71
(1) + (2) + (3) + (4) / kw.hr. g. }	10.3	7.4	8.2	7.1

The yield of the main reaction product is shown in Table 5.

Mean percentage of each compounds in the reaction product was as follows: (1) Identified products: benzylalcohol 26-30%, benzaldehyde 13-20, benzoic acid 2-4%, *o*-cresol 25-28%; (2) unidentified products: solid deposit on the wall 9-10%, fraction 3 of the neutral part 4-5%, fraction 1 of the acidic part 1-4%, distillation residue 11-17%.

In the ozonizer, toluene was found to be oxidized more easily than benzene. It was converted to the extent of 3.5-8.6% to give benzylalcohol, benzaldehyde, benzoic acid and cresols as main products, by running it only one time in the ozonizer. (Effective length, 25-75 cm.). Solid brown deposit formation on the glass wall was very small in this case.

Oxidation of side chain (1) and nucleus (2) of toluene are the main reactions. The ratio of the two reactions (1)/(2) was about 1.6-1.9 in the above experiment. But it may somewhat vary according to the voltage applied, the effective length of the tube and the rate of the flow of gas.

Oxidation of Cyclohexane. (V)

By the oxidation in an ozonizer, cyclohexane gave a mixture of cyclohexanol and cyclohexanone with a fair conversion efficiency. Methods of experiments were almost the same as the above two cases. The results are summarized in Table 6.

Table 6

	Run 1	Run 2	Run 3
Magnitude of the tube (all glass (pyrex) ozonizer)			
Effective length, cm.	75	75	75
Space gap, cm.	0.25	0.25	0.25
Diameter (outer), cm.	3.5	3.5	3.5
Electrical factor			
Cycle	50	50	50
Volt (secondary), kV.	20	25	20
Primary kwhr.	1.7	2.4	1.35
Temp. of ozonizer, °C.	45-55	55-60	45-50
Composition of gas used, Vol. %			
Cyclohexane	7.7	6.9	6.0
Air	92.3	31.1	94.0
Temp. of gas, °C.	20-22	17-19	15-19
Gas pressure, mm.	740	740	740
Rate of flow, l./hr.	21.7	21.5	50.5
Time, hr.	50	50	40
Cyclohexane used, g.	314	282	456
Total product, g.	80.2	122	80.5
Cyclohexanol, g.	44.1 (55%)	54.1 (44%)	50.3 (63%)

Cyclohexanone, g.	14.7 (18%)	30.4 (25%)	17.7 (22%)
Adipic acid, g.	5.0 (6%)	6.1 (26%)	2.3 (13%)
Distillation residue, g.	16.4 (20%)	31.4 (25%)	10.2 (13%)
Conversion efficiency, %	25.5	43.3	17.7

In this case, the gas flowing out the ozonizer was cooled through a trap containing some cyclohexane to 5-10° to condense the total reaction product together with unconverted cyclohexane. The crude product, after driving off the unconverted cyclohexane by distillation, was subjected to fractional distillation into four fractions which had the properties shown in Table 7.

Table 7

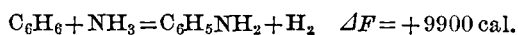
Fraction (B.p., °C.)	Properties	Note
1. (42-50) ₃₋₄	B.p., 155-158°C., $n_D^{20} = 1.4507$, M. p., 166-167°C.	Cyclohexanone semicarbazone Cyclohexanone
2. (50-60) ₃	B. p., 158-163°C., M. p., 80°C.	Cyclohexanol phenylurethane Cyclohexanol
3. (153-180) ₂	M. p., 148-150°C.	Adipic acid
4. Residue		

The oxidation of cyclohexane in the ozonizer was found to proceed very fast as compared with the case of aromatic hydrocarbons. The conversion efficiency reached to about 18-43% by running it one time in the ozonizer (effective length, 75 cm.). The reaction product consisted mainly of cyclohexanol and cyclohexanone and their content in the product were 44-63% and 18-25% respectively.

The results of these three researches offer a possibility of the use of silent discharge for the industrial preparation of (1) phenol from benzene, (2) benzylalcohol, benzaldehyde and cresols from toluene, and (3) cyclohexanol and cyclohexanone from cyclohexane respectively.

Synthesis of Aniline from Benzene and Ammonia.⁽²⁾ (I)

Benzene has also been studied in an ozonizer in the presence of ammonia in order to obtain aniline according to the following reaction.



(2) Already published in Japanese in *Jour. Chem. Soc. Japan*, 71, 343 (1950). So this description is an abstract of the result.

An example of the experimental conditions and results obtained are summarized in Table 8.

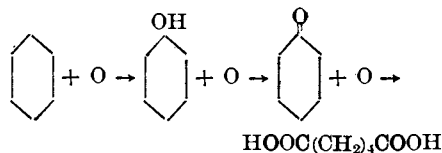
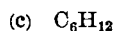
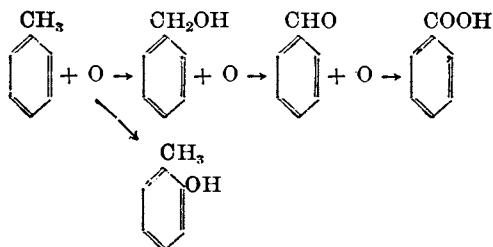
Table 8

Magnitude of the tube: all glass ozonizer; effective length, 30 cm.; space gap, 0.26 cm. Conditions: cycle, 50; volt (secondary), 13 kV.; current (secondary), 2.5 mA.; temp. of ozonizer, 30°C.; temp. of trap, -5°C.; gas pressure, 730 mm.; rate of flow, C_6H_6 8.2 L/hr. NH_3 34 L/hr.; composition of mixed gas, C_6H_6 /(total gas) $\times 100 = 20$; time, 63 hr. Results: C_6H_6 used, 1.8 kg.; NH_3 used, 1.6 kg.; liquid products subjected to fractional distillation, 14.08 g.

Fraction (B. p., °C.)	Yield, g.	n_D^{20}	Properties	Note
81-85	7.46	$\left\{ \begin{array}{l} 1.5410 \\ d_4^{20} = 1.000 \end{array} \right.$	Crystallized by absorbing CO_2 in air. Picrate and chloroplatinate- were formed.	Unconverted benzene (mainly)
85-100	0.23			Aliphatic amine or diamine
100-115	0.12			
(67-76) ₁₅	1.08	1.5410 $d_4^{20} = 1.000$	B.p., 175-182°C. M. p., of acet- anilide, 113°C.	Aniline
(91-92) ₁₅	0.14	1.5420	A crystal (M.p. 63°C.) was isolated	<i>m</i> -phenyl- enedi- amine
(111-114) ₁₅	0.28	1.5440		
(121-134) ₁₅	0.19	1.5390		
Residue	0.75			
Loss	3.83			Unconverted benzene

Summary

(1) By running a gas mixture of aromatic and hydroaromatic hydrocarbons and air in an ozonizer, following reactions were found to occur mainly.



(2) Conversion efficiency at one run under suitable conditions was found to be (a) 0.86-3.8% (effective length of ozonizer, 22 cm.), (b) 3.5-8.6% (effective length of ozonizer, 25-75 cm.), and (c) 18-43% (effective length of ozonizer, 75 cm.), respectively. The yield of each compound produced (grams of each compound produced/grams of total reaction product $\times 100$) was as follows: (a), phenol 25-30%; (b), benzylalcohol 26-30%, benzaldehyde 13-20%, benzoic acid 2-4%, *o*-cresol 25-28%; and (c), cyclohexanol 44-63%, cyclohexanone 18-25%.

(3) In the case of the oxidation of benzene, the yield of phenol could be increased to above 60% of the total reaction product by the special method.

(4) Aniline and other basic compounds were obtained by the reaction of benzene and ammonia in an ozonizer.

In conclusion, one of the authors (K. Sugino) wishes to express his hearty thanks to Prof. M. Suzuki of Tokyo Municipal University for his sincere friendship which facilitated this research. The authors also extend their thanks to Dr. K. Odo, Lecturer of Tokyo Institute of Technology and Mr. K. Shirai, Assistant of the same Institute, for their valuable collaboration on the analytical work. Thanks are also due to their collaborators, H. Yamada, M. Hattori and H. Yamakawa, who gave earnest assistance in the investigations. The cost of this research has been defrayed from the Grant in Aid for Fundamental Scientific Research of the Ministry of Education and from the funds of the Nippon Carbide Industries Inc. to which thanks are due.

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Dipole Moments of Halogen-Derivatives of Hinokitiol

By Yukio KURITA, Tetsuo NOZOE and Masaji KUBO

(Received January 26, 1951)

Introduction

In the previous paper,⁽¹⁾ we reported the results of measurements on the dipole moments of tropolone,⁽²⁾ hinokitiol(4-isopropylcycloheptatriene-2,4,6-ol-2-one-1)⁽³⁾ and their derivatives. We arrived at the conclusion that these molecules resonate among various electronic structures contributing to the normal states of these molecules and that the cycloheptatrienolone ring is planar. We found that the dipole moment of hinokitiol is nearly pointing along the line from the center of the ring to the C-atom at 2-position with a positive end at the ring, as shown in the Figure 2 in the next paper.⁽⁴⁾

We have prepared another halogen-derivatives of hinokitiol and carried out, besides investigations in the field of organic chemistry, measurements on the dipole moments of these compounds to determine the position of substituents in these compounds.

Experimental Method and Materials

The dipole moments were measured in benzene solution at 25°. The apparatus and the method of measurements were the same as described in the previous report.⁽¹⁾ The materials used were prepared by one of us and his collaborator. They are: β -monobromohinokitiol, m. p. 42°, α -monochlorohinokitiol, m. p. 117.5-8.5°, β -monochlorohinokitiol, m. p. 47.6-8.5°, γ -monochlorohinokitiol,⁽⁵⁾ m. p. 44-46°, and α -dichlorohinokitiol,⁽⁶⁾ m. p. 126.7°.

Experimental Results

For the extrapolation of molecular polarization to infinite dilution, Hedestrand's method⁽⁷⁾ was used, i.e.,

$$\epsilon_{12} = \epsilon_1 + \alpha w_2,$$

$$d_{12} = d_1 + \beta w_2,$$

$$p_{2\infty} = p_1 \left(1 - \frac{\beta}{d_1}\right) + \alpha C,$$

$$C = \frac{3}{d_1(\epsilon_1 + 2)^2},$$

where p and w denote specific polarization and weight fraction respectively. Other notations have their usual significances. For benzene at 25°, we have

$$p_1 = 0.3414 \text{ cc./g.},$$

$$d_1 = 0.8727 \text{ g./cc.},$$

$$C = 0.1883 \text{ cc./g.},$$

which can be used throughout the whole calculation. The results are shown in Table 1, in which P and R_D denote molecular polarization and molecular refraction for D-line respectively.

Table 1
Dipole Moments of Halogen-Derivatives
of Hinokitiol, 25°

β -monobromohinokitiol			
$w_2, \%$	ϵ_{12}	d_{12}	
0	2.273	0.8727	
0.629	2.329	0.8749	
1.118	2.374	0.8767	
1.382	2.393	0.8777	
$\alpha = 8.87, \beta = 0.35, P_{2\infty} = 455.6 \text{ cc.}$			
$R_D = 54.1 \text{ cc.}, \mu = 4.40 \text{ D}$			
α -monochlorohinokitiol			
0	2.273	0.8727	
0.697	2.301	0.8744	
1.116	2.319	0.8756	
1.957	2.356	0.8778	
$\alpha = 4.13, \beta = 0.26, P_{2\infty} = 202.0 \text{ cc.}$			
$R_D = 51.2 \text{ cc.}, \mu = 2.70 \text{ D}$			
β -monochlorohinokitiol			
0	2.273	0.8727	
0.546	2.330	0.8741	
1.075	2.389	0.8755	
1.855	2.473	0.8776	
$\alpha = 10.7, \beta = 0.26, P_{2\infty} = 447.8 \text{ cc.}$			
$R_D = 51.2 \text{ cc.}, \mu = 4.38 \text{ D}$			

(1) Y. Kurita, T. Nozoe and M. Kubo, This Bulletin, **24**, 10 (1951).

(2) T. Nozoe, S. Seto, Y. Kitahara, M. Kunori and Y. Nakayama, *Proc. Japan Acad.*, **26** (No. 7), 38 (1950).

(3) T. Nozoe, *Yakugaku (Science of Drugs)*, **3**, 172 (1949); *Proc. Japan Acad.*, **26** (No. 9), 30 (1950).

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(5) T. Nozoe, T. Mukai and K. Takase, *Proc. Japan Acad.*, **26** (No. 8), 19 (1950).

(6) T. Nozoe, K. Kikuchi and T. Ando, *Proc. Japan Acad.*, **26** (No. 10), 32 (1950).

(7) G. Hedestrand, *Z. physik. Chem.*, **B 2**, 428 (1929).

γ -monochlorohinokitiol

0	2.273	0.8727
0.465	2.332	0.8739
0.919	2.386	0.8750
1.467	2.457	0.8764

 $\alpha=12.5$, $\beta=0.25$, $P_{2\infty}=515.9$ cc., $R_D=51.2$ cc., $\mu=4.74$ D α -dichlorohinokitiol

0	2.273	0.8727
0.610	2.331	0.8745
1.196	2.388	0.8765
1.675	2.430	0.8779

 $\alpha=9.50$, $\beta=0.31$, $P_{2\infty}=468.3$ cc., $R_D=56.1$ cc., $\mu=4.46$ D

Discussion

We have already measured the dipole moment of hinokitiol and determined the direction of the moment in the molecule. The conceivable position of substituent in bromohinokitiol are 3 (ortho), 5 (para) or 7 (ortho') as justified by molecular orbital treatment,⁽⁴⁾ which have shown that π -electron distribution is concentrated at C-atoms 3, 5 and 7. The cycloheptatrienolone ring is planar. We may, as a first approximation, assume that the ring has a regular heptagon form. Assuming the bond moment $\mu(C-Br)=1.48$ D as before, we can calculate the theoretical moments for 3-bromo-, 5-bromo- and 7-bromohinokitiol to be 4.8 D, 2.6 D and 4.32 D⁽⁸⁾ respectively. Comparing these values with the observed one, it is concluded that the position of substituent in β -monobromohinokitiol is 3 (ortho).

The bond moment $\mu(C-Cl)$ is 2.0 D in aliphatic compounds and 1.5~1.7 D in benzene derivatives. Assuming $\mu(C-Cl)=1.7$ D, we can calculate the theoretical moments for monochloro- and dichlorohinokitiols. The results are: 3-monochlorohinokitiol, 4.95 D; 5-monochlorohinokitiol, 2.4 D; 7-monochlorohinokitiol, 4.4 D; 3,5-dichlorohinokitiol, 3.6 D; 3,7-dichlorohinokitiol, 4.8 D; and 5,7-dichlorohinokitiol, 2.8 D. Comparing these values with the observed ones, it is concluded that the position of substituents in α -monochlorohinokitiol is 5 (para), in β -monochlorohinokitiol 7 (ortho'), in γ -monochlorohinokitiol 3 (ortho) and α -dichlorohinokitiol is 3, 7-dichloroderivative. The results are summarized in Table 2.

Table 2

The Position of Substituents in Halogenated Hinokitiols

Hinokitiol derivatives	$\mu_{obs.}$	$\mu_{calc.}$	Position of substituents
α -monobromo-	4.32 D	(4.32 D)	7 or o'
β -monobromo-	4.40 D	4.8 D	3 or o
γ -monobromo-	—	2.6 D	5 or p
α -dibromo-	4.27 D	4.7 D	3, 7 or oo'
β -dibromo-	3.14 D	2.9 D	5, 7 or o'p
dibromo-	—	3.7 D	3, 5 or op
α -monochloro-	2.70 D	2.4 D	5 or p
β -monochloro-	4.38 D	4.4 D	7 or o'
γ -monochloro-	4.74 D	4.95 D	3 or o
α -dichloro-	4.46 D	4.8 D	3, 7 or oo'
β -dichloro-	—	2.8 D	5, 7 or o'p
dichloro-	—	3.6 D	3, 5 or op

These conclusions are in conformity with and supported by the results of structural determinations in organic chemistry carried out by one of us (Nozoe) and his collaborators.^{(5),(6),(9)}

Summary

The dipole moments of halogen-derivatives of hinokitiol (4-isopropylcycloheptatriene-2, 4, 6-ol-2-one-1) were measured in benzene solution at 25°. The values obtained are: β -monobromohinokitiol (3-bromo-), 4.40 D; α -monochlorohinokitiol (5-chloro-), 2.70 D; β -monochlorohinokitiol (7-chloro-), 4.38 D; γ -monochlorohinokitiol (3-chloro-), 4.74 D; α -dichlorohinokitiol (3,7-dichloro-), 4.46 D. By analysing the results obtained, the position of substituents in the halogenated hinokitiols were determined and are given immediately after each name of these compounds in parentheses.

We wish to express our cordial thanks to Mr. T. Mukai, Mr. K. Kikuchi and Mr. T. Ando of the Tohoku University for collaborating with us in the syntheses of these new compounds. Our thanks are also due to the Ministry of Education in aid of this research.

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(8) α -Monobromohinokitiol ($\mu=4.32$ D) was assigned to 7-mono-bromohinokitiol from considerations in organic chemistry.^{(8),(9)}

(9) T. Nozoe, Y. Kitahara and K. Doi, *Proc. Japan Acad.*, **26** (No. 10), 25 (1950).

A Note on the Theory of Solution of Hydrated systems

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The Solution of Electrolytes

It is well-known that the Debye-Hückel's theory of solution of strong electrolytes does not hold good any longer for the solutions of the concentration greater than 0.01 mols per litre. But taking the hydration of solute into account we can interpret the experimental results almost up to the concentration of saturation for any sort of solution.

Fundamental Equations.—Now, this theory is based on the following three assumptions:

1. The complete dissociation of electrolyte is assumed for simplicity.

2. The second, the most essential of this theory, is that the hydration water attached to an ion in a co-ordinated position by its strong field can not play the rôle of solvent in an ordinary sense; hence the number of molecules of free solvent in an aqueous solution of the concentration m represented in molality, namely mols of solute per 1000 g. of solvent, may be reduced to

$$55.51 - (\nu_+ \alpha_+ + \nu_- \alpha_-)m,$$

where ν_+ and ν_- are the number of positive and negative ions created by the dissociation of one molecule of salt, while α_+ and α_- being the hydration number of positive and negative ions respectively and assumed to be constants at a given temperature characteristic of the sorts of ion and solvent throughout the whole range of concentration.

3. The third is that the water outside of hydration shell, within which the dielectric saturation takes place, behaves normal. Furthermore, for simplicity it is assumed that the interactions between hydrated ion and molecules around it are independent of concentration. In this model, therefore, the solution is composed of the hydrated ions and of the free water molecules bearing themselves quasi-ideal, if the electrostatic interactions were ignored.

Upon taking the hydration into consideration the partial molal free energy of solute, $\bar{F}_1$, can be expressed in the following form:

$$\bar{F}_1 = \bar{F}_1^\circ + RT \ln f_{\pm}^{\nu_+ + \nu_-} \times$$

$$\frac{(\nu_+ m)^{\nu_+} (\nu_- m)^{\nu_-}}{[55.51 - (\nu_+ \alpha_+ + \nu_- \alpha_-)m + (\nu_+ + \nu_-)m]^{\nu_+ + \nu_-}} \\ = \bar{F}_1^\circ + RT \ln \nu_+^{\nu_+} \nu_-^{\nu_-} (\gamma_{\pm} m)^{\nu_+ + \nu_-}, \quad (1)$$

where $\bar{F}_1^\circ$ and $\bar{F}_1^{\circ'}$ are the standard free energies, which differ from the ordinary ones owing to hydration, R , gas constant, T , absolute temperature, $f_{\pm}$, Debye-Hückel's mean activity coefficient of salt (in which only the interionic attractions are taken into account), and $\gamma_{\pm}$, stoichiometrical mean activity coefficient of salt (in which both effects of interionic attractions and of hydration are taken into consideration).

Upon introducing into Eq. (1) the usual convention of $f_{\pm} = \gamma_{\pm} = 1$ at infinite dilution i. e., $m \rightarrow 0$, the relations

$$\bar{F}_1^{\circ'} = \bar{F}_1^\circ - (V_+ + V_-)RT \ln 55.51 \\ \ln \gamma_{\pm} = \ln f_{\pm} \\ - \ln \left[1 - \frac{1}{55.51} \{ (\nu_+ \alpha_+ + \nu_- \alpha_-)m - (\nu_+ + \nu_-)m \} \right] \quad (2)$$

may be obtained. According to Debye and Hückel,

$$\ln f_{\pm} = - \frac{z_+ z_- e^2}{2DkT} \cdot \frac{\kappa}{1 + a\kappa}, \\ \kappa^2 = \frac{8\pi e^2 N\omega}{1000DkT}, \quad (3)$$

where z_+ and z_- are the ionic valencies of positive and negative ions respectively, e , the electronic charge, D , the dielectric constant of solvent in solution, k , Boltzmann's constant, a , the mean distance of approach of two hydrated ions, N , Avogadro's number, and ω , the ionic strength.

In a similar way we can define the partial molal free energy $\bar{F}_0$ of free solvent in aqueous solution of a single sort of salt as,

$$\bar{F}_0 - \bar{F}_0^\circ = RT \ln f_0 \\ \times \frac{55.51 - (\nu_+ \alpha_+ + \nu_- \alpha_-)m}{55.51 - (\nu_+ \alpha_+ + \nu_- \alpha_-)m + (\nu_+ + \nu_-)m} \\ \equiv RT \ln a_0, \quad (4)$$

where $\bar{F}_0^\circ$ is the standard free energy of solvent, and a_0 is the activity of free solvent. And f_0 is the electrostatic activity coefficient of the free solvent of the following formula

$$\ln f_0 = + \frac{V_0 \kappa^3}{24\pi} \cdot \frac{3}{x^3} \left[1+x - \frac{1}{1+x} - 2 \ln(1+x) \right],$$

($x = \kappa a$) (5)

where V_0 is the molecular volume of solvent. It may easily be shown that the hydration has strictly no effect upon $\bar{F}_0^\circ$.

Now the practical osmotic coefficient, ϕ , may be defined as follows:

$$\begin{aligned} \phi &= - \frac{55.51(\bar{F}_0 - \bar{F}_0^\circ)}{(\nu_+ + \nu_-)mRT} = - \frac{55.51}{(\nu_+ + \nu_-)m} \ln a_0 \\ &= - \frac{55.51}{(\nu_+ + \nu_-)m} \ln f_0 \\ &\times \left[\frac{55.51 - (\nu_+ \alpha_+ + \nu_- \alpha_-)m}{55.51 - (\nu_+ \alpha_+ + \nu_- \alpha_-)m + (\nu_+ + \nu_-)m} \right]. \end{aligned}$$

(6)

Table 1

The Activity Coefficients of Sodium Chloride and the Logarithms of Activity of Water at 25°C. (1), (2), (3)

m	$\gamma_{\pm}$	$\gamma_{\pm}$ obs.		$1 + \log a_0$	$1 + \log a_0$ obs.	
		calc.*	(1) (2)		calc.**	(2) (3)
0.1	0.780	0.786	0.781	0.9985	0.9985	0.9985
0.2	0.736	0.741	0.737	0.9971	0.9971	0.9971
0.3	0.712	0.717	0.713	0.9956	0.9957	—
0.5	0.686	0.688	0.685	0.9927	0.9928	0.9928
0.7	0.673	0.674	0.671	0.9898	0.9898	—
1.0	0.664	0.664	0.661	0.9853	0.9853	0.9854
1.2	0.663	—	0.651	0.9822	0.9823	—
1.4	0.664	—	0.658	0.9790	0.9792	—
1.6	0.667	—	0.659	0.9758	0.9760	—
1.8	0.670	—	0.662	0.9725	0.9727	—
2.0	0.675	0.672	0.667	0.9691	0.9694	0.9695
2.5	0.691	—	0.686	0.9606	0.9605	—
3.0	0.712	0.713	0.713	0.9515	0.9511	0.9514
3.5	0.737	—	0.746	0.9419	0.9409	—
4.0	0.767	0.772	0.785	0.9319	0.9301	0.9314
4.5	0.801	—	0.832	0.9215	0.9184	—
5.0	0.839	—	0.884	0.9104	0.9061	—
5.2	0.857	0.859	—	—	—	0.9044
6.0	0.935	—	1.007	0.8868	0.8793	—

* $a = 4.32 \text{ \AA.}$, $\alpha_+ + \alpha_- = 6.0$

** $a = 4.32 \text{ \AA.}$, $\alpha_+ + \alpha_- = 3.$

If the hydration does not exist, i.e., in the case of $\alpha_+ = \alpha_- = 0$, all the equations cited above may be reduced to the ordinarily known formulae.

However, these equations contain two constants, a and $\nu_+ \alpha_+ + \nu_- \alpha_-$, of which exact values are not obtainable at present by purely theoretical bases. Therefore, they must be determined at present as parameters so as to give agreements between the observed and calculated values. It is evident, however, that they are in the closest relation with each other and must be reduced ultimately to one.

The Comparison between the Calculated and Observed Values of $\gamma_{\pm}$ and ϕ at 25°.

—The calculations for about 31 electrolytic aqueous solutions at 25° were made by the writer. Some of these results are compared in Table 1, Fig. 1 and Fig. 2.

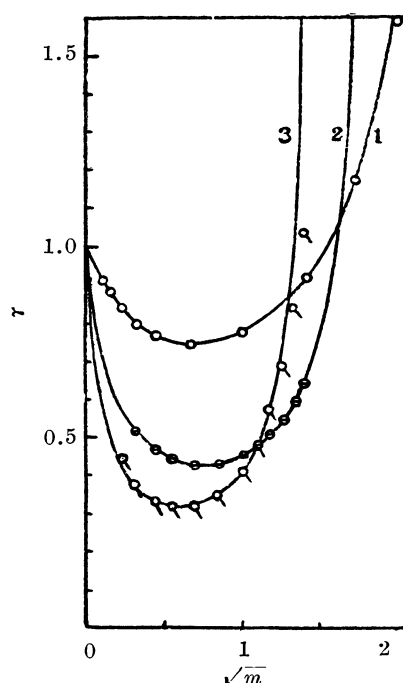


Fig. 1.—The activity coefficients of 1-1, 2-1 and 3-1 electrolytes at 25°C. Observed values: O, LiCl; O with dot, SrCl₂; O with cross, PrCl₃. Full line is calculated by Eqs. (2) and (3): curve 1 (LiCl), $a = 5.26 \text{ \AA.}$, $\alpha_+ + \alpha_- = 11$; curve 2 (SrCl₂), $a = 4.68 \text{ \AA.}$, $\alpha_+ + 2\alpha_- = 18$; curve 3 (PrCl₃), $a = 6.14 \text{ \AA.}$, $\alpha_+ + 3\alpha_- = 28$.

The agreements between calculated and observed values are satisfactorily excellent over the wide range of concentration: the deviations being within 1% for most uni-uni valent salts of the concentration up to 4 M (but to 3 M in case of HCl and LiCl) and for CaCl₂ type

(1) Landolt, Börnstein, "Physic. Chem. Tabellen," Erg. Bd. III, Berlin, 1936, p. 2153.

(2) G. Scatchard, W. Hamer and S. E. Wood, *ibid.*, **60**, 3061 (1938).

(3) Landolt, Börnstein, "Physik. Chem. Tabellen," Erg. Bd. II, 1931, p. 1126.

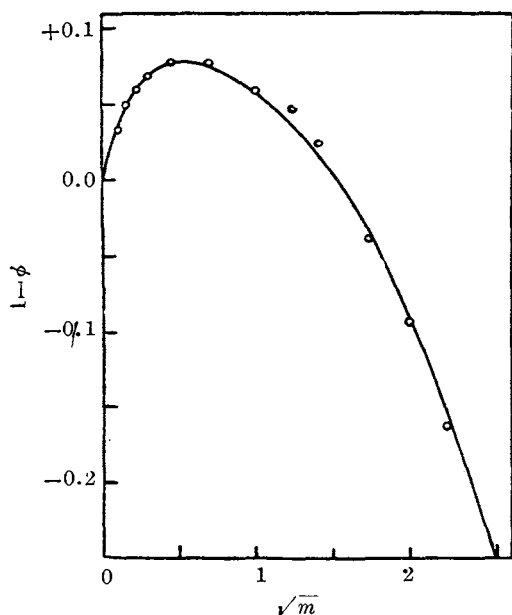


Fig. 2.—The osmotic coefficient of NaCl at 25°C.: O, observation. Full line is calculated by Eqs. (5) and (6): $a = 4.32 \text{ \AA.}$, $\alpha_+ + \alpha_- = 3$.

salts of the concentration up to 2 *M* (but to 0.5 *M* in case of ZnCl_2), and the deviations being within 2 % for LaCl_3 type salts of the concentration up to 1.6 *M*. The best fit values of a and $\nu_+ \alpha_+ + \nu_- \alpha_-$ for activity coefficients are tabulated in Table 2, in which the fourth row refers to the literatures with which the values are compared.

For all nitrates, sulphates and for a few of chlorides such as ZnCl_2 and CdCl_2 , both the a values and $\nu_+ \alpha_+ + \nu_- \alpha_-$ values are either exceedingly small or not satisfactorily obtainable. This probably might be due to the fact the ions of these salts, as compared with the other salts, are so liable to associate or to form the complexes even in the dilute solution that the apparent concentration of these ions becomes small enough to cancel the effects of hydration on the activity coefficients. If these contributions are taken into consideration the values in Table 2 might slightly be altered. And in addition to them the effects of the change of the dielectric constants of solution by varying the concentration⁽⁶⁾ must be taken into consideration in order to make the theory more complete.

Considering the sizes of molecules and ions the hydration number of an ion would probably be less than 12 for most monovalent simple ions. According to Bernal and Fowler⁽⁷⁾, it must be 4 for all the monovalent simple ions, and 6 or 8 for divalent ions. But from the lowering of the dielectric constant of aqueous salt solutions, Hasted, Ritson and Collie⁽⁸⁾ have estimated the minimum hydration number of positive ions at 10 for H^+ , 6 for Li^+ , 4 for Na^+ , K^+ and Rb^+ ; 14 for Mg^{++} and Ba^{++} ; and 22 La^{+++} .

Finally, however, it is not yet understood why the most favorable values of a and $\nu_+ \alpha_+ + \nu_- \alpha_-$ for $\gamma_{\pm}$ and for ϕ do not agree with each other.

Table 2

The Values of the Mean Distance of Approach of Ions, and of the Molecular Hydration Number.⁽⁴⁾⁽⁵⁾

$z_+ = 1$	HCl	KOH	LiCl	LiBr	LiI	NaCl	KCl	RbCl	CsCl	NH_4Cl	K_2SO_4
$a, \text{\AA.}$	5.26	3.51	5.26	5.80	6.86	4.32	3.72	3.14	2.30	3.07	3.00
$\nu_+ \alpha_+ + \nu_- \alpha_-$	12	10	11	12	14	6	4	4	4	5	(10)
Lit. No.	(5)	(3)	(3)	(4)	(4)(5)	(1)(2)	(2)(4)	(4)	(4)	(3)	(5)
$z_+ = 2$	MgCl_2	NiCl_2	CoCl_2	CaCl_2	MnCl_2	BaBr_2	SrCl_2	CuCl_2	BaCl_2	ZnCl_2	MgSO_4
$a, \text{\AA.}$	6.14	5.16	5.00	5.10	5.10	4.93	4.68	4.65	4.42	5.28	2.93
$\nu_+ \alpha_+ + \nu_- \alpha_-$	22	22	22	20	18	18	18	14	14	(2)	11
Lit. No.	(4)(5)	(5)	(5)	(5)	(5)	(5)	(5)	(5)	(5)	(5)	(5)
$z_+ = 3$	AlCl_3	ScCl_3	YCl_3	LaCl_3	CeCl_3	PrCl_3	NdCl_3	SmCl_3	EuCl_3		
$a, \text{\AA.}$	6.60	6.50	6.39	6.22	6.20	6.14	6.14	6.48	6.58		
$\nu_+ \alpha_+ + \nu_- \alpha_-$	34	32	30	28	28	28	28	28	28		
Lit. No.	(5)	(5)	(5)	(5)	(5)	(5)	(5)	(5)	(5)		

(4) Landolt, Börnstein, "Physik. Chem. Tabellen," Erg. Bd. III, 1936, p. 2138.

(5) R. A. Robinson and H. S. Harned, *Chem. Rev.*, **28**, 419 (1941).

(6) E. Hückel, *Physik. Zeits.*, **26**, 93 (1925).

(7) J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

(8) J. B. Hasted, D. M. Ritson and C. H. Collie, *J. Chem. Phys.*, **16**, 1 (1948).

The Solution of Non-Electrolytes

The van't Hoff's theory of dilute solution does not hold good any longer for the concentration higher than 0.1 mol per liter, while the hydration theory is applicable also for the interpretation of the properties of the solutions of non-electrolytes. The mechanism of hydration of non-electrolytes, different from that of electrolytes, is due chiefly to the hydrogen bond formation between solute and water molecules. As the strength of the hydrogen bond between water and hydroxyl radicals of organic compounds is assumed, in many cases, to be somewhat stronger than that of water⁽⁹⁾, the function of water as solvent might be somewhat diminished when the hydration occurs. Thus the activity coefficient γ and the osmotic coefficient ϕ of the aqueous solution on the molality (mols of solute per 1000 g. of solvent) scale can be calculated by the following equations (cf. Eqs. (2) and (6)),

$$\ln \gamma = -\ln[1 - (\alpha - 1)m/55.51] \quad (7)$$

$$\phi = -\frac{55.51}{m} \ln \frac{55.51 - \alpha m}{55.51 - \alpha m + m} \quad (8)$$

by adjusting only one parameter α , the number of hydrated water molecules per one molecule of solute.

Some of the results are shown in Fig. 3 and Table 3. The agreements between calculated and observed values are excellent up to 2 *M* with each characteristic α value, but unsatisfactory in the region of high concentration, as is seen in Fig. 3. It seems here that α value decreases with increasing concentration, suggesting that the association of the solute begins to play some rôles. The behaviors of solutes

Table 3
The Osmotic Coefficients of Aqueous
Solution of Sucrose at 25°C.⁽²⁾

<i>m</i>	ϕ calc. $\alpha=5$	ϕ obs.	<i>m</i>	ϕ calc. $\alpha=5$	ϕ obs.
0.1	1.008	1.007	1.2	1.108	1.108
0.2	1.016	1.015	1.4	1.128	1.128
0.3	1.024	1.023	1.6	1.149	1.149
0.4	1.033	1.032	1.8	1.170	1.169
0.5	1.042	1.041	2.0	1.195	1.189
0.6	1.051	1.050	2.5	1.255	1.236
0.7	1.059	1.059	3.0	1.322	1.282
0.8	1.069	1.069	3.5	1.397	1.326
0.9	1.078	1.078	4.0	1.482	1.369
1.0	1.088	1.088	5.0	1.686	1.448

(9) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, New York, 1940, pp. 284-334.

such as urea,⁽¹⁰⁾ urethane,⁽¹⁰⁾ acetamide,⁽¹⁰⁾ acetone,⁽¹¹⁾ methyl- and ethyl-alcohols⁽¹¹⁾ are

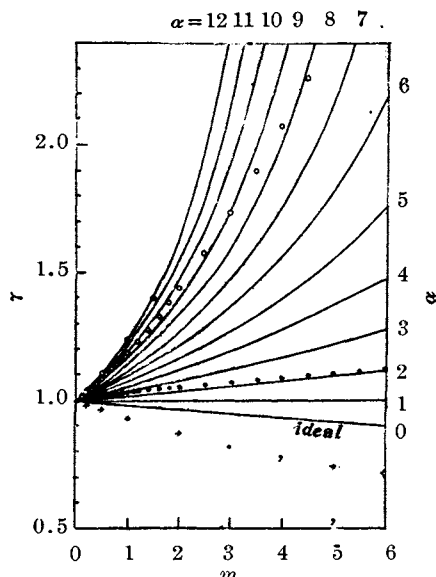


Fig. 3.—The activity coefficients of non-electrolytes at 25°C. ○, Sucrose; ●, Glycerol; +, Urea. Full line is calculated by Eq. (7).

Table 4
The Hydration Numbers of Some Organic Compounds.

Name of solute	No. of free OH radicals	α	Temp., °C.	Obtained from	References
Glycerol	2	3	0	γ (Fr)	(11)
		3	25	γ (p)	(2)
		1	25	ϕ (p)	(2)
Erythrit	4	4	0	γ (Fr)	(11)
Methyl Glucoside	4	3	0	p	(12)
		5	0	P	(13)
Glucose	5	4	0	γ (Fr), P	(11), (13)
Mannit	6	2	20	r (p)	(11)
		12	0	γ (Fr)	(11)
Sucrose	8	5	0	p, P	(12), (13)
		9~10	25	r (p)	(2)
		5	25	ϕ (p)	(2)
		4~5	25	p	(12), (14)
		5	30	P	(13), (15)
		4	55.7	P	(13), (15)
		4	100	p	(12)

(Fr...Freezing point depression; p...Vapor pressure; P...Osmotic pressure.)

(10) H. M. Chadwell and F. W. Politt, *J. Am. Chem. Soc.*, **60**, 1292 (1938).

(11) Landolt, Börnstein, "Physik. Chem. Tabellen," Erg. Bd. II, Berlin, 1931, p. 1130.

(12) "International Critical Table," Bd. III, p. 293.

(13) *ibid.*, Bd. IV, p. 429.

(14) Landolt, Börnstein, "Physik. Chem. Tabellen," Erg. Bd. III, 1936, p. 2496.

(15) *ibid.*, Erg. Bd. III, 1936, p. 2664.

exceptional in that their activity coefficients are, even in dilute solution, always below the ideal line. Therefore, such solutes must always be in associated states, because the activity coefficient is diminished by association.

The Hydration Number and the Structure of Solute.—In order to get the most probable value of the hydration number, we must determine it from the activity observed in the solution as dilute as possible, in which the association of the solute can be neglected. The best fit values of α are tabulated in Table 4. Here, it is possible to imagine a certain relation between α and the structural configuration of the solute molecule: a rough correspondence exists between α and the number of hydrogen-bond-forming radicals in the molecule of solute, although some exceptions such as mannitol exist.

It is inexplicable in this case too, the reason why some of the values of α estimated from γ are approximately two times of those estimated from ϕ .

Summary

(1) Upon taking the hydration into consideration the thermodynamical properties of solutions of electrolytes and non-electrolytes can be well represented over the wide range of concentration.

(2) The values of hydration number of non-electrolytes seem to be related to the configuration of solute molecules. The hydration number was determined for 37 solutes.

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Fungus and Enzyme. Preparation of *Aspergillus Oryzae* Amylase and its Use in Bread Making

By Taichi HARADA

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Introduction

The degree of panary ferment which is caused by yeast depends largely upon the presence of fermentable sugar produced by the action of diastatic enzyme in flour. The amount of diastase in the flour is, therefore, one of the important factors in bread making. Flour deficient in diastatic activity can not be baked into a desired large loaf of bread unless a sufficient amount of sugar is added to the dough. It is known that to supplement the deficiency, wheat is mixed with a little sprouting one⁽¹⁾ and is milled in the usual manner or the flour is mixed with corn flour⁽²⁾ having a high diastatic activity or with malt preparation.

In the experiment, it is observed that the use of fungal amylase preparation, taka-diastase, in bread making gives an undesirable effect, caused not by the true amylase of such preparation but by the proteolytic enzyme accompanying the amylase. That is to say the proteolytic

enzyme is not only responsible for a reduction of gas retaining power of the dough but also for the characteristic bread disease "Ropiness".⁽³⁾

Therefore, it is desirable to prepare the diastatic enzyme preparation as free as possible from the proteolytic enzyme.

Discussion

The present author⁽⁴⁾ has shown that the diastatic enzyme solution passes through a colloidal membrane, indicating that it possesses a relatively small molecule. The enzyme preparation prepared by this method was tried in bread making but this was abandoned since it was not economical. There are many methods for the separation or purification of amylase but they are not applicable to the industry from the same stand point.

Although it was thought that alkaline or acidic of the culture medium, bran, might

(1) Sherwood and Bailey, *Cereal Chem.* **3**, 163 (1926).

(2) Sapozhnikova, *C. A.* **43**, 7569 (1949).

(3) Unpublished observation by the author at Takamine Laboratory, Inc., Clifton, N. J., U. S. A. (1930).

(4) T. Harada, *Ind. Eng. Chem.* **23**, 1424 (1931).

influence the production of proteolytic enzyme, a few experiments has proved otherwise. The best method is to find the special strain of the fungus which does not produce any of the enzyme in question in its growth, but such is almost impossible at present.

In the previous paper⁽⁵⁾ the present author reported that in precipitating the enzyme with 70 volume percent alcohol when the precipitate becomes gum-like it may be adjusted to a desired precipitate by cutting down the amount of alcohol. However, in this case this will cause a loss of diastatic enzyme preparation. When the precipitating diastase preparation of this dilute alcohol was determined for diastatic and proteolytic (casein-digesting) enzymes, a relatively large amount, in other words, a strong proteolytic enzyme (Fuld-Gross' method) was present in comparison to that of diastatic enzyme

in the control.

Therefore, it is interesting to note here that the proteolytic enzyme could be removed by this simple fractional precipitating process, and that the diastase preparation, free or almost free from the enzyme in question is possible to be used in the bread making industry instead of malt preparation not only more economically but in producing fine loaves of bread. It is seen that the amount of diastase and protease in the flour or the dough in bread making becomes a real problem.

Fraction

It was shown that a fractional precipitation by alcohol serves to a certain degree as separation or purification of the amylase; that is, in the first fraction, with around 57 volume

Table 1

The Influence of Fractional Alcoholic Precipitation upon Diastase and Proteolytic Enzyme

Origin of fungus strain*		Yield, g.	L. V.	% L. V.**	Total L. V., %	T. V.	Total T. V.	T. V. in 100% L. V.
A	1. Koji extract 100 +alc. 150 (61%)	1.40	1100	73.3	102.6	111.1	155.5	151.6
	2. The filtrate of No. 1 225+alc. 215 (77.6%)	2.99	5651	376.7	1126.3	3.2	9.6	0.9
	3. Koji extract 100 +alc. 375 (75%)	4.12	4100	273.3	1126.0	41.7	171.8	15.3
B	1. Koji extract 100 +alc. 115 (51%)	0.9	125	8.3	7.5	47.6	42.8	573.5
	2. The filtrate of No. 1 205+alc. 230 (74%)	1.2	1967	131.1	157.3	37.0	44.4	28.2
	3. Koji extract 100 +alc. 350 (74%)	2.0	1283	85.5	171.0	47.6	95.2	55.7
	1. Koji extract 125 +alc. 188 (57%)	1.2	125	8.4	10.1	25.7	30.8	306.0
	2. The filtrate of No. 1 290+alc. 270 (75%)	1.1	2117	141.1	155.2	8.9	9.8	6.3
	3. Koji extract 125 +alc. 438 (74%)	2.2	1034	68.9	155.1	22.2	48.8	32.2
	1. Koji extract 110 +alc. 190 (60%)	1.4	190	12.7	17.8	111.1	155.4	874.8
	2. The filtrate of No. 1 275+alc. 230 (72%)	2.0	535	35.7	71.4	15.4	30.8	43.1
	3. Koji extract 110 +alc. 350 (72%)	3.0	480	320	96.0	66.7	200.1	208.4
C	1. Koji extract 100 +alc. 137 (55%)	0.6	230	8.7	5.2	8	4.8	92.0
	2. Whole filtrate of No. 1+alc. 270 (79%)	0.7	4600	306.7	214.7	6	4.2	2.0
	3. Koji extract 100 +alc. 375 (75%)	1.1	3240	216.0	237.6	8	8.8	3.7

* Origin of fungus strain A, *Asp. oryzae* strain of Takamine Laboratory; B, *Asp. oryzae*, a mixed strain; C, *Asp. oryzae* B. strain of the Sakaguchi Laboratory of this institute.

** 100% = 1500 L. V.

percent alcohol of Koji water extract, it gives a relatively strong tryptic but weak diastatic enzyme preparation, and in the second fraction, with 72 percent alcohol or over, it gives a preparation, fairly free from the proteolytic enzyme with a strong diastatic power, in comparison to the first fraction and the control.

It is seen that as total L. V. (Table 1), the diastase preparation may greatly be lost in the first fraction but this loss may be collected in the second fraction to make it up to about 70 volume percent or over. Further purification might be carried out by dissolving the precipitate and by repeating the process of the fraction but it is industrially not economical. The degree of purity, of course, depends largely upon the strength of the extract and the origin of the fungus strain as shown in the experiment.

Selective Use of the Fraction

The rich proteolytic but poor diastatic enzyme content preparation in the first fraction may be superior than that of an ordinarily prepared taka-diastase or the control when used internally such as for stomach disturbance but the proteolytic freed rich diastatic enzyme preparation is superior than malt preparation in the bread making industry.

Experiment

(a) One hundred cc. (Table 1, A) of the water extract of *Asp. oryzae* fungus Koji (free from spore) No. 1 and 3 were treated with 150 and 375 cc. of about 95 percent alcohol to give about 61 and 75 volume percent respectively in a 500 cc. capacity Erlenmeyer flask, mixed well, left standing one hour or so, then supernatant liquid decanted to another flask. The bottom liquid mixture with precipitate was transferred to a precipitation tube, centrifugalized and separated. The precipitate was washed with 95 percent alcohol and filtered

rapidly by suction, washed with ether and finally it was dried in a calcium desiccator. On the other hand (No. 2), the whole (225 cc.) alcoholic liquid part, the filtrate of No. 1, was treated with further addition of alcohol (215 cc.), mixed, precipitated again, and this second precipitation was washed with 95 percent alcohol, finally dried in a calcium desiccator. Table 1, B and C are the results of the similar treatment for the samples of different origins.

(b) When the amylase, fairly free from proteolytic enzyme, was tried number of times in bread making (flour, 350: diastase, 50 L. V. in total) by the method⁽⁶⁾ of Bailey, the result was quite a satisfactory bread in every respect. The characteristic fermentation (bread-disease) does not easily set in comparison with that prepared by the Takamine's method. This publication will soon follow.

Summary

1. The fungal amylase preparation containing rich proteolytic but poor diastatic enzyme has been prepared by precipitating Koji water extract with the amount of alcohol which gives around fifty to sixty volume percent solution.

2. A strong fungal amylase but very weak proteolytic enzyme preparation has been prepared by fractional precipitation of the filtrate of 1 by adding further alcohol up to seventy percent or over.

3. The possibility of utilizing fungal diastase preparation in the bread making industry has been pointed out.

The author thanks the Sakaguchi Laboratory for the *Asp. oryzae* B. strain which was kindly given for this investigation.

Scientific Research Institute, Ltd., Tokyo

(6) Bailey, *J. Ind. Eng. Chem.*, 8, 53 (1916).

Amperometric Titration of Potassium with Sodium Dipicrylamine

By Yoshikazu YASUMORI

(Received September 15, 1950)

Amperometric titration of potassium with sodium dipicrylamine has been studied by B. Sandberg⁽¹⁾ and A. Langer *et al.*,⁽²⁾ but the details are not given. In the present paper

(1) B. Sandberg, *Svensk. Kem. Tid.*, **58**, 197 (1946); *C. A.*, **41**, 349 (1947).

(2) A. Langer and D. P. Stevenson, *Ind. Eng. Chem., Anal. Ed.*, **14**, 770 (1942).

the analytical procedure is shown and the results are discussed.

Experimental

Chemicals and Apparatus Used.—Sodium Dipicrylamine was Hexyl Natrium made by Nippon Kasei Chemical Industries Limited. The polarograph used by the author was a Heyrovsky-Shikata type made by Yanagimoto Co., Kyoto. For amperometric titration both the portable electronic instrument of Delahay's type⁽³⁾ and the arrangement as shown in Fig. 1 were used.

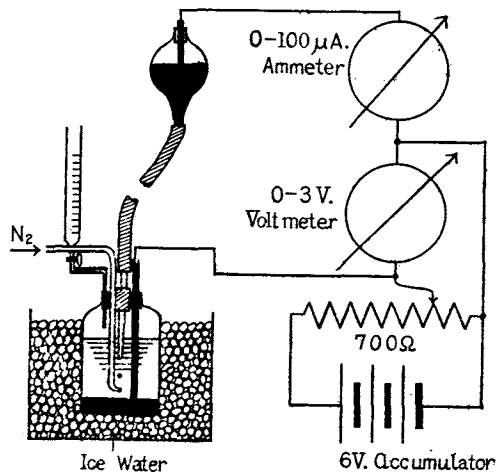


Fig. 1.

Polarographic Behavior of Sodium Dipicrylamine.—A polarogram of sodium dipicrylamine in Palitzsch's borate buffer solution (pH 8.98) is shown in Fig. 2. Three waves were obtained, the first small, the second obscure and the third was a large wave with maximum. The wave-height of the first was not proportional to the concentration of dipicrylamine. The maximum in the third wave was not suppressed by gelatin, but the

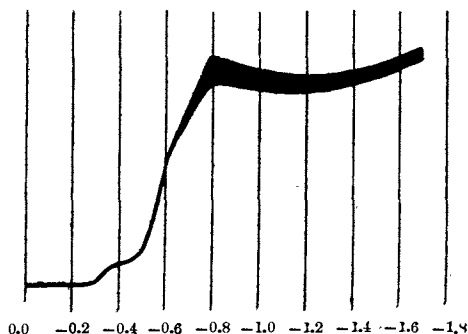


Fig. 2.—A polarogram of sodium dipicrylamine in Palitzsch's borax buffer solution (pH 8.98): Sensitivity, 1/100; concentration, 16.4×10^{-5} ; anode, Hg-pool.

diffusion currents of dipicrylamine in the above mentioned buffer solution at -1.60 V. applied *vs.* mercury pool were proportional to its concentration smaller than 3×10^{-5} .

Procedure.—A measured volume of the sample was introduced into the cell, neutralized with sodium hydroxide and 50ml. of the buffer solution were added. After passing nitrogen gas for ten minutes and cooling in an icewater-bath, the -1.60 V. *vs.* mercury pool was applied to the cell and the current was measured. $N/10$ sodium dipicrylamine solution was added successively with a microburette. After each addition the content in the cell was mixed by passing nitrogen gas for ten minutes and the current was recorded. During the titration, the electrolyte must be cooled in an icewater-bath at $0^\circ - 2^\circ$. In all cases the values of the current, corrected for the volume change, were plotted against the amount of reagent added.

Results

Results obtained in the titration are given

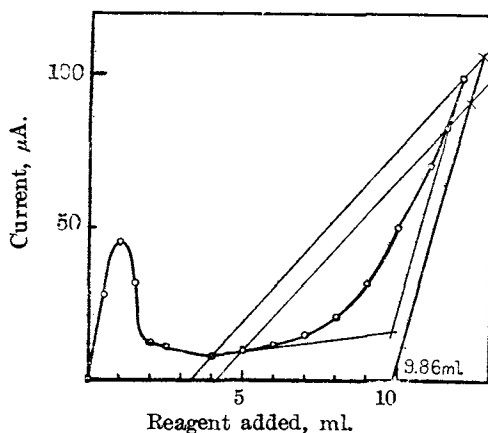


Fig. 3.—Titration curve of sample No. 1.

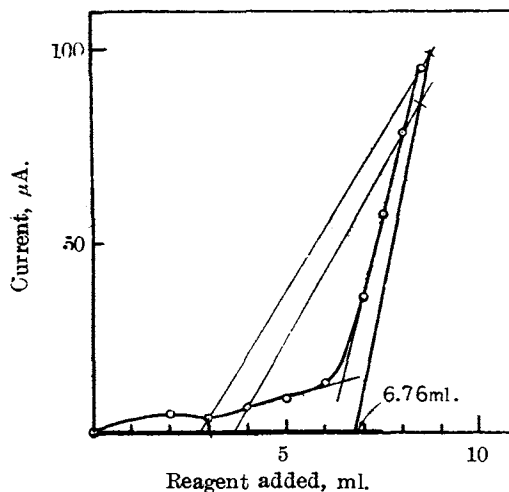


Fig. 4.—Titration curve of sample No. 2.

(3) P. Delahay, *Anal. Chem.*, **21**, 1425 (1949).

in Table 1 (Figs. 3, 4, 5, 6, 7, 8 and 9). The point obtained by the intersection of the tangents became different from the point obtained by the intersection of the asymptotes

Table 1

Sample No.	Used, mg.	End-point obtained, ml.	K found, mg.
1	K 39.1 Na 17.3	9.86 (9.80)	39.1 (38.9)
2	K 27.6 Na 17.3	6.76 (6.49)	26.8 (25.8)
3	K 72.7 Na 17.3	18.36 (16.97)	72.9 (67.4)
4	K 52.2 Na 412.6	13.18 (12.67)	52.3 (50.3)
5	K 26.4 Na 412.6	6.31	25.0
6	K 34.7 Na 336.4	8.68	34.5
7	K 51.4 Na 17.3 Fe 43.2 Al 22.3	12.97 (12.28)	51.5 (48.8)

The values obtained by the intersection of tangents were given in brackets. No. 7 was titrated, using a microammeter of 100 microamperes in full scale.

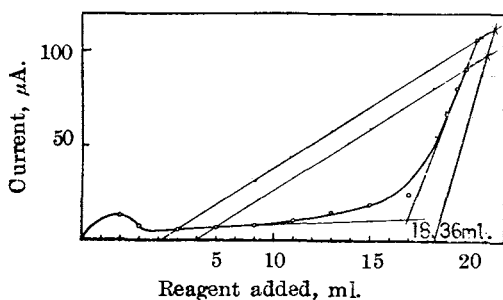


Fig. 5.—Titration curve of sample No. 3.

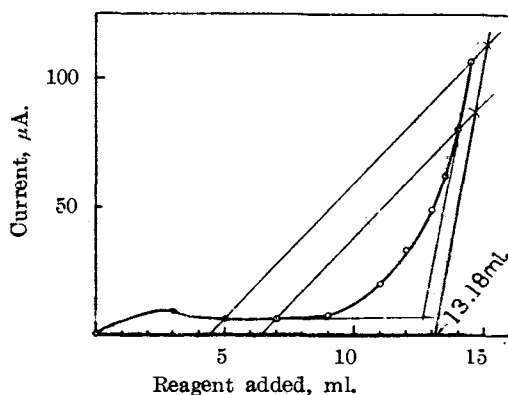


Fig. 6.—Titration curve of sample No. 4.

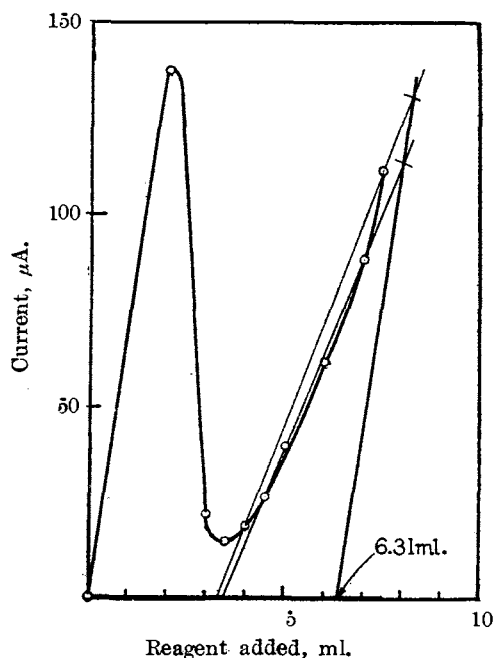


Fig. 7.—Titration curve of sample No. 5.

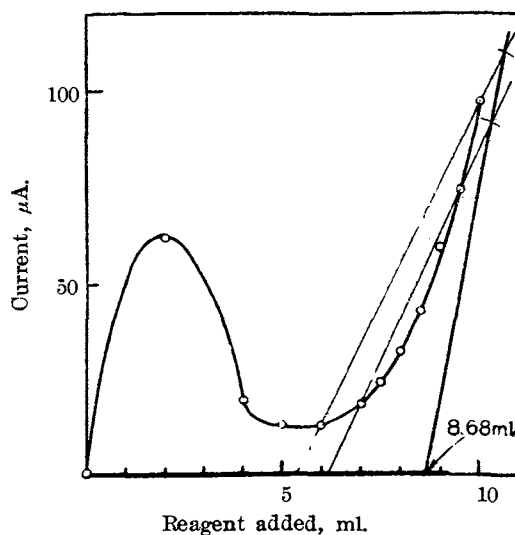


Fig. 8.—Titration curve of sample No. 6.

of titration curve according to Langer *et al.* When the end-point was located on the point obtained by the intersection of the asymptotes, the results obtained showed coincidence with that calculated. At the beginning of titrations supersaturation was held, so that when there was no more than 30 mg. K, the portion of the titration curve before the end-point was not complete enough to obtain an asymptote. The presence of 350 mg. Na did not interfere and in presence of aluminate and precipitate of ferric hydroxide the titration was not affected.

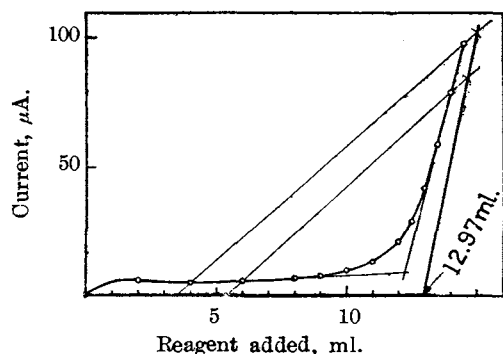


Fig. 9.—Titration curve of sample No. 7
(A 100-microammeter was used).

The great diffusion current of dipicrylamine made a microammeter of 100 microamperes in full scale useful instead of a galvanometer.

Discussion

Mercury pool was used for the anode, for the reason that if calomel electrode was used, potassium ion might stray into the cell and

that the diffusion current of dipicrylamine was so great that the potential drop through the connecting bridge would not be negligible. Applied potential should be changed with the composition of sample. When the sample was chloride, -1.60 V. was applicable. Although dipicrylamine seemed to be not completely dissociated, in the present work the end point was located neglecting the undissociated dipicrylamine.

Summary

In the amperometric titration of potassium with dipicrylamine, the end-point located by the theory of Langer *et al.* showed satisfactory results. The accuracy was within 1 mg. with more than 30 mg. K. In presence of 350 mg. Na, or aluminate and precipitate of ferric hydroxide the titration was not affected.

In conclusion the author wishes to express his sincere thanks to Mr. S. Sato in this laboratory for his kind advice.

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Phenomenological Theory of Intermediate Intensity Reciprocity-Law Failure at and near the Optimum in Photographic Exposure

By Eiichi MIZUKI and Shin FUJISAWA

(Received March 3, 1951)

Introduction

One of the most important problems in the latent image formation in photographic process is the phenomenon known as the reciprocity-law failure corresponding to the breakdown of Bunsen-Roscoe's law for a photo-chemical reaction. As is well known, the developed density of a photographic emulsion does not depend only upon the exposure of light, namely the product of the intensity and time factors. In most cases, there exists an optimal intensity at which the photographic process proceeds most efficiently.

This phenomenon is in general represented graphically by a reciprocity-failure curve. The curve A in Fig. 1 shows a typical case of it, in which the log exposure (It) required to produce a constant developed density is plotted

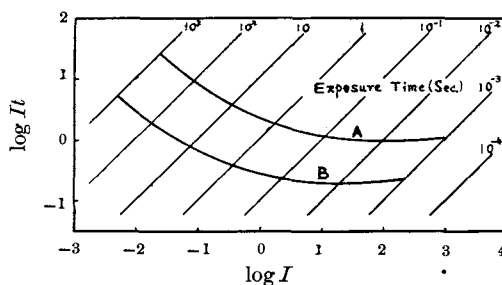


Fig. 1.—Reciprocity-failure curves for different degrees of after-ripening: curves A and B correspond to low and high degrees of after-ripening respectively.

against the log intensity (I).

The drop in photographic efficiency at intensities higher than the optimum, which is termed as the high intensity failure, is caused by the

relative sluggishness of the ionic process compared with the high rate of the production of the photo-electrons and the limited electric capacity of the electron traps.⁽¹⁾ On the other hand, the failure of reciprocity-law at intensities lower than the optimum arises from the fact that the thermal agitation impedes the creation of the silver specks in the initial stages of the latent image formation.^{(1), (2)}

These interpretations are qualitatively acceptable, but it is highly desired from both theoretical and practical standpoints to develop this theory, especially so as to interpret quantitatively the shape of the reciprocity-failure curve. This is the reason why the problem in this field has received so much discussion in recent years. Katz⁽³⁾ and Webb,⁽⁴⁾ for instance, have succeeded independently in deriving the theoretical curves in the region of very low intensities. Their methods are based upon the following considerations: (1) the assumed existence of the stable speck in the initial stages of latent image formation and (2) the statistical fluctuation of the number of light quanta absorbed by a grain. Their separate treatments arrived at the same conclusion that the shape of the curve at very low intensities is a straight line, and this is in good agreement with the experimental results.

In the above treatments by Katz and Webb, they attempt to extend their treatments so as to include the region of intermediate intensities below the optimum. However, it seems⁽⁵⁾ that in their extensions they do not fully appreciate the interplay of ionic and electronic processes at intermediate intensities below the optimum.

In such a region of exposure intensities special attention must be given to what becomes of the photo-electrons after they have been captured by the electron traps. In some cases, some of such trapped electrons may not be neutralized by ionic process, but, due to thermal motion, escape from the trapping states. Thus these two possibilities may act competitively on the trapped electrons (hereafter referred to as the competitive action).

It is the purpose of this paper, therefore, to point out that there is a more appropriate treatment in the region of intermediate intensities at and near the optimum. The present authors emphasize that in such a region the competitive action should be taken into account.

Moreover, by assuming the accumulation of the trapped electrons in an electron trap throughout exposure, the present authors have phenomenologically formulated a dynamical equation for the rate of increase in the number of the trapped electrons. On the basis of this, analytic expression for the log exposure required to produce the developable image has been derived. Finally, by means of adjustable parameters, comparison has been made to see how this theoretical curve is compatible with the experimental data.

A phenomenon which produces strong evidence for our viewpoint is that the reciprocity-failure curve is shifted as a whole in a definite way in accordance with the changes in various factors such as the degree of the after-ripening, the ionic conductivity, the temperature, etc.

For instance, as the after-ripening is prolonged in its earlier stages, the reciprocity-failure curve at intermediate intensities is in most cases shifted as a whole toward lower intensity along the direction of lines of constant exposure times (hereafter referred to as the diagonal shift).⁽⁶⁾ The experimental reciprocity-failure curves at different degrees of after-ripening are shown in Fig. 1, where the curve B refers to the emulsion subjected to a longer after-ripening than that of the curve A. This diagonal shift seen here which is composed of the vertical descent component as well as the traverse shift component would be inexplicable by any idea, unless the competitive action were taken into account.

It seems to be also the case with the similar shift caused by the temperature changes, although Katz⁽³⁾ and Webb⁽⁴⁾ have some remarks on this point without being aware of the importance of the competitive action at intermediate intensities.

It is to be noted, therefore, that the treatment given in this paper is especially suitable for interpreting the bodily shifts of the whole curves at intermediate intensities.

Derivation of the Equation Representing the High Intensity Failure Component

Exposure of silver halide grains of the photographic emulsion releases electrons from the bromide ions or the local absorption centers and raises them up to the conduction levels of the crystal lattice. Such electrons move through the lattice and then may be captured by the electron traps (sensitivity specks) distributed haphazardly on the grains.

Let us consider first the process of electron

(1) R. W. Gurney and N. F. Mott, *Proc. Roy. Soc., A* **164**, 151 (1938).

(2) J. H. Webb and C. H. Evans, *J. Opt. Soc. Am.*, **28**, 431 (1938).

(3) E. Katz, *J. Chem. Phys.*, **17**, 1132 (1949).

(4) J. H. Webb, *J. Opt. Soc. Am.*, **40**, 3 (1950).

(5) S. Fujisawa and E. Mizuki, to appear in *J. Opt. Soc. Am.*, (L).

(6) E. Mizuki, *Kagaku Butsuri* (in Japanese), **1**, 49 (1949); E. Mizuki and S. Fujisawa, to be published.

trapping. We assume that the electron trap responsible for the latent image formation may be capable of capturing several electrons simultaneously. In this case, however, owing to their electrostatic repulsion against subsequent electrons, the capture cross section σ of an electron trap diminishes with increasing the number n of the electrons already captured, in accordance with the relation

$$\sigma = \beta n^{-\gamma}, \quad (1)$$

where β and γ are the numerical constants, the former being one of parameters determining the position of the reciprocity-failure curve and the latter one of adjustable parameters which serve to fit the shape of the theoretical curve to the experimental one. It is on this account that the present treatment is to be considered as essentially phenomenological.

Secondly, we now suppose the existence of the competitive action on the trapped electrons. The electrons staying in the electron trap may be either neutralized by the ionic migration (mobile silver ions or vacant anion sites) owing to their negative charge, or ejected on to the conduction band by the thermal motion (leading to inefficiency). These two possibilities should be considered as competing (simultaneously existing) so long as the lifetime of a trapped electron is of the same order as the time of neutralization by ionic migration. Under the existence of such competitive action, the rate of increase in the number of trapped electrons during exposure with intensity I is given by the equation,

$$dn/dt = P\beta n^{-\gamma}I - (Q+R)n. \quad (2)$$

Herein P is the constant proportional to the product of the grain area and the light absorption factor of the grain; the factor $\beta n^{-\gamma}$ is given by Eq. (1); Q is the constant proportional to ionic conductivity for the ionic process playing a role in the neutralization of trapped electron; R is the probability of an electron escaping from an electron trap, or the reciprocal of average lifetime of a trapped electron, having the relationship,

$$R = \nu \exp(-\Delta E/kT). \quad (3)$$

In this relation ΔE is the thermal depth of the electron trap, and ν the frequency with which a trapped electron collides with the potential walls of the electron trap, k the Boltzmann constant and T the temperature.

It should be remarked about Eq. (2) that the present authors deal only with the case where the magnitude of the first term $P\beta n^{-\gamma}I$

is larger than that of the second term $(Q+R)n$. If, however, the ionic migration is so rapid that the second term surpasses the first term even when the magnitude of the factor R is very small, the accumulation of trapped electrons in an electron trap will not occur. Accordingly, Eq. (2), therefore the present treatment will be meaningless, but the extensions attempted by Katz and Webb will be found the good approximations in such a case.

Integrating Eq. (2), we have

$$n^{1+\gamma} = \{\beta PI/(Q+R)\}[1 - \exp\{(1+\gamma)(Q+R)t\}]. \quad (4)$$

When the factor $(1+\gamma)(Q+R)$ is large enough, Eq. (4) shows that the value of n approaches the saturation value $n_s(I)$ given by,

$$n_s(I) = \{\beta PI/(Q+R)\}^{1/(1+\gamma)}, \quad (5)$$

as soon as the grain is exposed. Then we can tentatively assume that the number of the trapped electrons in an electron trap remains constant throughout the whole exposure time, but increases slowly with increasing the exposure intensity I in accordance with the relation (5). On this assumption, the number N of the silver atoms produced by the neutralization process during exposure time t can be calculated by the following equation

$$N = \int_0^t Qn_s(I)dt. \quad (6)$$

Substituting for $n_s(I)$ from Eq. (5) and then integrating, we obtain the following equation after a slight rearrangement,

$$\log It = \frac{\gamma}{1+\gamma} \log I - \log \frac{Q}{N} - \frac{1}{1+\gamma} \log \frac{\beta P}{Q+R}. \quad (7)$$

Eq. (7) expresses the log exposure required to produce the N silver atoms. Eq. (7) plotted on the $\log It$ versus $\log I$ type of diagram gives a straight line having a positive slope, and thus represents only the component of the high intensity failure.

Consideration of the Low Intensity Failure Component

It is believed that the cause of the low intensity failure is found in the initial stages of latent image formation. Thermal vibration of the crystal lattice impedes the creation of the silver specks in the initial stages of latent image formation.

We now assume that the silver speck will begin to form only when the number of the trapped electrons in an electron trap at which the silver speck will be formed exceeds a critical value n_c , and that the silver speck so formed is stable to thermal agitation (the stable speck). Such interpretation is very similar to; but slightly different from that proposed by Gurney and Mott.⁽¹⁾

Since the silver speck can not be formed under the condition that the intensity of exposure is so low that the value of $n_s(I)$ is less than a critical value n_c ($n_s(I) < n_c$), where $n_s(I)$ is the average number of trapped electrons given by Eq. (5), the slope of the reciprocity-failure curve should become suddenly infinite at a critical intensity in the lower intensity side of the curve. Most experimental results, however, do not show such an abrupt upturn in the curve. It seems quite reasonable that the fluctuation of light quanta absorbed by a grain should be taken into account to interpret the non-existence of such an abrupt upturn in the lower intensity failure curve. This step has been already taken by many workers.⁽⁷⁾

Even if the average intensity of light is sufficiently low, its momentary value may be raised up because of the fluctuation phenomenon. Accordingly, it may be assumed⁽⁸⁾ that the momentary number of trapped electrons may become larger than n_c , although its average number can not exceed n_c . Therefore, it is expected that even at such low intensities there exists the possibility of formation of a stable speck, and this possibility will decrease as the average intensity of light is lowered.

Let us now calculate the exposure required to produce the stable speck at intermediate intensities with considering the low and high intensity failure component simultaneously. We believe that Eq. (6) can answer our purpose if such modification is made on it as is based on the afore-said considerations. This modification is made in the following way: When the average number of trapped electrons existing in an electron trap is $n_s(I)$, the probability $P(n)$ of n electrons existing in an electron trap can be represented by the use of the Poisson equation,

$$P(n) = \exp\{-n_s(I)\} \{n_s(I)^n / n!\}. \quad (8)$$

By summing this expression for all n values

from n_c to infinity, we can obtain a factor $F\{n_s(I)\}$ corresponding to the probability of at least n_c electrons existing in an electron trap

$$F\{n_s(I)\} = \exp\{n_s(I)\} \sum_{n=n_c}^{\infty} \{n_s(I)^n / n!\}. \quad (9)$$

The above mentioned modification will be made when $n_s(I)$ in Eq. (6) is multiplied by the factor F so obtained. Thus we can calculate approximately the exposure required to produce the stable speck (the number of silver atoms in it is N_s) by means of the equation

$$N_s = \int_0^{t_s} QF\{n_s(I)\} n_s(I) dt. \quad (10)$$

Substituting for $n_s(I)$ from Eq. (5) and then integrating, we obtain the following equation after a slight rearrangement,

$$\log It_s = \frac{\gamma}{1+\gamma} \log I - \log \frac{QF\{n_s(I)\}}{n_s} - \frac{1}{1+\gamma} \log \frac{\beta P}{Q+R}. \quad (11)$$

This equation expresses the log exposure (It_s) required to produce the stable speck in the initial stages of latent image formation. The value of $F\{n_s(I)\}$ for a given value n_c (say two), which can be calculated by the graphical method, begins to decrease less than unity as $n_s(I)$ is lowered. In addition, $n_s(I)$ varies with the intensity I in accordance with Eq. (5), and thus following relation will be given,

$$\Delta \log n_s(I) = \left(\frac{1}{1+\gamma} \right) \Delta \log I. \quad (5')$$

Using this relation we can easily get an idea of how the factor $F\{n_s(I)\}$ varies with the intensity I . It follows that the curve of Eq.

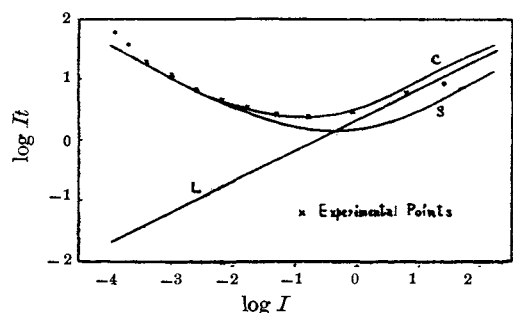


Fig. 2.—Theoretical reciprocity-failure curves for: (S), initial stages; (L), later stages; (C) total stages. Comparison of theoretical composite curve C with experimental curve.

(7) L. Silberstein, *J. Opt. Soc. Am.*, **29**, 432 (1939); P. C. Burton and W. F. Berg, *Phot. J.*, **86B**, 2 (1946); references (3) and (4).

(8) As has been stated, it is assumed that the saturation of the electron concentration in an electron trap is achieved as soon as the grain is exposed.

(11) plotted on $\log It$ versus $\log I$ type of diagram has its optimum point (the optimal intensity). Its schematic curve is shown by the curve S in Fig. 2. It has been derived, therefore, that the reciprocity-failure curve for the initial stages of formation of the latent image (the stable speck formation) has the optimal intensity.

Composite Reciprocity Failure Curve

In order that the stable speck may be brought up to the developable size, there are still required some additional silver atoms N_a . Then, we assume that this process takes place in that later stages of the latent image formation in which there is no influence of the low intensity failure component, but of the high intensity failure component. Therefore, in order to calculate the further exposure (It_a) required to produce N_a additional silver atoms, Eq. (7) can be directly applicable. Thus we obtain the equation,

$$\log It_a = \frac{\gamma}{1+\gamma} \log I - \log \frac{Q}{N_a} - \frac{1}{1+\gamma} \log \frac{\beta P}{Q+R}. \quad (12)$$

Since Eq. (12) does not contain the factor F , the shape of its reciprocity-failure characteristic is a straight line having a slope $\gamma/(1+\gamma)$ as shown by the line L in Fig. 2.

Finally, the log total exposures (It) required to produce the developable latent image from unexposed state will be

$$\log It = \log (It_s + It_a), \quad (13)$$

where It_s and It_a are given by Eqs. (11) and (12) respectively. Summation in Eq. (13) can be easily carried out by the graphical method. A composite reciprocity-failure curve so obtained is schematically shown by the curve C in Fig. 2. Using adjustable parameters γ , n_c , and N_a/N_s , we can fit the shape of the theoretical curve to that of experimental curve at and near the optimal intensity. The other parameters β , N_s , N_a , P , Q and R determine the position of the curve C in Fig. 2. The theoretical curve having $\gamma = 1$, $n_c = 2$ and $N_a/N_s = 2$ is shown here together with the measured points of the experimental reciprocity-failure curve.

Discussion of Theoretical Results

Discrepancies at Lower and Higher Intensities.—As is shown in Fig. 2, the theo-

retical curve C does not perfectly agree with the experimental points in the region of lower and higher intensities. The discrepancy at lower intensities is probably connected with the fact that in such a region the trapped electron in an electron trap can not be accumulated continually during the entire course of exposure, therefore the fundamental Eq. (2) will lose its meaning. On the other hand, the discrepancy in the region of higher intensities presumably arises from the following fact: The present theoretical curve representing the log exposure required to produce only one just-developable speck in a grain is worthy of comparing with the experimental results obtained under the special condition that only the grains having a just-developable speck can initiate the development. In the region of higher intensities, however, the grains having the sub-speck whose size is too small to be developable for a short duration of development are likely to be formed together with the grains having the developable one. This tendency will progressively predominate with increasing the intensity. Thus, it is expected that the development conditions exert strong influence upon the shape of the curve in the region of higher intensities at and beyond the optimum. Accordingly, the experimental curves would be more compatible with the theoretical curves, if the exposed emulsions were developed for a shorter period by means of a weaker developer.

Bodily Shift of the Whole Curve.—It is to be emphasized that the important feature of this theory is the strong dependence of the position of the whole curve in diagram upon the factors such as β , P , Q and R . An interesting conclusion theoretically derived on the basis of this is that the position of the reciprocity-failure curve will make a bodily shift if the value of the above factors is changed.

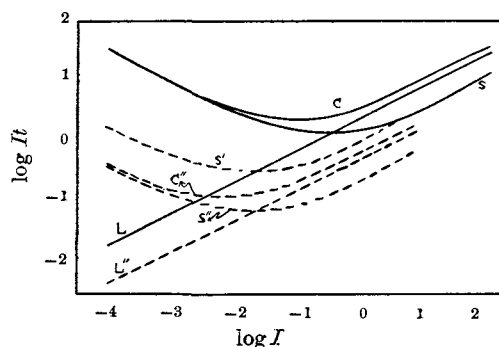


Fig. 3.—Bodily shift of the whole curve caused by the change in the magnitude of the factor R .

This conclusion has been reached in the following way: Let us consider, for instance, the case of the factor R , which is also applicable to the case of the factors β , P and Q with slight modifications. When the thermal depth ΔE of electron trap is increased, the probability R of an electron escaping from the electron trap will be decreased in accordance with the relation (3). This decrease in the R factor exerts an influence upon the factors $n_s(I)$ in accordance with the relation (5). If the value of $\beta P/(Q+R)$ is increased by a factor λ due to a decrease in the R factor, it is easily seen that the value of $n_s(I/\lambda)$ after this change equals to that of $n_s(I)$ before this change, and thus leaving the value of the F factor unchanged. In Eq. (11), because of the existence of the term containing the F factor, the position of the minimum point in the curve S will be shifted toward lower intensities along a straight line having a slope $\gamma/(1+\gamma)$ by an amount whose projection on the abscissa is $\log \lambda$ (as shown by the shift $S \rightarrow S'$ in Fig. 3). It is to be noted here that the curves S and S' have the same shape. Hence, the magnitude of the vertical descent of the upturn portion of the curve S will be $\{\gamma/(1+\gamma)\} \log \lambda$. In addition, the curve S' will vertically descend as a whole by an amount $\{1/(1+\gamma)\} \log \gamma$ (the shift $S' \rightarrow S''$), since Eq. (11) has the last term containing the R factor. This shift will change the shape of the composite curve. However, the straight line L will only vertically descend by the same amount originating in the last term

in Eq. (12) (the shift $L \rightarrow L''$), which does not contain the F factor. Accordingly, the shape of the composite curve does not change. The vertical descent of the upturn portion of the composite curve (the shift $C \rightarrow C''$) will be $\log \lambda$ after all. Thus, the composite curve will be shifted toward lower intensities diagonally (along the direction of 45-degree lines of constant exposure times) as a whole, since the vertical descent equals to the traverse shift in their magnitudes.

The present authors maintain that the above theoretical conclusion is tenable,⁽⁹⁾ since it is consistent with the experimental facts concerning the diagonal shifts caused by the prolongation of after-ripening in its earlier stages. The detailed effects of after-ripening upon the position and shape of the reciprocity-failure curves will be discussed in our forthcoming publication.⁽⁹⁾ It is to be added here that the measurements⁽⁹⁾ of the reciprocity-failure curves of the photographic emulsions having the different ionic conductivities respectively are consistent with the theoretical conclusion derived by means of changing the factor Q in the theory of this paper.

We are indebted to Prof. S. Makishima for helpful discussions concerning several points.

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Minami-ashigara-cho, Kanagawa-ken*

(9) S. Fujisawa and E. Mizuki, *Bull. Soc. Sci. Phot. Japan*, (in press).

LETTER

On the New Method for Increasing the Sensitivity in Polarographic Analysis. The Use of Rotating Current Alternator

By Masayoshi ISHIBASHI and
Taitiro FUJINAGA

(Received March 1, 1951)

Previously, the authors reported the use of rotating current alternator for the differential

polarographic technique.⁽¹⁾

In this paper, the authors report the method for increasing the sensitivity in the ordinary polarography using the same apparatus. Fig. 1 shows the scheme of the circuit. As seen in this figure, the voltage of E is applied to the cell and the reduction current flows through the galvanometer. The next instant when the alternating switch is half rotated, the circuit is shorted through the galvanometer and the oxidation current due to the dissolution of the

(1) M. Ishibashi and T. Fujinaga, This Bulletin, **23**, 261 (1950).

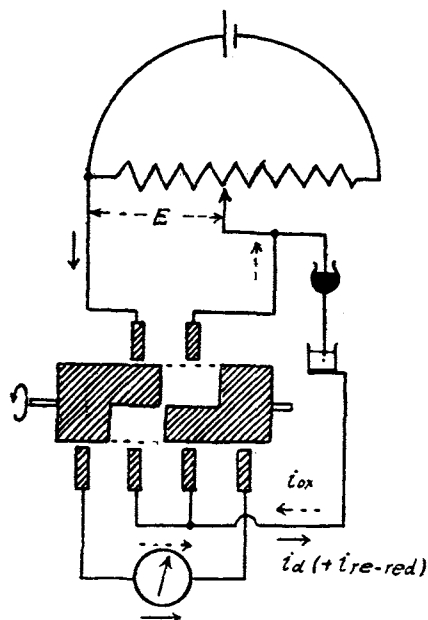


Fig. 1.

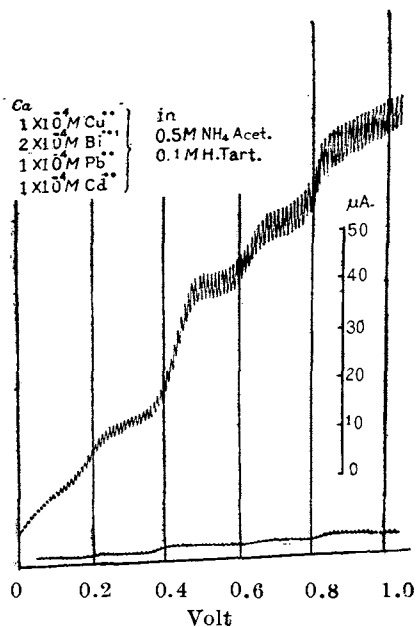


Fig. 2.

the change of the concentration of the solution before and after the electrolysis is thought to be smaller than that in the ordinary method in spite of the larger current. Fig. 2 shows the polarogram taken with the switch rotated (the new method) and that, taken with the switch stopped (the ordinary polarogram) using the galvanometer of the same sensitivity. Some other interesting characteristics and the circuits using this rotating switch will be submitted later.

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deposited metal flows additively through the galvanometer and moreover in the next half rotation, the dissolved ion is reduced again together with the diffused ion. So concentration of the ion occurs on the electrode surface instead of the diffusion layer. The total current is practically *ca.* twenty times greater than the ordinary diffusion current (hundreds microamperes per millimolar ion). By this method,

Chemical Analysis by the Measurement of Nuclear Moment. (Nuclear Momentscope Analysis)

By Shizuo FUJIWARA

(Received April 11, 1951)

An apparatus for observing the nuclear magnetic resonance has been constructed as an extension of the researches on the high-frequency titrimetry,⁽¹⁾ and the utility for the qualitative and quantitative analysis has been studied, although this resonance experiment has been already carried out for the precise measurement of the moments⁽²⁾ or of the magnetic field.⁽³⁾

The sample is mounted in a coil of the receiver circuit and the coil is placed in the magnetic field with its axis perpendicular to the field direction. The radio-frequency waves of constant frequency (15.25 MC; with the modulation unit of 280 C. P. S.) are supplied to this circuit and the strength of the magnetic field is varied very slowly. The transitions occur which result in an absorption of energy from the radiofrequency field when the radio-frequency coincides with the Larmor precessional frequency of the atom. As the moment of ${}^1\text{H}^1$ is close to that of ${}^9\text{F}^{19}$, the absorption lines of the two elements have been compared with each other. The intensity of the energy absorption which is measured by the voltage drop of the out-put power from the detector circuit has shown good correspondence to the amount of the each element in the sample, as it is given in Table 1, when the sensitivity of

(1) S. Fujiwara and S. Hayashi, *Report of Univ. of Electro-Communications*, 1, 112 (1950).

(2) J. E. Mack, *Rev. Modern Phys.*, **22**, 64 (1950).

(3) N. J. Hopkins, *Rev. Sci. Instr.*, **20**, 401 (1949).

Table 1

No.	Sample		Intensity of the energy absorption	
			$^1\text{H}^1$, volt	$^19\text{F}^{19}$, volt
1	Paraffin + Na_2SiF_6	0 g.	-0.10	0
2	"	0.1	-0.10	-0.08
3	"	0.3	-0.10	-0.27

the apparatus has been held appropriate. When the sensitivity of the apparatus is sufficiently raised, the energy absorption line has been easily observed with one-tenth milligramme of fluorine.

With the improvements in the apparatus, it will be possible to utilize the method for the chemical analysis, especially, of the solids, or for the determination of isotopes of heavy metals as an only suitable method.

The author expresses his sincere thanks to Mr. S. Hayashi for his devoted cooperation and heartily willing assistance, and also to Dr. K. Terasawa, the president of the Univ. of Electro-Communications, Dr. K. Kimura, the professor of Tokyo Univ. and Mr. K. Kambe, the assistant professor of the Univ. of Electro-Communications, for their interests and encouragements during this work. He wishes to thank also Dr. S. Wada of Tokyo-Shibaura Electric Co., and Mr. H. Yamada for their kindnesses shown in the construction of the magnet.

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served. The different phases of luminescence indicate the presence of different trace elements acting as luminescence activators; $\text{Ca}_3(\text{PO}_4)_2$ of the bones working as the luminophoric base.

The conclusion that the intense bright red luminescence is due to the $\text{Ca}_3(\text{PO}_4)_2$ -Bi phosphor and thus indicates the presence of Bi in the bones mentioned is drawn from the following facts:—

(1) If the specimens are boiled for more than 12 hrs. with 5% NaCl or 1% KOH solution at the beginning, then the color of luminescence is very faint blue even when treated in the same manner as mentioned above. Boiling for more than 12 hrs. with CHCl_3 or water does not alter the red luminescence.

(2) Pure $\text{Ca}_3(\text{PO}_4)_2$ is prepared with elaborate care and heated at 950° for 2 hrs. The luminescence obtained is the same as in (1). But when Bi is chemically added to the $\text{Ca}_3(\text{PO}_4)_2$ in the ratio 10^{-6} : 1 and the same heat treatment is given, the same bright red luminescence as mentioned above is produced.

(3) Bi was microchemically detected in the above NaCl extract. A solution in which Bi is concentrated was obtained from 320 g. of the bones of *Paralichthys olivaceus*. A drop of the solution when added to the specimen of (1), reproduces the bright red luminescence. This solution also gives CaS, the well known violet blue luminescence of CaS-Bi phosphor.

(4) When Bi is chemically added to the specimen of (1) in the ratio 10^{-6} : 1, the bright red luminescence is also reproduced.

The same bright red luminescence is also observed in the case of human teeth when treated in the same manner as in the case of the vertebrae mentioned above.

A decayed tooth showed no such bright red luminescence.

The writers surmise that Bi may be a "nutritional trace element" which is indispensable in the metabolism of $\text{Ca}_3(\text{PO}_4)_2$ in the animal body. With respect to this point, further research is still being done. The cathodo-luminescence method will offer a convenient method for studying the manner of the trade of Bi in bones and teeth.

The Presence of Bismuth in Fish Bones and Human Teeth as Revealed by Cathodo-luminescence Method of Analysis

By Shin'ichiro HAKOMORI and
Shohei TAMURA

(Received April 16, 1951)

The vertebrae of *Cololabis saira* and *Paralichthys olivaceus* are well washed with water, dried and heated at 950° for 2 hrs. The specimens are excited with cathode ray and the colors of luminescence produced are ob-

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The Photochemical Reaction of Cyclooctatetraene (C₈H₈)

By Ikuzo TANAKA, Seinosuke MIYAKAWA and Shoji SHIDA

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Introduction

The properties of cyclooctatetraene (C. O. T.) have been lately investigated by several physicochemical methods. We have calculated the energy levels of C. O. T. as the symmetry of D_{2d},⁽¹⁾ D₄,⁽²⁾ and D_{4d}⁽³⁾ by the HLSP method⁽⁴⁾ and the GMS method,⁽⁵⁾ and then its electronic structure has been discussed in comparison with the experimental results of thermochemical data⁽⁶⁾, magnetic susceptibility⁽⁷⁾ and absorption spectra.⁽⁸⁾

We have newly found that C. O. T. undergoes the photochemical reactions by the mercury vapor lamp. Hence, C. O. T. was excited by mercury lamp and the gaseous products were examined by their absorption spectra. The quantum yield for benzene in the product was spectrographically determined, and the increase in the pressure of non-condensable producing gas was measured by a Bourdon gauge. The purpose of the present paper is to report these experimental results.

Electronic Structure of C. O. T.

The energy levels of C. O. T. was calculated as the most probable symmetry of D_{2d} by the HLSP method and the GMS method and are

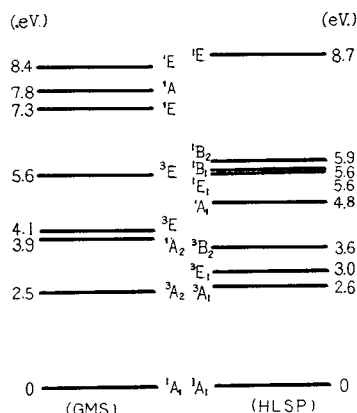


Fig. 1.

shown in Fig. 1. The absorption band below 2000 Å. was ascribed to the ¹A₁ → ¹E transition and the shoulder at 2800 Å. of the absorption band of longer wave length to the ¹A₁ → ¹A₁ or ¹A₁ → ¹A₂ transition. The levels which are calculated by the HLSP method for non-polar structures do not include the ¹A₂ level. But the ¹A₂ level appears in the calculation when it is only polar structures. The wave length of the transition ¹A₁ → ¹A₂ is calculated to be shorter than 2000 Å. according to Craig's estimation.⁽⁹⁾ But it is of interest as the property of approximate calculations that the levels appear on the lower or upper side; the molecular orbital introduces extra polar structures like GMS methods and makes the energy ¹A₂ lower, while the atomic orbital raises the level ¹A₂ made of polar structures.

There are some recent investigations about the interaction in the systems consisting of I₂ and aromatic compounds, especially benzene.⁽¹⁰⁾ The following results were recognized from the relation obtained in the systems of I₂ and C₈H₈,⁽¹¹⁾ namely, the absorption band at 2800 Å. for C₈H₈ (CCl₄ solution + I₂) has the order of ε = 450, which is about twice as large as that of heptane solution (ε = 250), but does not

(1) H. S. Kaufmann, I. Fankuchen and H. Mark, *J. Chem. Phys.* **15**, 414 (1947); H. S. Kaufmann, I. Fankuchen and H. Mark, *Nature*, **161**, 165 (1948); K. Hedberg and V. Schomaker, Annual Meeting of Am. Chem. Soc., 1949.

(2) E. P. Lippincott, R. C. Lord and R. S. MacDonald, *J. Chem. Phys.* **16**, 548 (1948); E. P. Lippincott, R. C. Lord and R. S. MacDonald, *Nature*, **166**, 227 (1950); O. Bastiaisen and O. Hassel, *Acta Scandinavica*, **3**, 209 (1949).

(3) O. Bastiaisen, O. Hassel and A. Langseth, *Nature*, **160**, 128 (1947); B. D. Saksena and H. Narain, *Nature*, **165**, 723 (1950).

(4) I. Tanaka and S. Shida, *This Bulletin*, **23**, 54 (1950).

(5) Y. Mori, I. Tanaka and S. Shida, *ibid.*, **23**, 168 (1950).

(6) D. W. Scott, M. E. Gross, G. D. Oliver and H. M. Huffman, *J. Am. Chem. Soc.*, **71**, 1634 (1949); E. J. Prosen, W. H. Johnson and F. D. Rossini, *J. Am. Chem. Soc.* **69**, 2068 (1947); E. J. Prosen, W. H. Johnson and F. D. Rossini, *J. Am. Chem. Soc.* **72**, 626 (1950); J. L. Cotrell and L. E. Sutton, *J. Chem. Phys.* **15**, 685 (1947).

(7) R. C. Pink and A. R. Ubbelohde, *Nature*, **160**, 502 (1947); R. C. Pink and A. R. Ubbelohde, *Trans. Faraday Soc.*, **44**, 708 (1948); F. R. M. MacDonnell, R. C. Pink and A. R. Ubbelohde, *Trans. Faraday Soc.*, **46**, 156 (1950); S. Shida and S. Fujii, Annual Meeting of Chem. Soc. Japan, 1950.

(8) A. Langseth and S. Broderon, *Acta Chemica Scandinavica*, **3**, 778 (1949); S. Miyakawa, I. Tanaka and T. Uemura, in process of publication.

(9) D. P. Craig, *Proc. Roy. Soc., A* **200**, 272, 390, 401 (1950).

(10) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2708 (1949); R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 600 (1950).

(11) unpublished.

increase more than fifty times as in the case of benzene. So it is concluded that the electronic structure of C. O. T., though it being a ring compound, is different from those of the aromatic compounds. This conclusion coincides with the experimental results of the previous reference papers.^{(1)-(6), (12)}

The Photochemical Reactions, Experimental

The sample of C. O. T. was prepared by Prof. S. Murahashi and Dr. N. Hagiwara in the Institute of Scientific and Industrial Research, University of Osaka and was used in our experiments. The C. O. T. was purified by four time fractional distillations in vacuum in which the more volatile and the heavier portions were discarded.

The experimental arrangement is shown in Fig. 2. The low pressure mercury arc was set against the cylindrical quartz tubes (reaction cell) of different lengths, where the gaseous C. O. T. was introduced by distillation from the sample tube at room temperature. The photochemical reactions of C. O. T. in the cell were carried out by light which passed a filter between the cell and the arc. On the other hand, another cell with plane quartz windows was set between Jobin-Yvon spectrograph and the hydrogen discharge tube that was connected with the first cell so that the gaseous C. O. T. and its products diffuse into the cell. Their absorption spectra could thus be obtained.

The quantum yield of the reaction where C. O. T. is decomposed into benzene was determined using the uranyl sulfate and oxalic acid as actinometer. Corrections were made for light reflection on quartz-air interfaces.

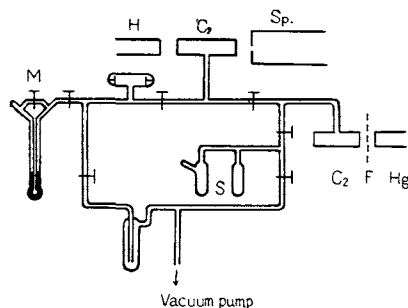


Fig. 2.—M, manometer; H, hydrogen discharge tube; C₁ and C₂, cell; Sp, spectrograph; S, sample; F, filter; and Hg, mercury lamp.

We have found the benzene as a product, hence the following process can be considered, $C_6H_6 + h\nu \rightarrow C_6H_6 + C_2H_2$. If this mechanism is true, it is expected that the pressure should increase as a result of the formation of C_2H_2 , non-condensed

at low temperature. In order to ascertain this consideration, a cylindrical quartz cell of 20 cc. capacity was connected directly to a gauge of the Bourdon type and the pressure change of non-condensable gas can be read with a cathetometer.

These experiments were carried out in the pressure range from 2 to 7 mm.Hg. of C. O. T. For the filter, glass (above 3300 Å.), P. V. A. (above 2300 Å.), etc. were used.

Results and Discussions

First of all, the results which were qualitatively observed by the absorption spectra of photochemical products of C. O. T. are shown as follows. The characteristic absorption bands of benzene (2610 Å., 2550 Å., 2480 Å., 2420 Å., ...) were observed in the spectra which could be obtained through the second cell of 50 to 95 mm. length, by illumination of mercury arc, for 10 to 60 minutes. In order to find other substances but benzene, by using the second cell of 200 mm. length, narrowing the slit and operating the mercury arc for 1 to 3 hours, new absorption bands which were not recognized in the case of the shorter cell, could be found at 2916 Å. (s), 2916 Å.~2885 Å. (diffuse), 2885 Å. (s), 2877 Å. (w), 2872 Å. (w), 2840 Å.~2700 Å. (diffuse), 2816 Å. (w) and 2800 Å. (w) (where the notation s means strong and w weak intensity).

In order to study what substances have given these absorption bands, the absorption spectra of pure gaseous styrene were taken. Its strong absorptions at 2885 Å., 2877 Å., 2872 Å., 2816 Å. and 2800 Å. could be confirmed to coincide with the above-mentioned bands, so we can conclude that the styrene, an isomer of C. O. T., is also produced in the photochemical reaction of C. O. T. We can not yet determine from which of reacting substances come those bands at 2916 Å. (s), 2916 Å.~2885 Å. (diffuse band) and 2840 Å.~2700 Å. (diffuse band) which are not observed in the spectra of styrene. We may, however, suppose that these bands may be dependent on some compounds like C. O. T. which contain some conjugated double bonds, since these substances will have absorption bands of longer wave lengths than 2000 Å. In order to determine whether benzene can be directly produced by the photodecomposition of C. O. T. or by the photodecomposition of styrene that is produced by the isomerization of C. O. T., the reaction products, which were produced from pure styrene in gaseous phase by the mercury lamp at the same condition as the case of the photoreaction of C. O. T., can be studied their absorption spectra. The reactions by the illuminations for 10 min., 30 min., and 60 min. gave no benzene at all, and

(12) Cf. R. M. Eliofson, *Anal. Chem.*, **21**, 917 (1949).

the intensity of the absorption spectra of styrene was only decreased. This fact is probably due to the photopolymerization of styrene. So that, we can ascertain that the photodecomposition to benzene is the direct one.⁽¹³⁾

If we compare the absorption spectra which were obtained in 200 mm. cell for the resultant of the photochemical reaction and the spectra that were respectively obtained from pure styrene in various pressures, we can recognize that the quantity of reaction of photodecomposing to benzene is larger than that of isomerizing to styrene, although this conclusion is not certain, because the styrene changes to polystyrene in small quantity.

It may be considered that the reason why the photodecomposition of C. O. T. to benzene is easier than the isomerization of C. O. T. to styrene is that after the excitation by photon the breaking of the single bonds ($=CH-CH=$) is easier than the displacement of the hydrogen atom.⁽¹⁴⁾

Next, to investigate the reaction $C_8H_8 + h\nu \rightarrow C_6H_6 + C_2H_2$, the results that are obtained for the non-condensable gas at low temperature will be illustrated. A trap which is prepared between the cylindrical quartz cell (20 cc.) and Bourdon Gauge, can be cooled after the exposition of the cell to light, in alcohol with dry ice to condense out C. O. T., benzene, styrene, and etc., and the pressure of non-condensable gas could be measured. The initial pressure of C. O. T. was 2.50 to 3.50 mm.Hg. An example is shown in Table 1.

Table 1

The initial pressure of C. O. T., mm.Hg	Filter	Pressure of non-condensable gas, mm.Hg		
		10 min.	30 min.	60 min.
2.60	None	0.06	0.14	0.25
2.92	P. V. A.	—	0.04	0.06
3.32	Glass	0	0	0

Conditions of above reaction: The cell is set parallel to mercury arc. (100 V., 5 Amp.) Temp. 25°.

The measured values of transmissions of the filters used are shown in Fig. 3. According to

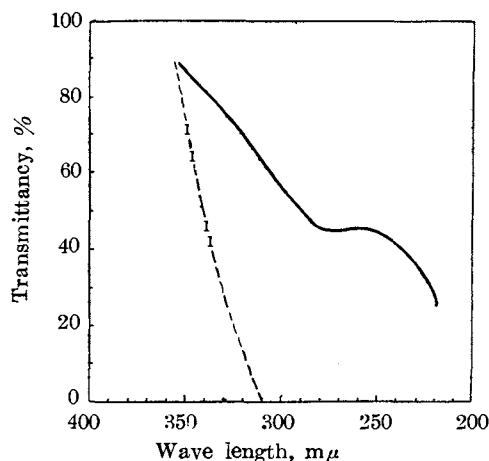


Fig. 3.—Transmission of the filters: —, PVA-filter; ---, glass.

these results that are given in Table 1, it is clear that besides C_6H_6 a non-condensable gas, probably C_2H_2 , is produced by the photochemical reaction. When the light below 3300 Å. was cut off by glass, C. O. T. did not decompose photochemically as well as the results of quantum yield of C_8H_8 as stated later will show. By comparing the reactions with and without filter P. V. A. it is clear that the light below 2500 Å is important for the photochemical decomposition.

Next, the quantum yield of reaction in which C. O. T. decomposes to benzene will be stated. The experimental arrangements are shown in Fig. 2.

In order to determine the quantity of benzene which is produced in the photochemical reaction, the extinction of pure benzene was first measured in various pressures by the microphotometry of the absorption spectra of gaseous benzene that were distilled three times in vacuum. The benzene which is produced by photochemical reaction in various conditions could be quantitatively determined. On the other hand, when we can measure the fraction of light that was absorbed by chemical actinometer, the quantum yield may be determined. An example of the experimental data is written in Table 2.

Table 2

The Photodecomposition of C. O. T. at 25°.

The initial pressure of C. O. T., mm. Hg	Filter	Pressure of benzene produced, mm. Hg		
		10 min.	30 min.	60 min.
5.0	None	0.18	0.47	0.70
5.0	P. V. A.	—	0.13	0.23
5.0	Glass	0	0	0

(13) B. L. Dunicz, *J. Am. Chem. Soc.*, **63**, 2461 (1941). It was reported that the characteristic bands of styrene was not found in the course of the photochemical reaction in acetylene-benzene mixture for irradiation. The authors are indebted to Z. Kuri for valuable discussions about this experiment.

(14) Norrish, *Trans. Faraday Soc.*, **30**, 103 (1934); Saltmarsh and Norrish, *J. Chem. Soc.*, 455 (1935); The interesting facts for shift of hydrogen atom about the photodecomposition of cycloketones were reported.

From the data of actinometry with uranyl sulfate and oxalic acid, the absorbed quanta are 5.1×10^{18} and the decomposed molecules are 0.41×10^{18} in a half hour. Then the quantum yield for decomposition to benzene is about 0.1 for light near 2537 Å. It is also seen in Table 2 that the light which is shorter than 2500 Å. is important for the photochemical decomposition, as we have already mentioned. The absorption bands below 2500 Å. can be considered as due to the $^1A_1 \rightarrow ^1E$ transition which was given by the calculation for the electronic structure of C. O. T. A configuration of a polyatomic molecule for an electronic state having orbital degeneracy can not be stable with respect to all displacements of the nuclei (Jahn-Teller effect).⁽¹⁵⁾ We can suppose that the Jahn-Teller effect will be very small in benzene, even if it occurs, as π -electrons have less contribution to the chemical binding than σ -electrons, then the decomposition is impossible by mercury lamp.⁽¹⁶⁾ We may consider that C. O. T. is not stable through the change of the shape of molecule as the Jahn-Teller effect is more effective for C. O. T. than for benzene and C. O. T. will be decomposed by light which has shorter wave length than 3000 Å.

(15) H. A. Jahn and E. Teller, *Proc. Roy. Soc., A* **161**, 220 (1937); H. A. Jahn, *ibid.*, **A 164**, 117 (1938).

(16) Kistiakowsky and Solomon, *J. Chem. Phys.* **5**, 609 (1937).

Summary

By the absorption spectra, it was found that benzene and styrene were independently produced from C. O. T. when C. O. T. was excited by the light shorter than 3000 Å., and that some unknown substances giving a sharp line at 2916 Å. and two diffuse bands at 2916 Å.~2885 Å. and 2840 Å.~2700 Å. were also produced. The gas like acetylene which can not be condensed by dry ice can be at the same time produced.

The quantum yield of reaction where C. O. T. is decomposed to benzene by light near 2537 Å. was about 0.1. And the light which has the shorter wave length than 2500 Å. mainly contributes to the reaction in which C. O. T. decomposes to benzene.

The authors deeply wish to express their appreciation to Prof. S. Murahashi and Dr. N. Hagiwara who have furnished them the C. O. T. and have also given many valuable advices and also to Prof. T. Uemura who has stimulated them. Authors' sincere thanks are also due to the Ministry of Education for the financial grant.

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On the Etched Surfaces of Nickel Single Crystals Revealed by Means of Electron Diffraction and Microscopy

By Shigeto YAMAGUCHI

(Received February 21, 1951)

The etched surfaces of nickel single crystals were here examined by means of electron diffraction and oxide replica of microscopy. The electron diffraction method identified the crystalline substances found in the etched surfaces of specimens and determined their crystallographic orientation. The oxide replica method of electron microscopy clarified the forms and orientation of the metal crystals on the etched surfaces of specimens. It was demonstrated in the present study that the combination of electron diffraction and microscopy made it possible to assign the crystallographic

indices to the etched surfaces of single crystals of nickel. It is important to ascertain the particular crystallographic arrangement characteristic to the atoms on the etched surface, because the physical and chemical properties (*e.g.*, catalysis,⁽¹⁾ corrosion-resistance⁽²⁾ *etc.*) of nickel crystal should be discussed in relation to the atomic arrangement experimentally determined.⁽³⁾

(1) O. Beeck, *Rev. Mod. Phys.*, **17**, 61 (1945).

(2) S. Yamaguchi, T. Nakayama and T. Katsurai, *J. Electrochem. Soc.*, **95**, 21 (1949).

(3) T. N. Rhodin, *J. Appl. Phys.*, **21**, 971 (1950).

Experiments

The three types of nickel single crystals⁽⁴⁾ employed in the present experiments were the three metal discs (diameter: 10 mm., thickness: 2 mm.) cut along the (001), (110) and (111) planes respectively. These specimens were named No. 1, 2 and 3 here. The surfaces of these three types of disc specimens were buffed and then etched with ethanol-bromine (10:1 by vol.) for 10-20 seconds. These specimens gave respectively different etching figures to naked eyes. These etched surfaces were observed at first by means of electron diffraction and then oxide replica method of electron microscopy.

The specimen No. 1 gave the diffraction patterns shown in Photos. 1-4. These diffraction patterns verified the existence of pure nickel crystal in the etched surface of specimen. Photo. 1 coincides with the diffraction pattern which should be given by the electron beam running parallel to the (001) and (110) planes of nickel single crystal. The electron beam in obtaining Photo. 1 was nearly parallel to the macroscopic surface of etched specimen. Photos. 2 and 3 were obtained from the specimen surfaces rotated respectively by 15° and 30° from the position of Photo. 1. Photo. 4 was obtained from the specimen whose macroscopic surface was inclined by 2° to the incident beam in the position of Photo. 2. These four diffraction patterns verified that the macroscopic etched surface of specimen No. 1 was approximately parallel to the (001) planes of nickel single crystal.

The etched surface giving the diffraction patterns of Photos. 1-4 was treated in an autoclave (water vapor pressure: 15-20 atm., duration of reaction: 5 hrs.) in order to form the structureless oxide film on the specimen surface. This oxide film was stripped from the substrate by Mahla-Nielsen's method⁽⁵⁾ with ethanol-bromine solution. The isolated film was magnified by means of electron microscopy. The electron micrograph obtained is shown in Photo. 5. It is seen in Photo. 5 that the crystals of cubic form (size: 30 mμ-300 mμ) are oriented in one direction. Some side planes of the single crystals recognized in Photo 5 are distinctively more opaque than the other planes. This means that the crystallographic indices for the opaque planes are different from those for transparent planes, since the former planes have been oxidized more deeply than the latter. It is, therefore, concluded in reference to the results of diffraction experiments described above that the etched surface of specimen No. 1 is composed of the (001) and (110) planes, as is shown in Fig. 1. It is surmised here that the (110) faces are more easily oxidized than the (001) planes.

The specimen No. 2 gave the diffraction patterns shown in Photos. 6-8. Many fine grooves arranged

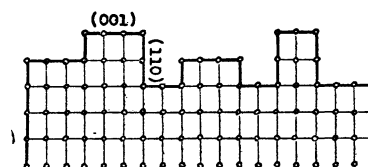


Fig. 1.—Profile of specimen No. 1 sectioned parallel to (110) plane. Atom distances: 3.52 Å. and 2.49 Å.

parallel with each other were observed by naked eyes on the etched surface of the specimen. The electron beam running parallel to these grooves gave the diffraction shown in Photo. 6. The beam intersecting at the angles of 45° and 90° to the direction of the grooves gave the patterns of Photos. 7 and 8 respectively. These diffraction patterns verified that the macroscopic surface of specimen No. 2 was parallel to the (110) planes of nickel crystal and the direction of the grooves was parallel to the (110) direction.

The etched surface of specimen No. 2 was magnified by means of electron microscopy, as is shown in Photo. 9. The long crystals oriented parallel to each other in Photo. 9 might be seen as etching grooves with naked eyes. In this way the profile of specimen No. 2 sectioned parallel to cube face was shown schematically in Fig. 2, i. e., the etched surface of specimen No. 2 is composed of the (110) and (110) planes.

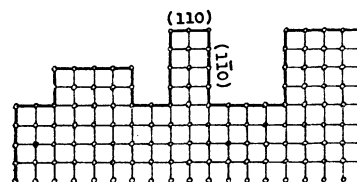


Fig. 2.—Profile of specimen No. 2 sectioned parallel to cube face. Atom distance: 2.49 Å.

Specimen No. 3 gave the diffraction pattern of Photo. 10. The incident electron beam in Photo. 10 is parallel to the (111) and (110) planes of nickel crystal. Since the incident beam was nearly parallel to the macroscopic surface of the etched specimen, the etched surface of the specimen was parallel to the (111) planes and perpendicular to the (110) planes. The Kikuchi-lines are found in Photo. 10. This means that the etched surface of the specimen is rather flat than thorny.

The magnified reprints of the etched surface of specimen No. 3 are shown in Photos 11 and 12. There are many lamellar crystals of triangular form in Photos 11 and 12. The faces of the lamellae had to be assigned with (111) indices in reference to the results of the diffraction experiments. The surface of specimen No. 3 was composed of the (111) and (110) planes, as is shown schematically in Figs. 3 and 4.

(4) These single crystals were prepared by S. Kaya, and J. Horiuti used these crystals for the samples in the experiments on chemical kinetics.

(5) E. M. Mahla and N. A. Nielsen, *J. Appl. Phys.*, **19**, 378 (1948).

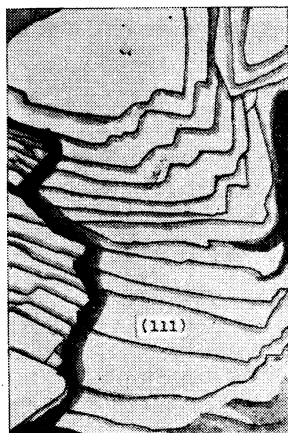


Fig. 3.—An exaggerated sketch of Photo 11.

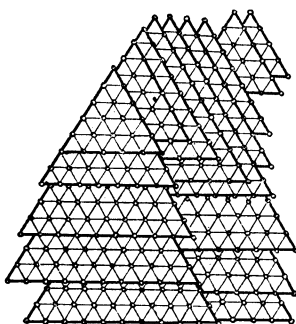


Fig. 4.—Projection of the etched surface of specimen No. 3 showing the (111) faces. Atom distances, 2.49 Å.

Discussion

The crystallographic assignment of the boundary planes of the powder crystals was able

to be carried out by means of electron microscopy and microscopic diffraction.⁽⁶⁾ In order to assign crystallographically the boundary planes of bulk single crystal, however, it was necessary to rely on the oxide replica method and the electron reflection method of diffraction as given in the present study.

The temper colors obtained on the etched surfaces of the specimens on exposure to the air were here observed. The etched surface of specimen No. 2, which was composed of the (110) and $(\bar{1}\bar{1}0)$ faces, became mat rapidly in the air at room temperature. On the other hand, the etched surface of specimen No. 3, which was composed of the (111) and $(\bar{1}\bar{1}0)$ faces, became mat very slowly in the air at room temperature. These facts indicated that the $(\bar{1}\bar{1}0)$ face, whose atomic arrangement is coarse, is chemically most active, and the (111) face, which consists of the closest packed atoms, is most inert among the principal faces of nickel crystal.

Summary

(1) It was possible to assign the crystallographic indices to the etched surfaces of single crystals by the combination of electron microscopy and diffraction.

(2) The (110) plane of nickel crystal was most active and the (111) plane was most inactive among the principal planes of crystal.

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31, Kamifujinae, Komagome, Bunkyo-ku, Tokyo

(6) A. C. Dorsten, H. Niendorp and A. Verhoeff, *Philips Tech. Rev.*, **12**, 33 (1959).

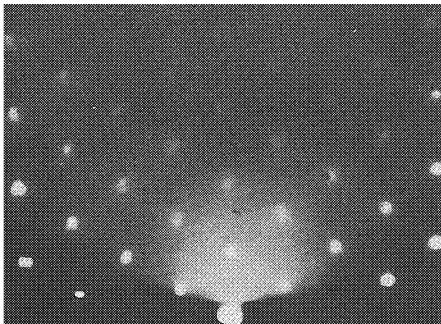


Photo. 1.—Incident beam is parallel to (001) and (110) planes. Macroscopic surface is parallel to (001) planes.

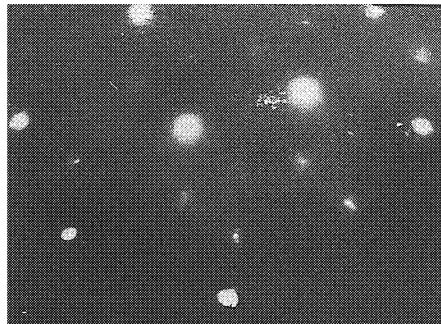


Photo. 2.—Diffraction from the specimen surface rotated by 15° from the position of Photo. 1.

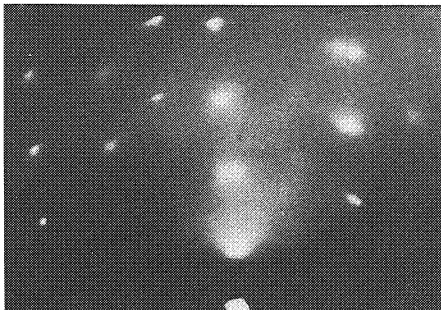


Photo. 3.—Diffraction from the specimen surface rotated by 30° from the position of Photo. 1.

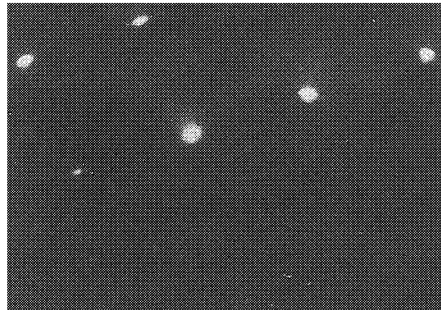


Photo. 4.—Diffraction from the specimen surface inclined by 2° to incident beam in the position of Photo. 2.

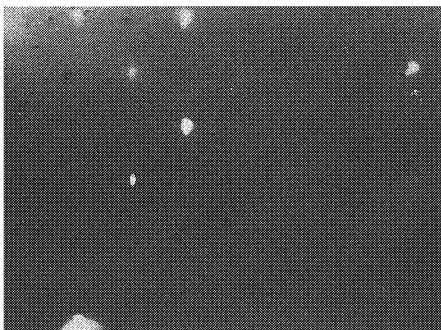


Photo. 6.—Diffraction of the incident beam parallel to the etching grooves of specimen No. 2.

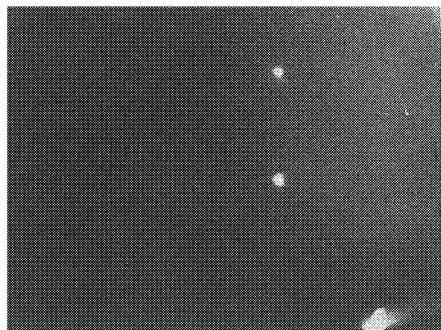


Photo. 7.—Diffraction from the specimen surface rotated by 45° from the position of Photo. 6.



Photo. 8.—Diffraction from the specimen surface rotated by 90° from the position of Photo. 6.

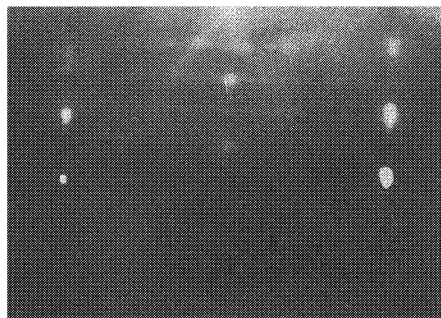


Photo. 10.—Diffraction from the etched surface of specimen No. 3. Macroscopic surface of specimen is parallel to (111) planes

[To face p. 124.]

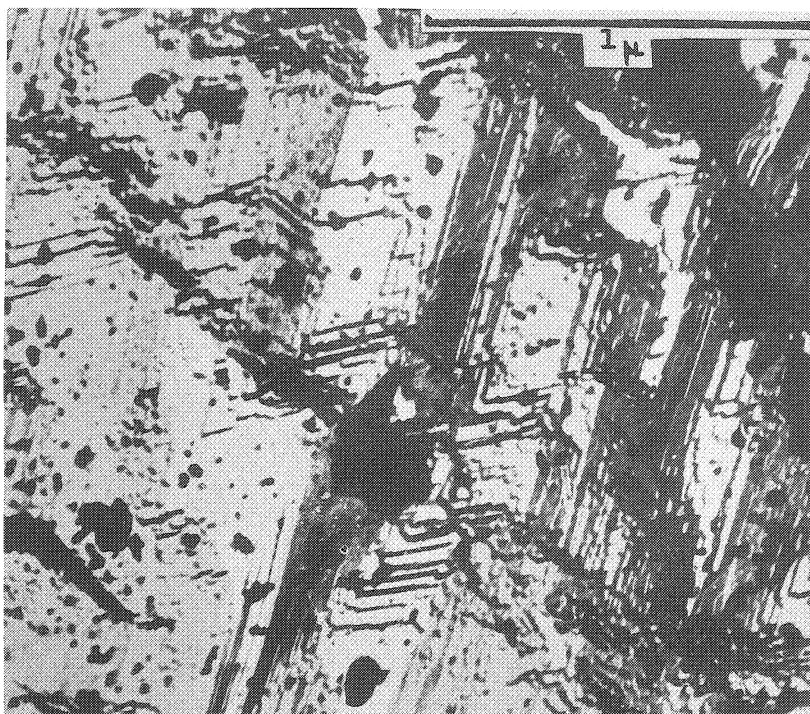


Photo. 5.—Electron micrograph of the etched surface of specimen No. 1.

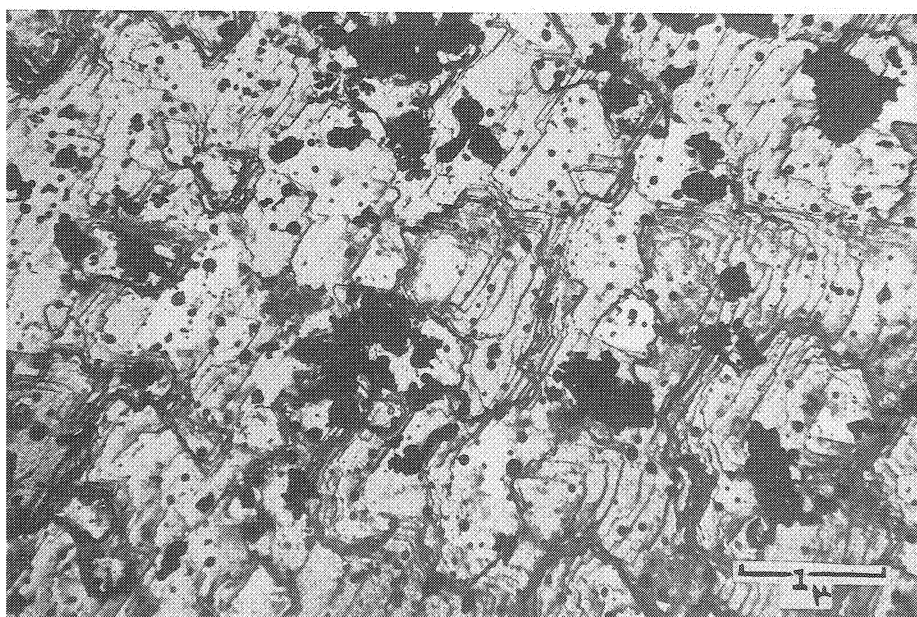


Photo. 11.—Electron micrograph of the etched surface of specimen No. 3.
There are many lamellar crystals.

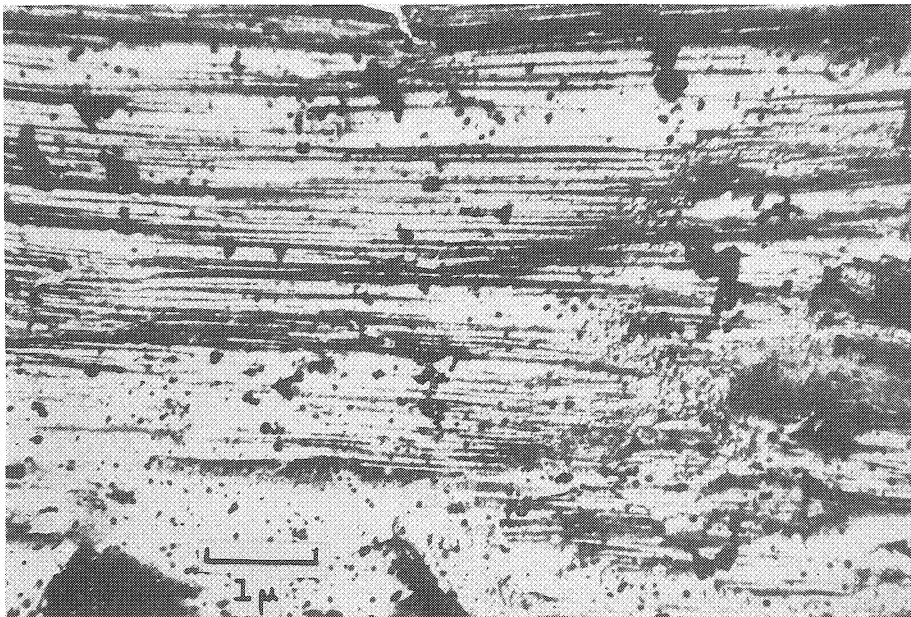
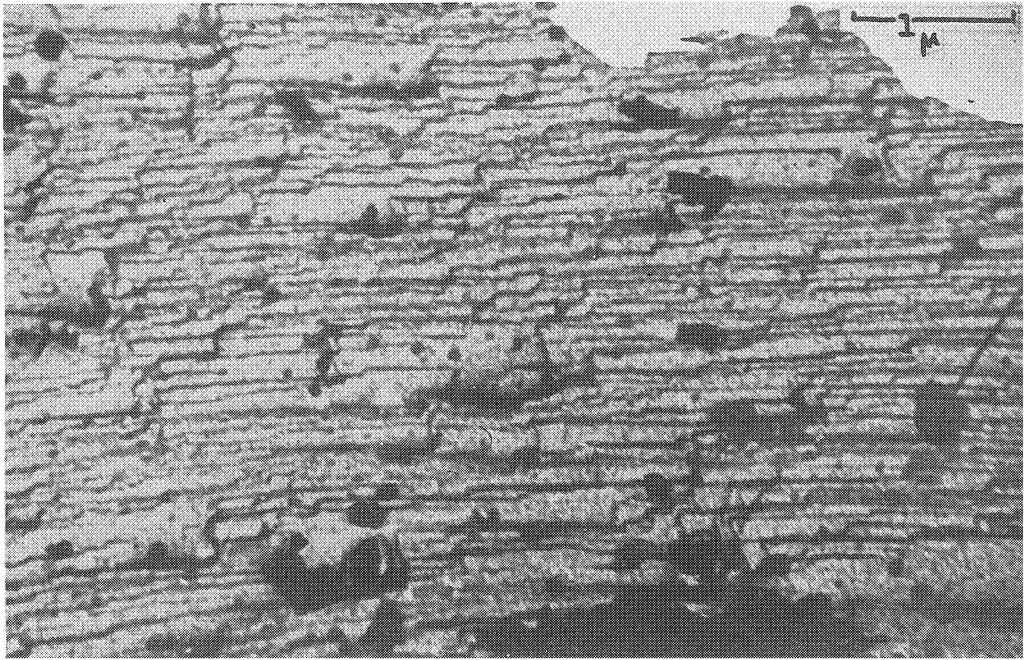


Photo. 9.—Electron micrographs showing etching grooves
on the surface of specimen No. 2.

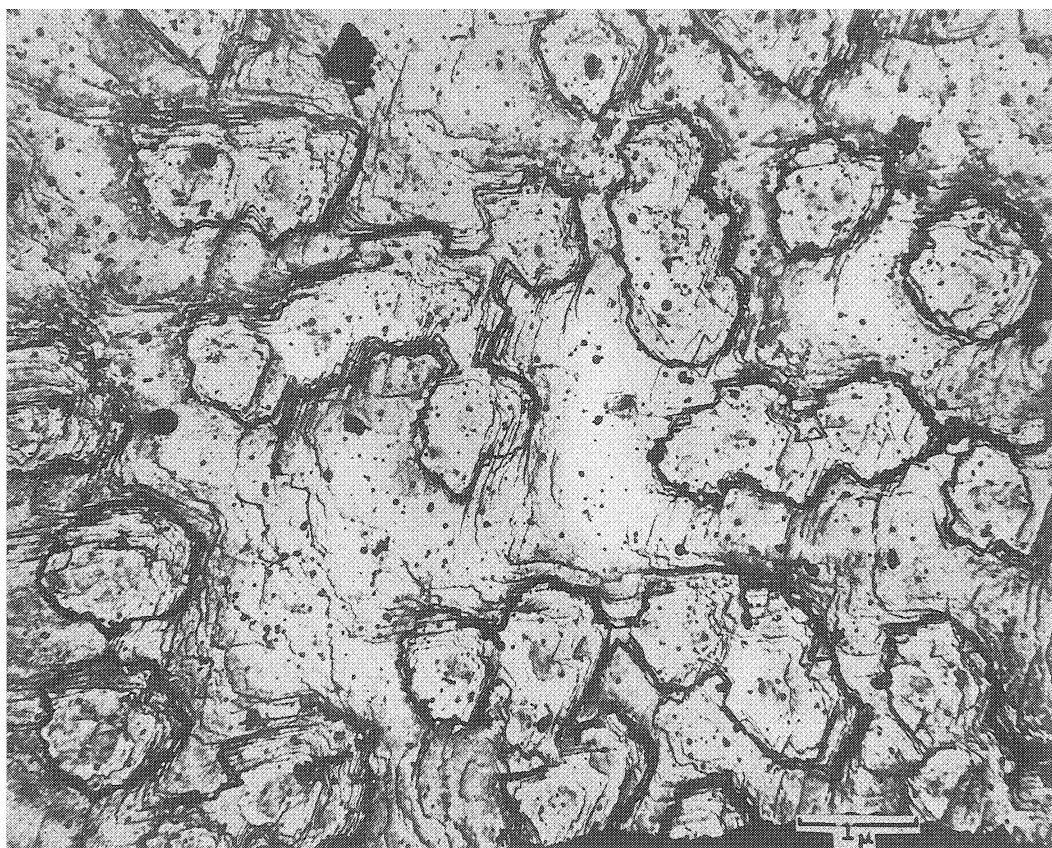


Photo. 12.—Electron micrograph of the etched surface of specimen No. 3.
There are lamellae of triangular form.

Researches on Dichroism of Planar Complexes. III. The Color and the Structure of the Crystals of Tetracyanoplatinates (II)

By Shoichiro YAMADA

(Received March 1, 1951)

Crystals of some tetracyanoplatinates (II) have been known to show unusually deep colors. For example, crystals of the barium and calcium salts are yellow, and those of the magnesium salt orange red; they show different colors for different degrees of hydration of the same cations, whose aqueous solutions are all colorless. Such unusual colors of the salts, which seem closely related to the anisotropic character of the planar tetracyanoplatinates (II), indicate that planar complexes in these crystals are in a condition quite different from their state in solution. On the colored crystals of tetracyanoplatinates (II) there have been reported several researches, which, however, have scarcely dealt with the relation between absorption and structure or bonding; nor has any plausible explanation as to the colors of the crystals of these compounds been presented.

This research was undertaken for the purpose of investigating the problem of the colors of magnesium, calcium and barium tetracyanoplatinates (II) in the crystalline state. In this work the dichroism of the crystals of $\text{BaPt}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$, $\text{CaPt}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$ and $\text{MgPt}(\text{CN})_4 \cdot 7\text{H}_2\text{O}$ was measured, and this phenomenon is discussed in relation to the crystal structure.

Experimental

Measurement.—Quantitative dichroism measurements of the crystals were carried out by the microscopic method with microcrystals, as described in the previous report⁽¹⁾. α denotes absorption coefficient per mm. of the crystal, and $\parallel$ - or $\perp$ -absorption represents that of polarized light with electric vector parallel or perpendicular, respectively, to the complex plane.

Extinction coefficients, ϵ , of barium tetracyanoplatinate (II) in aqueous solution were determined by the photographic method using a sector photometer⁽²⁾. Aqueous solutions of the complex

salt were 3.3×10^{-3} , 1.3×10^{-4} and 3.3×10^{-5} molar. Measurements were made at room temperature.

Materials.— $\text{BaPt}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$. The pure yellow compound was obtained as monoclinic prisms by recrystallizing a sample of the compound of commercial reagent grade. The crystal structure has been studied by Brasseur and de Rassenfosse⁽³⁾.

$\text{CaPt}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$. It was prepared from aqueous solutions of barium tetracyanoplatinate (II) and calcium sulfate as yellow, orthorhombic, prismatic crystals. The crystal structure has not been completely analyzed, although the lattice constants and the unit cell have been determined⁽⁴⁾.

$\text{MgPt}(\text{CN})_4 \cdot 7\text{H}_2\text{O}$. It was prepared from aqueous solutions of the barium salt and magnesium sulfate. Red, tetragonal, prismatic crystals with green metallic luster were obtained. The crystal structure has been studied by Pauling and Bozorth⁽⁵⁾.

Results and Discussion

The Crystal Structure of $\text{CaPt}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$.—The crystal structure of the calcium salt has not been determined as yet. Absorption spectrum of this crystal by polarized light perpendicular to the c -axis, however, bears a striking resemblance to $\parallel$ -absorptions of both barium and magnesium salts, each of them showing a sharp, characteristic absorption band

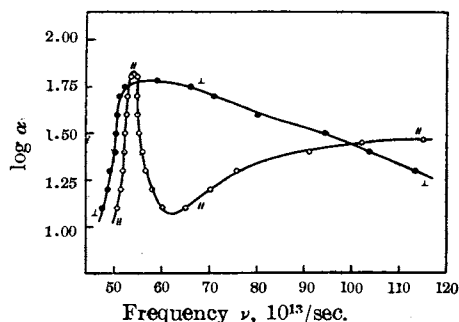


Fig. 1.—Dichroism of $\text{MgPt}(\text{CN})_4 \cdot 7\text{H}_2\text{O}$.

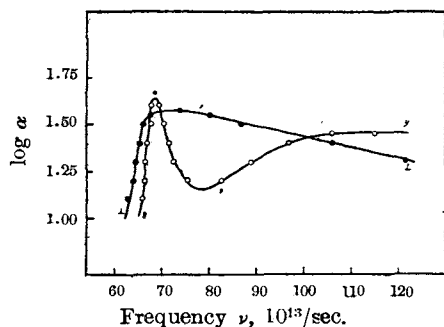
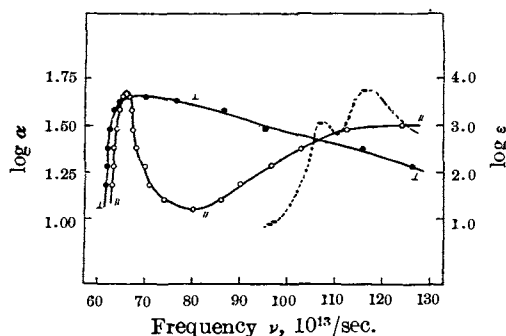
(1) S. Yamada, *J. Am. Chem. Soc.* **73**, 1182 (1951).

(2) The study of J. A. Khvostikov (*Physik. Z. Sowjetunion*, **9**, 211 (1936)) states that aqueous solutions of magnesium, barium and potassium salts show the same absorption spectra.

(3) H. Brasseur and A. de Rassenfosse, *Z. Krist.*, **88**, 210, 221 (1934).

(4) H. Brasseur and A. de Rassenfosse, *Bull. soc. roy. sci. Liège*, **4**, 24 (1935).

(5) R. M. Bozorth and L. Pauling, *Phys. Rev.*, **39**, 538 (1932).

Fig. 2.—Dichroism of $\text{CaPt}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$.Fig. 3.—Dichroism of $\text{BaPt}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ and absorption spectrum of aqueous solution (dotted curve).

of the same kind, which has scarcely ever been found in the crystals previously measured. On the other hand, the absorption spectrum of the calcium salt by polarized light parallel to the c -axis is similar to $\perp$ -absorption of the other salts. Now, according to the hypotheses that absorption by the calcium salt of polarized light perpendicular to the c -axis corresponds to $\parallel$ -absorption and that the other absorption corresponds to $\perp$ -absorption, its dichroism seems quite similar to that of the other salts. In consequence, tetracyanoplatinate (II) ions in the crystal of calcium salt are assumed to be arranged in the same way as in those of the barium or magnesium salt, in which planar ions, $\text{Pt}(\text{CN})_4^{--}$, are oriented parallel to each other and perpendicular to the c -axis, with platinum ions disposed in equal distances on straight lines parallel to the c -axis. On the basis of the above presumption was designated $\parallel$ - or $\perp$ -absorption for $\text{CaPt}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$ in Fig. 2.

The State of the Complex Ions in Crystals.—First, the fact that the crystals of these three compounds show similar dichroism, different from each other only in the position of the absorption band, suggests that the complex ions undergo quite similar effects in these

three compounds⁽⁶⁾. Secondly, it is recognized from the figures that $\perp$ -absorption is both more bathochromic and more hyperchromic than $\parallel$ -absorption in all of these compounds, showing that the complex ion in the crystalline state is influenced more effectively in the direction perpendicular to the complex plane than in the plane, and that the force is exerted perpendicularly upon it. Thirdly, the order of bathochromicity for the sharp bands of the $\parallel$ -absorptions (Table I) indicates that the effect

Table 1

Characteristic Bands of $\parallel$ -Absorption

	Shortest dist. between Pt ions	Frequency at abs. max. sec^{-1}	Half width, sec^{-1}
$\text{MgPt}(\text{CN})_4 \cdot 7\text{H}_2\text{O}$	3.13 ^(a) Å.	34.0×10^{12}	2.3×10^{13}
$\text{CaPt}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$	3.32 ^(b) Å.	68.6	5.4
$\text{BaPt}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$	3.27 ^(c) Å.	65.8	4.6
$[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$	3.21 ^(d) Å.		

(a) Ref. 5.

(b) This value was estimated on the basis of the crystal structure assumed in this report and from the data given in Ref. 3.

(c) Ref. 4.

(d) E. G. Cox, F. W. Pinkard, W. Wardlaw and G. H. Preston, *J. Chem. Soc.*, 1932, 2527.

upon the complex ion increases in the order Ca, Ba and Mg salts, since the larger the effect on the complex ion, the more bathochromically the absorption would be displaced. This order is in conformity with the increasing order of sharpness of the characteristic band (Table I), but differs from the order of strength of the cations expected from the periodic table.

From the foregoing considerations, it is concluded that the force on the complex ions in the crystal differs from the Coulombic force between the cation and the complex anion. As to the force in these crystals, direct interaction between complex ions, of the same kind as was suggested for Magnus' salt in the previous report⁽⁷⁾, is proposed. Thus, in these crystals, the mutual interaction between central platinum ions of planar complex ions is supposed to be exerted upon one another, where the pairs of electrons in coordination above and below the central platinum would contribute in a considerable degree. The considerably smaller interplatonic distance for the magnesium salt as compared with that for

(6) It is quite clear from comparison of the absorption spectra of the crystals and of the solution that complex ions in the crystals are in a condition quite different from their state in solution.

(7) S. Yamada, *J. Am. Chem. Soc.*, **73**, 1579 (1951)

Magnus' salt would allow us to expect larger interaction between complex ions in the former than in the latter. The distances in cases of both barium and calcium salts are considered to be short enough for direct interaction to be expected between complex ions.

Thus, it is concluded that, as the distance between platinum ions becomes smaller and, in consequence, the interaction stronger in the order of Ca, Ba and Mg salts (Table 1), the absorption is displaced toward longer wave-length and the characteristic band of // -absorption becomes sharper. It may be supposed that, as the interaction between platinum ions increases in the order Ca, Ba and Mg salts, the prismatic aggregates of $\text{Pt}(\text{CN})_4^{--}$ ions are more firmly connected together through platinum ions, with the result that a new electronic system is formed and the absorption suffers bathochromic effects, the characteristic band of // -absorption increasing in sharpness. The interaction between platinum ions in these tetracyanoplatinates (II) is extraordinary as compared to that in Magnus' salt; in the latter the interaction is reinforced by Coulombic attraction between complex ions of opposite electrical charges, while in the former there must be instead a repulsion between complex anions of the same sign.

Summary

The dichroism of crystals of $\text{BaPt}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$, $\text{CaPt}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$ and $\text{MgPt}(\text{CN})_4 \cdot 7\text{H}_2\text{O}$ has been measured in the visible and the near-ultraviolet region, and with the aid of results of this measurement, the state of the complex ions in the crystals has been discussed in relation to their crystal structures. These crystals show similar dichroism, with the characteristic sharp absorption band for // -absorption. It has been concluded that between adjacent tetragonal complex ions piled upon one another along the *c*-axis in these crystals there exists a sort of direct interaction, which is supposed to be related to the unusual colors of these compounds. It has been found that as the distance between platinum decreases in the order of Ca, Ba and Mg salts, the interaction between platinum ions becomes stronger, and that the characteristic band becomes sharper and is displaced towards longer wave-length. The interaction in these crystals is regarded as more remarkable than that in Magnus' salt.

The author wishes to express his sincerest thanks to Professor R. Tsuchida for his advices and encouragement throughout the work.

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Fundamental Studies on the Current-Voltage Curve in Polarography. IV.
On the Reduction Wave of Organic Compounds—Especially
on the Wave which Involves the “Kinetic Current”

By Reita TAMAMUSHI and Nobuyuki TANAKA

(Received March 5, 1951)

There exist many possible types of the redox reaction of organic compounds at the dropping mercury electrode surface, and the formulae of the polarographic current-voltage curve will take various forms according to the type of the reaction. In the present paper, the case in which the undissociated molecule of an organic acid is reduced at the more positive potential than the corresponding dissociated anion has been investigated. After deriving the general formulae for the current-voltage curve, the special case which involves the

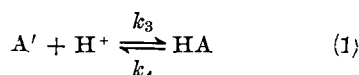
“kinetic current” has been considered, and the discussions on some properties of the polarographic waves of pyruvic acid⁽¹⁾ have been carried out.

Derivation of the General Formulae

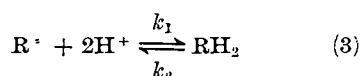
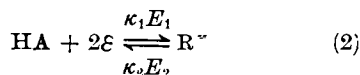
Let us consider that in the body of the solution the equilibrium between the dissociated

(1) R. Brdička, *Collection Czechoslov. Chem. Commun.*, **12**, 212 (1947).

anion, A' , and the undissociated molecule, HA , is kept according to the following equation:



On the other hand, at the electrode surface the undissociated molecule combines with the electrons and then the reduced ion, $R^{\cdot-}$, reacts with the hydrogen ions, getting the reduced molecule, RH_2 .



It is assumed that the equilibrium concentration of the undissociated molecule at the electrode surface is maintained by the diffusion process from the interior of the solution and by the recombination reaction at the electrode surface (the forward reaction of process (1)). Furthermore, accompanying these processes at the electrode surface, the diffusion process of the hydrogen ion between the body of the solution and the electrode surface comes into consideration. Under these conditions the current flowing at the electrode surface can be represented by the following equations:

$$\begin{aligned} I &= 2\varepsilon K_{HA}([C_{HA}]^{\circ} - [C_{HA}]) \\ &\quad + 2\varepsilon K_A([C_A]^{\circ} - [C_A]) \\ &= 2\varepsilon K_{HA}'([A_{HA}]^{\circ} - [A_{HA}]) \\ &\quad + 2\varepsilon K_A'([A_1]^{\circ} - [A_1]) \\ &= I_{HA} + I_k^{(2)} \end{aligned} \quad (4)$$

$$I = 2\varepsilon(\kappa_1 E_1 [A_{HA}] - \kappa_2 E_2 [A_{R^{\cdot-}}]) \quad (5)$$

$$\begin{aligned} I_k &= 2\varepsilon\sigma(k_3[A_1^+][A_1] - k_4[A_{HA}]) \\ &= 2\varepsilon(k_3'[A_A] - k_4'[A_{HA}]), \\ k_3' &\equiv \sigma k_3[A_1^+], \quad k_4' \equiv \sigma k_4 \end{aligned} \quad (6)$$

$$\begin{aligned} I &= 2\varepsilon\sigma(k_1[A_H^+]^2[A_{R^{\cdot-}}] - k_2[A_{RH_2}]) \\ &= 2\varepsilon(k_1'[A_{R^{\cdot-}}] - k_2'[A_{RH_2}]), \\ k_1' &\equiv \sigma k_1[A_H^+]^2, \quad k_2' \equiv \sigma k_2 \end{aligned} \quad (7)$$

$$\begin{aligned} I &= 2\varepsilon K_{RH_2}([C_{RH_2}]^{\circ} - [C_{RH_2}]) \\ &= 2\varepsilon K_{RH_2}'([A_{RH_2}]^{\circ} - [A_{RH_2}]) \end{aligned} \quad (8)$$

$$\begin{aligned} I &= 2\varepsilon K_H([C_{H^+}]^{\circ} - [C_{H^+}]) \\ &= 2\varepsilon K_H'([A_1^+]^{\circ} - [A_1^+]) \end{aligned} \quad (9)$$

σ : the constant concerning the nature of the electrode.

$[C]^{\circ}$, $[C]$: concentrations in the body of

the solution and at the electrode surface.

$[A]^{\circ}$, $[A]$: activities in the body of the solution and at the electrode surface.

K : the constant concerning the diffusion process.

$K' \equiv K/f$, f is the activity-coefficient.

$k_1' \sim k_4'$, $\kappa_1 E_1$, $\kappa_2 E_2$: the terms concerning the reaction rates of the corresponding processes.⁽³⁾

If the solution is well buffered, however, the diffusion process of the hydrogen ion can be neglected and $[A_1^+]$ is considered to be equal to $[A_1^+]^{\circ}$. In this paper such a case only has been dealt with.

Generally, the two constants, K_{HA} and K , concerning the diffusion coefficients of the undissociated molecule and the dissociated anion, are nearly the same, and can be written as K , so that Eq. (4) is reduced to

$$\begin{aligned} I &= 2\varepsilon K([C_A]^{\circ} - [C_A]) \\ &= 2\varepsilon K'([A_1]^{\circ} - [A_1]), \end{aligned} \quad (10)$$

where $[C_A]^{\circ}$ and $[C_A]$ are the analytical concentrations of the oxidized form in the body of the solution and at the electrode surface, which can be represented by the relations

$$\begin{aligned} [C_A]^{\circ} &= [C_{HA}]^{\circ} + [C_A]^{\circ}, \\ [C_A] &= [C_{HA}] + [C_A]. \end{aligned}$$

$[A_1]^{\circ}$ and $[A_1]$ are the activities of the corresponding terms. By eliminating $[A_{RH_2}]$, $[A_{R^{\cdot-}}]$ and $[A_{HA}]$ from these equations the formula

$$\begin{aligned} I/2\varepsilon &= \kappa_1 E_1 \frac{k_3'([A_1]^{\circ} - I) - K_1' I_k}{K_1'(k_3' + k_4')} \\ &\quad - \kappa_2 E_2 \frac{k_2'([A_{R^{\cdot-}}]^{\circ} + I) + K_2' I}{K_2' k_1'} \end{aligned}$$

is obtained. Now, let us introduce the relation

$$I_k = \rho I \quad (11)$$

where ρ is a proportional constant. Then the relation between the current and the electrode potential can be written as follows:

$$I/2\varepsilon = \frac{[A_1]^{\circ} - [E][A_{RH_2}]^{\circ}}{[\kappa_1 E_1] + \left(\frac{1}{K_1'} + \frac{\rho}{k_3'}\right) + [E]\left(\frac{1}{K_2'} + \frac{1}{k_4'}\right)} \quad (12)$$

(2) R. Brdička and K. Wiesner, *Collection Czechoslov. Chem. Commun.*, **12**, 138 (1947).

(3) The explanations for $\kappa_1 E_1$ and $\kappa_2 E_2$ were set down in the previous papers (N. Tanaka and R. Tamamushi, *Bull. Chem. Soc. Japan*, **22**, 187 (1949), etc.).

$$= \frac{[E]'[A_0]^\circ - [A_{RH_2}]^\circ}{[\kappa_2 E_2] + \left(\frac{1}{K_R'} + \frac{1}{k_2'} \right) + [E]' \left(\frac{1}{K_O'} + \frac{\rho}{k_3'} \right)} \quad (12')$$

where

$$[\kappa_1 E_1] \equiv \frac{k_3'}{k_3' + k_4'} \kappa_1 E_1, \quad [\kappa_2 E_2] \equiv \frac{k_2'}{k_1'} \kappa_2 E_2 \quad (13)$$

$$[E] \equiv \frac{[\kappa_2 E_2]}{[\kappa_1 E_1]}, \quad [E]' \equiv \frac{[\kappa_1 E_1]}{[\kappa_2 E_2]}$$

Eqs. (12) and (12') are the general formulae of the oxidation-reduction wave which appears according to the electrode processes (1)-(3).

The formulae for the various conditions can be derived by the same method as mentioned in the previous papers, because general formulae (12) and (12') are quite analogous with those of the complex metal ion.⁽⁴⁾ In the following section, the theoretical analysis of the wave will be set down under the condition that the terms k_2' and k_3' are comparable with K_O' and K_R' .

The Case When k_2' and k_3' are Comparable with K_O' and K_R'

Now, two special cases can be considered according to the relative magnitudes of the terms, k_2' , k_3' , K_O' , K_R' , $[\kappa_1 E_1]$ and $[\kappa_2 E_2]$. One of them is the case when k_2' , k_3' , K_O' , and K_R' are much smaller than $[\kappa_1 E_1]$ and $[\kappa_2 E_2]$ at the electrode potential where $[\kappa_1 E_1]$ is nearly equal to $[\kappa_2 E_2]$, and the other case is that in which the relation between these terms is reverse. The latter corresponds to the activation-controlled one, and only the discussion on the reduction wave obtained in such a case is carried out in the present paper.

If the rate-determining step of the over-all electrode process is the activation process which contains the transfer of the electrons, the condition that $1/[\kappa_1 E_1]$ is much larger than both of $1/K_O' + \rho/k_3'$ and $1/K_R' + 1/k_2'$ is satisfied at the electrode potential where $[\kappa_1 E_1]$ is nearly equal to $[\kappa_2 E_2]$. According to the value of the electrode potential the following three cases are considered, i. e., $[\kappa_1 E_1] \cong [\kappa_2 E_2]$ (Part A), $[\kappa_1 E_1] \gg [\kappa_2 E_2]$ (Part B), and $[\kappa_1 E_1] \ll [\kappa_2 E_2]$ (Part C).^{(4), (5)}

Part A. $[\kappa_1 E_1] \cong [\kappa_2 E_2]$

In this potential region the current flowing is represented as follows:

$$I/2\mathcal{E} = [\kappa_1 E_1][A_0]^\circ - [\kappa_2 E_2][A_{RH_2}]^\circ, \quad (14)$$

and the current is completely defined by the activation process. The equation for the potential where the current flowing is zero can be derived from the above equation.

Part B. $[\kappa_1 E_1] \gg [\kappa_2 E_2]$

$$(1) \quad 1/[\kappa_1 E_1] \cong 1/K_O' + \rho/k_3'$$

In this case the equations for the reduction wave,

$$I, 2\mathcal{E} = \frac{[A_0]^\circ}{[\kappa_1 E_1] + \left(\frac{1}{K_O'} + \frac{\rho}{k_3'} \right)} \quad (15)$$

or

$$[\kappa_1 E_1] = K_O' \frac{(I_l)_0}{(I_a)_0} \frac{I}{(I_l)_0 - I}$$

are derived, where $(I_a)_0$ equals $2\mathcal{E}K_O'[A_0]^\circ$ and $(I_l)_0$ represents the limiting current of the wave. The detailed discussion of the limiting current, $(I_l)_0$, will be carried out in the following.

$$(2) \quad 1/[\kappa_1 E_1] \ll 1/K_O' + \rho/k_3'$$

Now, the limiting current is obtained, and it is represented as follows:

$$(I_l)_0 = \frac{1}{K_O'} \frac{(I_a)_0}{\frac{1}{K_O'} + \frac{\rho}{k_3'}} = \frac{k_3'(I_a)_0}{k_3' + \rho K_O'}$$

Part C. $[\kappa_1 E_1] \ll [\kappa_2 E_2]$

This is the potential region for the oxidation wave,⁽⁶⁾ but all discussions on this part are omitted in this paper.

In the following section some discussions will be made on the properties of the reduction wave by means of the equations derived above.

Analysis of the Limiting Current.—It can be considered that the limiting current, (I_l) , is the sum of the term $(I_a)_{HA}$ due to the diffusion process of the undissociated molecule HA and the term I_k which is attributed to the recombination reaction (3), i. e.,

$$(I_l)_0 = (I_a)_{HA} + I_k \quad (17)$$

By the definition of ρ , previously mentioned, the relation

$$\rho = \frac{I_k}{(I_l)_0} = \frac{(I_l)_0 - (I_a)_{HA}}{(I_l)_0}$$

is derived, and if $[A_{HA}]^\circ$ is the activity of the undissociated molecule in the body of the solution the term $(I_a)_{HA}$ can be written as follows:

$$(I_a)_{HA} = 2\mathcal{E}K_O'[A_{HA}]^\circ$$

(4) R. Tamamushi and N. Tanaka, *Bull. Chem. Soc. Japan*, **23**, 110 (1950).

(5) R. Tamamushi and N. Tanaka, *ibid.*, **22**, 227 (1949).

Moreover, as it can be considered that in the body of the solution the dissociation equilibrium is maintained, ρ can be represented as below by means of the relations cited above.

$$\rho = \frac{\langle I_l \rangle_o - 2\varepsilon K_o' [A_o]^\circ \frac{[A_{H^+}]}{[A_{H^+}] + \Gamma}}{\langle I_l \rangle_o} \\ = \frac{(\langle I_l \rangle_o - \langle I_d \rangle_o) \frac{[A_{H^+}]}{[A_{H^+}] + \Gamma}}{\langle I_l \rangle_o} \quad (18)$$

Γ means the dissociation constant of the molecule, HA, and is equal to k_4/k_3 . When the terms $\langle I_d \rangle_o$, Γ and $[A_{H^+}]$ are known, the value of ρ can be calculated by Eq. (18). By introducing this relation into Eq. (16) we can write $\langle I_l \rangle_o$ in terms of $\langle I_d \rangle_o$, Γ and $[A_{H^+}]$, i. e.,

$$\langle I_l \rangle_o = \langle I_d \rangle_o \frac{k_3'(\Gamma + [A_{H^+}]) + K_o' [A_{H^+}]}{(k_3' + K_o')([A_{H^+}] + \Gamma)} \\ = 2\varepsilon \frac{K_o' [A_o]^\circ [A_{H^+}] \frac{\sigma k_3'(\Gamma + [A_{H^+}]) + K_o'}{\Gamma + [A_{H^+}]} + \sigma k_3 [A_{H^+}]}{K_o' + \sigma k_3 [A_{H^+}]} \quad (19)$$

This formula is quite the same as has been set down by R. Brdička for the "kinetic current."⁽²⁾ Furthermore, if we take into account the relation obtained by Brdička, the constant σ can be written as follows:⁽²⁾

$$\sigma = q \cdot \mu \cdot 10^{-3} \quad (20)$$

q : the surface area of the dropping mercury electrode in cm.²

μ : the thickness of the reaction layer at the electrode surface in cm.

On the Rate of the Recombination Reaction.—The following relation for k_3' is easily obtained from Eq. (16)

$$k_3' = \sigma k_3 [A_{H^+}] = \frac{K_o' \rho \langle I_l \rangle_o}{(\langle I_d \rangle_o - \langle I_l \rangle_o)} \quad (21)$$

Therefore, if $\langle I_d \rangle_o$, $\langle I_l \rangle_o$, K_o' , and ρ are known from the experimental data and others, the terms k_3' , σk_3 , and μk_3 can be calculated from Eqs. (20) and (21). If we use the theoretical expression for μ obtained by J. Koutecky and R. Brdička⁽⁷⁾

$$\mu = \sqrt{\frac{D}{k_3 \Gamma}}$$

the equation for k_3 ,

$$k_3 = \frac{(\mu k_3)^2 \Gamma}{D} \text{ sec.}^{-1} (\text{mol/liter})^{-1}, \quad (22)$$

is obtained, where D is the diffusion constant of the depolarizer. Hence the value of k_3 can be determined from the experiments.

Moreover, by means of the ratio, $\langle I_l \rangle_o / \langle I_d \rangle_o = T$, the equation

$$k_3' = \frac{K_o' [T \Gamma - [A_{H^+}](1 - T)]}{(\Gamma + [A_{H^+}])(1 - T)} \quad (23)$$

is derived.

The Relation between V and $\log I / (\langle I_l \rangle_o - I)$.—This relation is a straight line whose tangent is $0.059/2\alpha$ volt at 25° , if the value of α is constant. From this tangent the value of α can be calculated.

Half-wave Potential.—By introducing the relation, $I = \langle I_l \rangle_o / 2$, for the current at the half-wave potential, the equation

$$[\kappa_1 E_1]_{1/2} = \frac{k_3' K_o'}{k_3' + \rho K_o'} \quad (24)$$

is obtained from Eq. (15), and, furthermore, this formula can be written as follows by means of relation (13) and the definition of Γ ,

$$V_{1/2} = \frac{RT}{2\alpha F} \left(\ln s \frac{kT}{h} - \ln K_o' \right) \\ - \frac{RT}{2\alpha F} \ln \frac{\sigma k_3'([A_{H^+}] + \Gamma)}{\sigma k_3 [A_{H^+}] + \rho K_o'} - \frac{\Delta F_1}{2\alpha F} \\ = \text{const.} - \frac{RT}{2\alpha F} \ln \frac{\sigma k_3'([A_{H^+}] + \Gamma)}{\sigma k_3 [A_{H^+}] + \rho K_o'} \quad (24')$$

s : the constant concerning the nature of the electrode.

It can be said that $V_{1/2}$ is constant and independent of the activity of the substance concerned, if pH , α and the ionic strength of the solution remain constant. If the values of K_o' , k_3' , Γ , ρ , α , and others are known, the free energy of the activation, ΔF_1 , can be calculated from the formula mentioned above.

Now, let us consider the relation between $V_{1/2}$ and pH . Representing the half-wave potentials corresponding to the hydrogen ion concentrations $[A_{H^+}]_a$ and $[A_{H^+}]_b$ by $(V_{1/2})_a$ and $(V_{1/2})_b$, respectively, then for the shift of the half-wave potential with respect to the change of pH the following relation is obtained:

$$(V_{1/2})_a - (V_{1/2})_b = \Delta V_{1/2} \\ = \frac{RT}{2\alpha F} \ln \frac{([A_{H^+}]_b + \Gamma) (\sigma k_3 [A_{H^+}]_a + K_o' \rho_a)}{([A_{H^+}]_a + \Gamma) (\sigma k_3 [A_{H^+}]_b + K_o' \rho_b)} \quad (25)$$

(6) In this case the unit of the concentration is mol per liter.

(7) J. Koutecky and R. Brdička, *Collection Czechoslov. Chem. Commun.*, **12**, 337 (1947).

It is found from Eqs. (24') and (25) that when the value of pH is large the value of $V_{1/2}$ becomes independent of pH and reaches a constant value, and this can be thought as a special character of the reduction wave which is obtained under the condition mentioned above (Fig. 1).

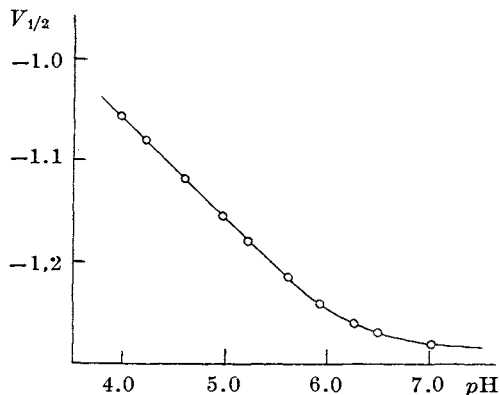


Fig. 1.

Hitherto, the case, in which K_O' , K_R' , k_2' and k_3' have the values nearly of the same order, has been discussed. The important character in such a case is that the limiting current is not represented only by the rate of the diffusion process but also by the term concerning the reaction rate such as k_3' . For such a limiting current, it is obvious that the application of the Ilkovič equation fails, and the "kinetic current" mentioned by Brdička corresponds to this current. We can distinguish the "kinetic current" from the ordinary "diffusion current" by its dependence on the nature of the electrode, temperature and so forth.^{(1), (2)}

As for the example of the application of the theoretical results obtained above, the shift of the half-wave potential and the calculation of the free energy of the activation, ΔF_1 , of the reduction process of pyruvic acid are discussed in the following section.

Discussion on the Properties of the Reduction Wave of Pyruvic Acid⁽¹⁾

The polarographic study on the pyruvic and phenylglyoxylic acids was carried out, at first, by O. H. Müller,⁽⁸⁾ and recently by R. Brdička.⁽¹⁾ The latter has explained the appearance of the double-wave by introducing the conception of the "kinetic current." However, the shift of the half-wave potential accompanying the change of pH has not yet been interpreted.

By means of the theoretical equations described above, the discussion on the half-wave potential and the calculation of the value of ΔF_1 can be carried out. The experimental data obtained by Brdička have been used for the present calculation.

Calculation of the Shift of the Half-wave Potential.—First, the linear relations have been found between V and $\log I/(I_t - I)$ for the actual polarograms of pyruvic and phenylglyoxylic acids. From these relations the value of α for each case has been calculated. While the value of α for pyruvic acid has been nearly constant and equal to 0.28, on the other hand, that of phenylglyoxylic acid varied from 0.54 to 0.34 according to the change of pH . Unless the value of α remains constant, it is quite doubtful whether Eqs. (24') and (25) can be applicable or not for the present purpose, so only the calculation for pyruvic acid will be carried out in the following.

After having been determined the value of α , the term μk_3 has been calculated from Eqs. (20) and (21), the mean value of which over the range of pH 4.95-6.81 is 3.2×10^3 . The terms ρ , K_O' and $m^{2/3} t^{1/6}$ (the capillary constant) have been obtained from the polarograms observed by Brdička, and for the value of I , 4×10^{-3} has been used. Then, the shift of the half-wave potential with the change of pH has been calculated from Eq. (25), and the results have been compared with the experimental data obtained by Brdička (Table 1). The half-wave potential of the wave at $pH=5.20$ (-1.180 volts)

Table 1

pH	$\Delta V_{1/2}$ calc., mV.	$\Delta V_{1/2}$ obs., mV.	pH	$\Delta V_{1/2}$ calc., mV.	$\Delta V_{1/2}$ obs., mV.
3.95	127	114	5.59	-35	-35
4.19	102	90	5.91	-60	-60
4.58	61	65	6.24	-79	-80
4.95	24	28	6.48	-89	-80
5.20	—	—	6.64	-93	—

has been taken as the standard for the present calculation. It has been shown by the experimental results that half-wave potential of such a wave tends to reach the constant value when pH increases. This property can be completely interpreted by Eq. (25), and the calculated limiting value of the half-wave potential for pyruvic acid is obtained to be -1.287 volts. From this result it can be said that the theoretical treatment mentioned above can interpret the properties of the wave of pyruvic acid at least qualitatively.

Calculation of ΔF_1 .—Introducing the values.

(8) O. H. Müller, *J. Am. Chem. Soc.*, **61**, 590 (1939).

of α , σk_3 , ρ , and others to Eq. (24') the value of the free energy of the activation for the forward reaction of the process (2), ΔF_1 , can be calculated.⁽⁹⁾ In the case of pyruvic acid the results obtained over the range of pH 4.95-6.48 are shown in Table 2.

Table 2

pH	$V_{1/2}$, volt	ΔF_1 , joule
4.95	-1.152	9.5×10^4
5.20	-1.180	9.5×10^4
5.59	-1.215	9.6×10^4
5.91	-1.240	9.6×10^4
6.24	-1.260	9.6×10^4
6.49	-1.260	9.5×10^4
		mean value..... 9.6×10^4

Summary

Of the oxidation-reduction reaction of organic compounds, the case, in which the undissociated molecule of an organic acid is reduced at the more positive potential than the corresponding dissociated anion and the equilibrium

concentration of the reducible form at the electrode surface is kept by the diffusion process and the recombination reaction at the electrode surface, has been taken into consideration. Under such conditions, the general formulae for the polarographic current-voltage curve have been derived, and the special case which involves the "kinetic current" has been investigated. The theoretical discussions on the limiting current and the shift of the half-wave potential with the change of pH have been carried out. Moreover, the results obtained have been applied to interpret the properties of the wave of pyruvic acid observed by R. Brdička. A considerably good agreement between the experimental data and the theoretical results has been obtained, and it is probably said that the properties of the various polarographic waves and the mechanism of the electrode process can be investigated by the analogous treatment mentioned above.

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(9) The constant s in Eq. (24') is assumed to be equal to the constant σ .

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Effect of Gelatin on the Polarographic Waves of *p*- and *o*-Nitroanilines

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Several literatures have been published on the studies on polarographic reduction waves of nitroanilines. In 1932, M. Shikata and E. Taguchi⁽¹⁾ reported on the reduction potentials of *o*-, *m*- and *p*-nitroanilines measured by the 45° tangent method in a wide range of *pH* with buffered and non-buffered solutions, and they discussed the relation between the reduction potentials and the constitutions. Recently O. D. Shreve and E. C. Markham⁽²⁾ reported on the effect of ethyl alcohol on the polarographic waves of nitroanilines. Y. Yasumori⁽³⁾ tried

to apply the polarographic waves of *p*- and *o*-nitroanilines to the simultaneous determination of these compounds in their mixtures, when he employed the double waves of these compounds which were obtained in supporting electrolyte of a suitable *pH* and a suitable concentration of ethyl alcohol. However, these researchers told of nothing concerning the effect of gelatin on the reduction waves of these compounds.

In the present paper are reported the effect of gelatin on the polarographic waves of *p*- and *o*-nitroanilines and its application to the determination of these compounds. The experiments and discussions on the characteristics of the polarographic waves themselves of these compounds and the reduction mechanisms will be reported elsewhere.

(1) M. Shikata and E. Taguchi, *J. Agricul. Soc. Japan*, **8**, 1225 (1932).

(2) O. D. Shreve and E. C. Markham, *J. Am. Chem. Soc.*, **71**, 2993 (1949).

(3) private communication.

Experimental

Apparatus.—A Heyrovsky-Shikata type polarograph was employed. A dropping mercury electrode was employed for the cathode, and a normal calomel electrode, for the anode. The capillary constant, $m^{2/3} t^{1/6}$, was 1.124 ($\text{mg.}^{2/3} \text{ sec.}^{-1/6}$), measured in distilled water free from oxygen without applied potential. All measurements were carried out in a thermostat of 25° or 30°.

Reagents.—*p*- and *o*-Nitroanilines were kindly given by Nippon Kasei Chemical Industries Limited, which have the melting points of 148.0–148.5° and 72.0–72.5° respectively. Their standard solutions were prepared by dissolving them in distilled water, the concentrations of which were about 1 millimol per liter.

The Clark and Lub's buffer of pH 9.0 was used as a supporting electrolyte solution, its actual pH value being 8.8 determined with an antimony electrode.

Results and Discussion

The polarographic waves of *p*- and *o*-nitroanilines measured in the supporting electrolyte containing no gelatin are shown in Fig. 1, on which distinct maxima appeared. These maxima were suppressed by adding 0.005–0.01% of gelatin to the supporting electrolyte. When

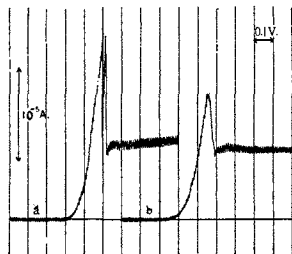


Fig. 1.—Polarograms of *p*- and *o*-nitroanilines in the supporting electrolyte containing no gelatin; (a) *p*-nitroaniline ($0.5 \times 10^{-5} M$), (b) *o*-nitroaniline ($0.5 \times 10^{-5} M$). Each polarogram begins at -0.4 volt vs. N. C. E.

the concentration of gelatin increased more than about 0.01%, it was found that the wave of nitroaniline splitted into two waves. The total height of the double wave was almost constant independently of the concentration of gelatin. The ratio of the wave height of the second wave to the first one became greater with the increase of the concentration of gelatin contained in supporting electrolyte. These phenomena are shown in Figs. 2 and 3.

In addition to the fact it became clear that the ratio of the second wave to the first one was different between *p*- and *o*-compounds when the supporting electrolyte contained the

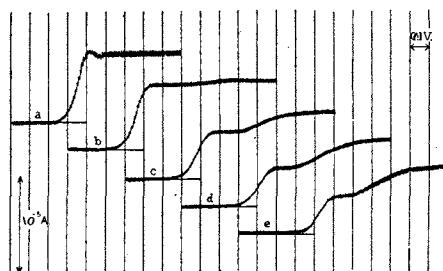


Fig. 2.—Polarograms of *p*-nitroaniline ($0.5 \times 10^{-3} M$) in the supporting electrolytes containing gelatin of, (a) 0.005%, (b) 0.01%, (c) 0.02%, (d) 0.05% and (e) 0.1%. Each polarogram begins at -0.4 volt vs. N. C. E.

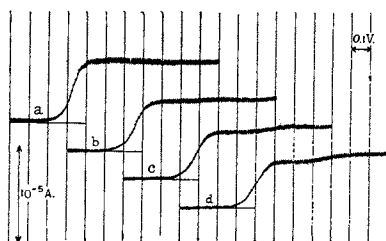


Fig. 3.—Polarograms of *o*-nitroaniline ($0.5 \times 10^{-3} M$) in the supporting electrolytes containing gelatin of, (a) 0.005%, (b) 0.01%, (c) 0.02% and (d) 0.1%. Each polarogram begins at -0.4 volt vs. N. C. E.

same concentration of gelatin.

The linear relations were held between the concentrations and the wave heights of both the first and the second waves of each compound, as shown in Figs. 4 and 5. Therefore,

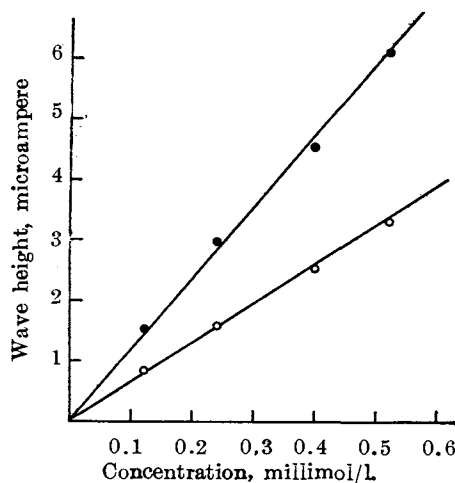


Fig. 4.—Relation between the wave height and the concentration of *p*-nitroaniline: —○—, indicates the wave height of the first wave; and —●—, the total wave height of the first and the second waves.

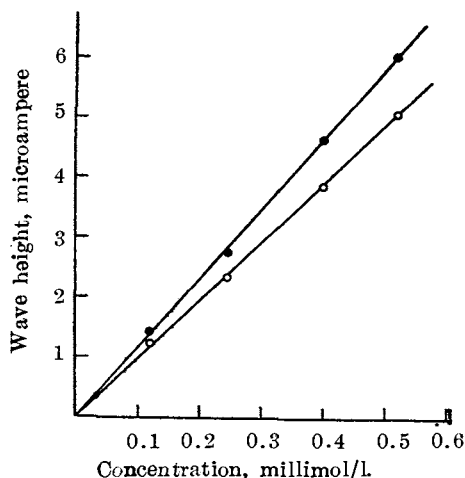


Fig. 5.—Relation between the wave height and the concentration of *o*-nitroaniline: —○—, indicates the wave height of the first wave; and —●—, the total wave height of the first and the second waves.

these double waves seemed possible to be applied to the simultaneous determination of both compounds, which will be described later.

The relations of $\log I/(I_a - I)$ vs. V held straight lines, but their slopes were far less than those expected from the reversible reduction. They should hold straight lines with slopes of about 10 millivolts, if the reduction proceeded reversibly and if the numbers of electrons necessary to the reduction were six as reported by Shreve and Markham and as confirmed by the authors.

The half-wave potentials were almost independent of the concentration of the reducible substances, but shifted to negative potential with increasing concentration of gelatin, which are indicated in Tables 1 and 2.

Table 1

Concentration, millimol/l.	<i>p</i> or <i>o</i>	$V_{1/2}$ vs. N.C.E., volt	Slope of $\log I/(I_a - I)$ vs. V , volt
0.12	<i>p</i>	-0.820	0.062
	<i>o</i>	-0.791	0.066
0.24	<i>p</i>	-0.814	0.061
	<i>o</i>	-0.785	0.068
0.40	<i>p</i>	-0.821	0.062
	<i>o</i>	-0.789	0.068
0.52	<i>p</i>	-0.828	0.071
	<i>o</i>	-0.797	0.073

Supporting electrolytes contained 0.1% of gelatin.

Table 2

Concentration of gelatin, %	<i>p</i> or <i>o</i>	$V_{1/2}$ vs. N.C.E., volt	Slope of $\log I/(I_a - I)$ vs. V , volt
0.005	<i>p</i>	(-0.74)	—
	<i>o</i>	(-0.73)	—
0.01	<i>p</i>	-0.750	0.057
	<i>o</i>	-0.756	0.069
0.02	<i>p</i>	-0.772	0.064
	<i>o</i>	-0.780	0.076
0.05	<i>p</i>	-0.795	0.068
	<i>o</i>	-0.787	0.075
0.1	<i>p</i>	-0.815	0.069
	<i>o</i>	-0.801	0.078

Concentration of *p*- and *o*-nitroanilines are 0.5 millimol per liter.

The numbers of electrons necessary to the reduction were calculated from the polarogram by means of the Ilkovič equation and the diffusion constant. For the latter, 8.79×10^{-6} cm.²sec.⁻¹, the value given by Shreve and Markham, was employed. The result showed that the reduction of *p*- and *o*-nitroanilines, including the second wave if the wave splitted into two waves, was of the six-electron reduction, as the same as reported by Shreve and Markham.

It seems important to answer the problems of why the wave splits by the addition of gelatin and of why the ratio of the wave height of the second wave to the first one increases with the increase of the concentration of gelatin. It has been reported that nitro compound often gives a double wave in the certain condition. Being the case, the first wave corresponds to the reduction of nitro compound to hydroxylamine, (that is, a four-electron reduction), while the second wave corresponds to the reduction of hydroxylamine (that is, a two-electron reduction).

The present case, no doubt, did not correspond to such a case, because the ratio of both waves changed continuously with increasing concentration of gelatin. The authors would like to infer that some changes at the electrode interface occurring by the addition of gelatin caused the wave splitting. Such a case has been recently reported by E. L. Colichman⁽⁴⁾ in regard to the reduction waves of the several inorganic compounds, which are greatly influenced by surface active substances, such as gelatin and cetyltrimethylammonium bromide.

(4) E. L. Colichman, *J. Am. Chem. Soc.*, **72**, 4086 (1950).

In the present study, however, the authors could not confirm the idea, but as the result of some experiments, they did not prove the phenomenon to be explained by the idea of the formation of intermediate reduction substances and also by that of kinetic current.

Analytical Application

Since it was found out that the wave heights are proportional to the concentration and that the ratio of wave height of the second wave to the first one is different between *p*- and *o*-compounds in the supporting electrolyte containing the same concentration of gelatin, the double waves were applied to the simultaneous determination of these compound. The concentration of gelatin contained in the supporting electrolyte was decided to be 0.1%, considering that, in the case, the difference of the ratio of the second wave to the first one was the greatest between *p*- and *o*-compounds. The relations of the wave heights and the concentrations were obtained in this condition, as shown in Figs. 4 and 5. From the result the following equations were obtained to express the concentration of each of these compounds contained in the solution electrolyzed.

$$C_p = \frac{7.9 h_2 - 11.6 h_1}{38.3} \quad (\text{millimol/l.})$$

$$C_o = \frac{11.6 h_1 - 6.4 h_2}{38.3} \quad (\quad , \quad),$$

where C_p and C_o represent the concentrations of *p*- and *o*-nitroanilines and h_1 and h_2 , the first wave height and the total wave height both measured in microampere.

Some synthetic samples were analyzed with the procedure with the results shown in Table 3. The results were not so good, but it was concluded that an approximate content of each compound can be estimated with the procedure.

Summary

The effect of gelatin on the polarographic waves of *p*- and *o*-nitroanilines has been investigated,

(1) Maxima of the polarographic waves of these compounds which occur in the supporting electrolyte without gelatin were suppressed by adding 0.005-0.01% of gelatin to the supporting electrolyte.

(2) The wave of each of these compounds splitted into two waves when the supporting electrolyte contained more than 0.01% of gelatin.

(3) The ratio of the wave heights of the second wave to the first increased with increasing concentration of gelatin, and it was different between *p*- and *o*-compounds in the supporting electrolyte containing the same concentration of gelatin.

(4) The wave heights of the first and the second waves of each compound were proportional to the concentration.

(5) These double waves were applied to the simultaneous determination of both compounds, with the result that the procedure was available for rough estimation of content.

The authors are grateful to Nippon Kasei Chemical Industries Limited that gave them purified samples of *p*- and *o*-nitroanilines. The cost of this study has been partly defrayed from the Grant in Aid from the Ministry of Education.

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Table 3

Simultaneous Determination of Synthetic Samples

Ratio of <i>p</i> : <i>o</i> in synthetic samples, (<i>p</i> : <i>o</i>)		Concentration present, millimol/l.	Concentration found, millimol/l.
1:1	$\left\{ \begin{array}{l} p \\ o \end{array} \right.$	0.24	0.27
		0.24	0.18
2:1	$\left\{ \begin{array}{l} p \\ o \end{array} \right.$	0.32	0.35
		0.16	0.18
4:1	$\left\{ \begin{array}{l} p \\ o \end{array} \right.$	0.32	0.32
		0.08	0.06
5:1	$\left\{ \begin{array}{l} p \\ o \end{array} \right.$	0.40	0.46
		0.08	0.09
1:2	$\left\{ \begin{array}{l} p \\ o \end{array} \right.$	0.16	0.17
		0.32	0.27
1:3	$\left\{ \begin{array}{l} p \\ o \end{array} \right.$	0.08	0.08
		0.24	0.23
1:5	$\left\{ \begin{array}{l} p \\ o \end{array} \right.$	0.08	0.10
		0.40	0.39

Études spectrochimiques du cyclooctatétraène (C_8H_8) et du $C_{10}H_{10}$

par Seinosuké MIYAKAWA, Ikuzo TANAKA et Taku UÉMURA

(Reçu le 20 mars, 1951)

Introduction

Les propriétés du cyclooctatétraène (C.O.T.), dont la structure est théorétiquement intéressante, ont déjà été étudiées par plusieurs chimistes et physiciens.⁽¹⁾ Nous avons récemment publié un mémoire dans ce bulletin sur les études de la réaction photochimique et de la structure électronique de la même substance.⁽²⁾ Nous avons mesuré maintenant l'absorption visible et ultraviolette du C.O.T. et du composé $C_{10}H_{10}$ en solution et à l'état gazeux. Nous avons étudié les influences sur le spectre d'absorption du C.O.T. dans sa solution de heptane normal et celle de tétrachlorure de carbone lorsqu'on y ajoute l'iode. Ces influences d'iode sur le C.O.T. peut être comparées à celles sur le benzène.

Procédé expérimental et spectres d'absorption

Le C.O.T. et le $C_{10}H_{10}$ qui sont employés dans nos expériences sont préparés par Prof. S. Murahashi et Dr. N. Hagiwara à l'Institut de Recherche scientifique et industrielle de l'Université d'Osaka. Les échantillons sont purifiés par les distillations fractionnaires exécutées quatre fois *in vacuo* par lesquelles les parties plus volatiles et plus lourdes sont exclues. L'alcool méthylique, l'alcool éthylique, le cyclohexane, l'heptane normal et le tétrachlorure de carbone sont utilisés comme dissolvants, et purifiés par des procédés ordinaires. Nous nous sommes servis du spectrographe en quartz "QF-60" construit par Shimazu, de celui construit par Jobin et Yvon et du spectrophotomètre Spekker de Shimazu en employant 1 cm. d'épaisseur de solution pour la détermination du spectre d'absorption. Pour mesurer l'absorption de l'échantillon gazeux du C.O.T., nous avons pris, comme auparavant, l'appareil indiqué dans la figure 1.

Les conditions expérimentales que nous avons adoptées sont les suivantes, savoir: les tubes d'absorption ajoutés à deux côtés les plaques en quartz sont changés sa longueur à 4.95, 6.7 et

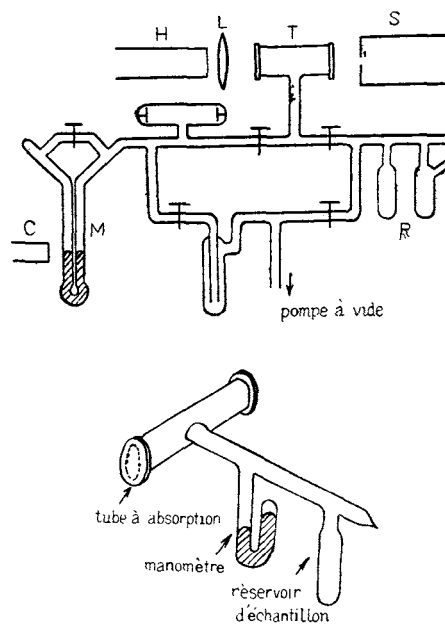


Fig. 1.—H, tube à décharges d'hydrogène; L, lentille en quartz; T, tube à absorption; S, spectrographe; C, cathétomètre; M, manomètre; R, réservoir d'échantillon.

20.0 cm. en variant la grandeur d'extinction. Nous avons utilisé comme source lumineuse un tube à décharges d'hydrogène et nous avons employé des plaques photographiques "Fuji" (marque japonaise) et celles pour rayons cosmiques préparées spécialement au laboratoire de la compagnie Fuji-Film pour la région à 230-195 $m\mu$ au lieu d'employer celles de Schuman.

Pour mesurer le coefficient d'absorption, on prend sept spectres sur une plaque photographique à la même durée d'exposition constante, toujours égale à 10 minutes. Six d'entre eux sont obtenus en traversant le rayon au tube à l'absorption évacué d'avance, et ont des intensités logarithmiquement variées qui sont entre elles comme 10, 6.31, 3.98, 2.51, 1.59, 1, par le diaphragme employé pour le spectrophotomètre. Le septième obtenu par l'échantillon gazeux introduit, dans le tube à absorption sous une tension moyenne entre 3 et 6 mm. Hg et cette tension est lue sur le manomètre en mercure à l'aide du cathétomètre.

Il suffit normalement de microphotomètre:

(1) Voir les bibliographies indiquées dans ce bulletin 24, 119(1951).

(2) Ikuzo Tanaka et Shoji Shida, ce bulletin, 23, 54 (1950); Yuji Mori, Ikuzo Tanaka et Shoji Shida, *ibid.*, 23, 168 (1950); Ikuzo Tanaka, Seinosuké Miyakawa et Shoji Shida, *ibid.*, 24, 119(1951).

ces spectres, pour obtenir une courbe de noircissement de la plaque à l'aide de ces six premiers spectres; le septième donne l'extinction gazeuse par la méthode d'interpolation. La figure 2 donne la courbe d'absorption du C. O. T. à l'état gazeux.

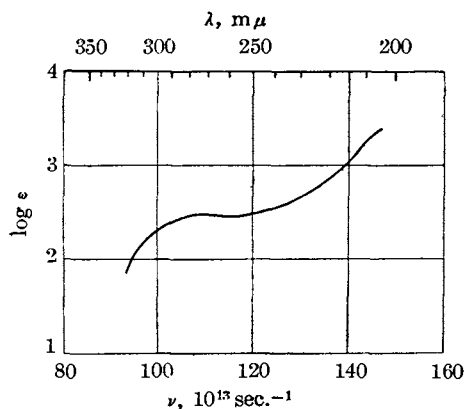


Fig. 2.—Spectre d'absorption du C. O. T. à l'état gazeux.

Dans cette figure nous avons pris le coefficient d'absorption comme celui moléculaire ϵ du C. O. T. à l'état gazeux pour faire facilement comparer au cas de solution. La valeur ϵ est égale à $\log I_0/I \cdot cd$, où $\log I_0/I$ est l'extinction gazeuse déjà indiquée, d la longueur d'épaisseur et c la concentration représenté par mol/l. Nous avons utilisé une cuve spéciale pour mesurer l'absorption entre 230 mμ et 200 mμ. Cette cuve consiste de trois parties, savoir: un tube à absorption ayant la longueur à 4.95 cm. attaché les fenêtres en quartz à deux côtés, un manomètre en mercure et un réservoir pour l'échantillon. Le C. O. T. est condensé dans ce réservoir par distillation en vide et ensuite l'appareil est complété par le détachement en fondant le tube de verre. Après avoir obtenu l'appareil, on fait modérer la tension du C. O. T. par l'abaissement de la température. L'extinction de cet échantillon est mesuré par l'appareil Spekker en utilisant comme source lumineuse une décharge d'étincelles entre électrodes de l'argent et de l'alliage de Cu-Zn-Al. Nous mettons ensuite les spectres obtenus sur une plaque photographique pour rayons cosmiques. Comme l'extinction du C. O. T. est très grande en région de la longueur d'onde vers 200 mμ, il est nécessaire de la mesurer sous basse tension de vapeur. On fait donc baisser la température de l'échantillon au-dessous de -10° , tandis qu'on maintient celle du tube à absorption à la température ordinaire.

Le changement de la température de l'ab-

sorption du C. O. T. dans la solution a déjà été publié,⁽³⁾ tandis que notre présent mémoire donne les résultats exécutés à l'état gazeux. Nous avons examiné le spectre d'absorption en utilisant le tube dont les deux côtés ont été joints avec les fenêtres en quartz fondues. Nous en avons changé la température entre 110° et 10° , mais avons trouvé peu d'influence de température à la bande d'absorption.

Les spectres d'absorption du C. O. T. et du C₁₀H₁₀ en solution sont tous obtenus au moyen du spectrophotomètre Spekker ou encore celui de Nutting appliqué spécialement en région visible. Nous avons étudié que la structure fine soit existée dans la bande d'absorption du C. O. T. et du C₁₀H₁₀, et l'avons examinée par la méthode de Hartley-Baly en utilisant comme source lumineuse l'étincelle sous l'eau

Table 1

Absorption lumineuse du C. O. T. et du C₁₀H₁₀.

Composé	Dissolvant	λ , mμ	ϵ
C. O. T.	alcool méthylique	280	350
	alcool éthylique	280	435
	tétrachlorure de carbone	288	320
	heptane normal	280	235
	cyclohexane	283	255
C ₁₀ H ₁₀	alcool méthylique	280	2100
		230	26400
	alcool éthylique	280	2900
	tétrachlorure de carbone	280	2100
	heptane normal	280	2100

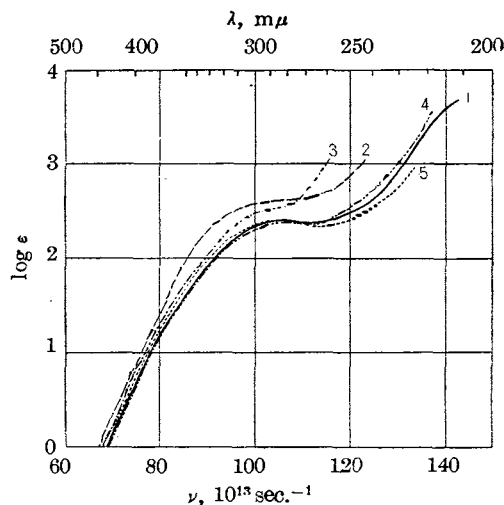


Fig. 3.—Spectre d'absorption du C. O. T. Les chiffres à la courbe montrent les dissolvants employés: 1, alcool méthylique; 2, alcool éthylique; 3, tétrachlorure de carbone; 4, heptane normal; 5, cyclohexane.

(3) A. Langseth et S. Brodersen, *Acta Chemica Scandinavica*, **3**, 778 (1949); *Chem. Abstr.*, **44**, 2369 (1950).

qui donne un spectre continu très fort dans la région ultraviolette voisine. Cet appareil de l'étincelle sous l'eau a été récemment construit à notre laboratoire⁽⁴⁾. Nous avons encore employé les plaques photographiques étant sensibilisées par l'acide aminé G ainsi que celles pour rayons cosmiques. Les résultats sont montrés dans la table 1 et par les figures 3 et 4.

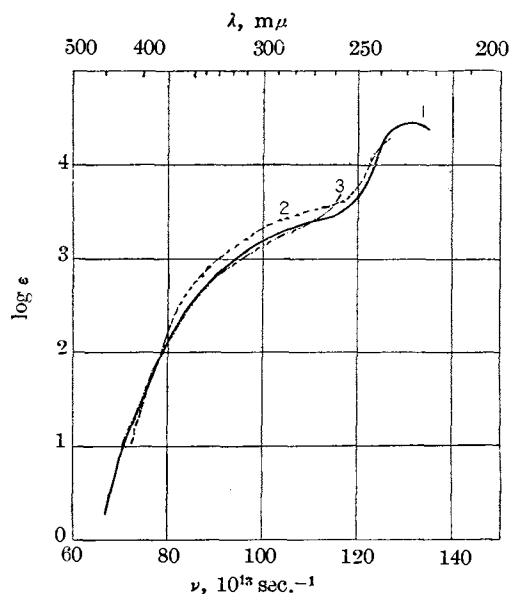


Fig. 4.—Spectre d'absorption du $C_{10}H_{10}$.

L'absorption du $C_{10}H_{10}$ à l'état gazeux est encore mesurée à la température élevée au moyen de la cuve employée dans l'expérience exécutée ci-dessus, parce que la tension de $C_{10}H_{10}$ est trop basse pour obtenir l'extinction moyenne.

Comme on le voit, dans la figure 3, toutes les courbes d'absorption du C.O.T. dans plusieurs dissolvants donnent un maximum vers 280 $m\mu$ et ne montrent pas l'absorption sélective en région visible tandis que le C.O.T. est jaune à l'état liquide et en solution. La couleur du C.O.T. est donc attribuée à l'absorption terminale étendue à la région visible dont le maximum se trouve à la région ultraviolette. La courbe d'absorption montrée à la longueur d'onde plus courte que celle vers 280 $m\mu$ monte jusqu'à 200 $m\mu$ en manquant de maximum d'absorption, mais on peut supposer l'existence d'absorption maxima vers 200 $m\mu$ par l'inclinaison de la courbe diminuée rapidement à la longueur d'onde un peu plus élevée que 200 $m\mu$. La courbe d'absorption du C.O.T., soit à l'état

gazeux, soit en solution, n'a pas la structure fine qu'on peut trouver à l'absorption du benzène.

Pour examiner la structure fine en absorption du C.O.T. à la température basse, nous avons photographié le spectre d'absorption du C.O.T. dissout dans l'heptane normal à la température d'environ -40° . Nous avons obtenu cette température basse par le refroidissement causé par la neige carbonique, mais nous n'y voyons pas de structure fine à pareille température.

L'absorption lumineuse du C.O.T. en solution⁽⁵⁾ est influencée par le dissolvant employé, c'est-à-dire, la position de l'absorption maxima est seulement déplacée vers le rouge et son coefficient d'extinction grandit plus que l'état gazeux. Cet effet de dissolvant est le plus grand à l'alcool éthylique qui est le plus polaire dans nos dissolvants employés, et le moindre à l'heptane normal. L'extinction en solution de tétrachlorure de carbone est plus grande qu'on la prévoit au point de vue de sa polarité. Cette anomalie peut être aussi observée au cas de benzène dissous dans ce dissolvant.⁽⁶⁾

Le spectre d'absorption du $C_{10}H_{10}$ est semblable à celui du C.O.T. et n'a ni de structure fine, ni de bande sélective dans la région visible. Nous pouvons probablement conclure que les bandes d'absorption produites par le $C_{10}H_{10}$ à 280 $m\mu$ et à 280 $m\mu$ correspondent respectivement aux bandes de 280 $m\mu$ et de 200 $m\mu$ déjà montrées par C.O.T.. La couleur du $C_{10}H_{10}$ est jaune plus foncée que celle du C.O.T.. L'extinction moléculaire du $C_{10}H_{10}$ est 18 à la longueur d'onde 400 $m\mu$, tandis que celle du C.O.T. est 8. L'extinction moléculaire dans la région ultraviolette est donnée à la table 1.

Nous avons encore étudié l'influence de l'iode sur le spectre d'absorption du C.O.T.. Le coefficient d'absorption du C.O.T. donne une tendance à croître dans sa solution de heptane normal et celle de tétrachlorure de carbone lorsqu'on y ajoute l'iode, savoir: dans la solution de heptane normal, quand la concentration du C.O.T. est 2.03×10^{-3} mol/l. et celle d'iode est 1.97×10^{-3} mol/l, l'extinction moléculaire ϵ du C.O.T. change à 315 à la longueur d'onde 280 $m\mu$. D'autre part, dans la solution de tétrachlorure de carbone, où la concentration du C.O.T. est 2.08×10^{-3} mol/l. et celle d'iode est 1.98×10^{-3} mol/l., du C.O.T. change de 250 à 430 à 280 $m\mu$. Ces valeurs de ϵ ,

(4) T. Uémura, Y. Inamura, Y. Kondo et K. Morinaga, *J. Chem. Soc. Japan* **72**, 650 (1951).

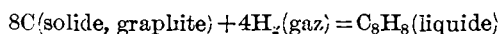
(5) B. H. Eccleston, H. J. Coleman et N. G. Adams, *J. Am. Chem. Soc.*, **72**, 3866 (1950).

(6) V. Henri, *J. phys. et rad.*, **3**, 181 (1922).

influencées ne sont qu'environ le double de celle du C.O.T. qui ne contient pas l'iode. Ces résultats nous montrent le peu d'influence de l'iode sur le C.O.T.. Mais, au cas du benzène, la valeur ε influencée par l'iode varie 30 fois plus que celle du cas sans l'addition de l'iode.⁽⁷⁾ Cette conclusion nous conduit à penser que la structure électronique du C.O.T. est différente de celle des composés aromatiques comme le benzène et le toluène, malgré que le C.O.T. ait les liaisons doubles conjuguées dans sa molécule.

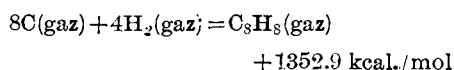
Discussion

Nous avons déjà calculé la structure électronique du C.O.T.⁽²⁾ et avons examiné le spectre d'absorption de la même substance. Nous n'exposons maintenant que son énergie de résonance. La chaleur de formation du C.O.T. est expérimentalement donnée par Prosen et ses collaborateurs.⁽⁸⁾



$$\Delta H(298.16^\circ K) = +60.82 \pm 0.32 \text{ kcal./mol}$$

On peut montrer la chaleur de formation aux états gazeux,



car les énergies de liaison pour C—C, C=C et C—H sont respectivement données par 60.3 kcal., 102.9 kcal. et 87.13 kcal., la chaleur de formation pour C₈H₈ est donc dérivée à 1350 kcal. en utilisant celles ci-dessus exposées. L'énergie de formation et celle de liaison. Cette énergie de résonance montre la valeur de 7-8% de celle de benzène.

Nous avons fait la calculation de l'énergie de résonance du C.O.T. par deux méthodes approximatives, une la méthode de HLSP,⁽⁹⁾ et l'autre, elle de HMM.⁽¹⁰⁾

(1) Méthode de HLSP

$$\alpha = \int \Psi_1(1)\Psi_2(2)\Psi_3(3)\Psi_4(4) \dots \\ H\tilde{\Psi}_1(2)\tilde{\Psi}_2(1)\tilde{\Psi}_3(3)\tilde{\Psi}_4(4) \dots d\tau \\ \alpha' = \int \Psi_1(1)\Psi_2(2)\Psi_3(3)\Psi_4(4) \dots \\ H\tilde{\Psi}_1(1)\tilde{\Psi}_2(3)\tilde{\Psi}_3(2)\tilde{\Psi}_4(4) \dots d\tau$$

Si on prend 1.5 e.V. pour la valeur de α , on a pour l'énergie de résonance suivante:

Table 2

	$\alpha' = 0.25\alpha$	$\alpha' = 0.3\alpha$	$\alpha' = 0.35\alpha$
énergie de résonance	1.73 kcal.	2.47 kcal.	3.46 kcal.

Comme on voit dans la table précédente, plus l'énergie commutative grandit, plus l'énergie de résonance augmente.

(2) Méthode de HMM⁽¹¹⁾

$$8 | \varepsilon(C_2H_2) | = 8\varepsilon_E \frac{1}{\sigma} (Q + R_1) = 23.606 \text{ e. V.}$$

$$| \varepsilon(C.O.T.) | = | 2\varepsilon_1 + 4\varepsilon_2 + 2\varepsilon_3 | \\ = 2 \frac{1}{\sigma_1} \{ Q - R_1 - R_7 \} + 4 \frac{1}{\sigma_2} \left\{ Q + \frac{1}{S} R_1 + \frac{k}{S} R_7 \right\} \\ + 2 \frac{1}{\sigma_3} \{ Q + R_1 + R_7 \} = 23.735 \text{ e. V.}$$

où

$$\varepsilon_i = \int \varphi_i H \varphi_i^* d\tau$$

$$Q = - \int I H I d\tau$$

$$R_1 = - \int I V_I I d\tau$$

$$R_7 = - \int I V_{VII} d\tau$$

comme les facteurs normalisés:

$$\sigma_1 = 1 + d_1 + d_7 + 2d_2$$

$$\sigma_2 = 1 + \frac{1}{S} d_1 + \frac{k}{S} d_7$$

$$\sigma_3 = 1 + d_1 - d_7 - 2d_2$$

$$\sigma = 1 + d_1$$

les intégrales sont les suivants:

$$d_1 = \int I II d\tau$$

$$d_2 = \int I III d\tau$$

$$d_7 = \int I VIII d\tau$$

L'explication des signes utilisés dans ces équations se trouve dans notre mémoire précédent.⁽¹⁰⁾

Par cette calculation l'énergie de résonance

(7) H. A. Benesi et J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2707 (1949); R. S. Mulliken, *ibid.*, **72**, 600 (1950).

(8) E. J. Prosen, W. H. Johnson et F. D. Rossini, *J. Am. Chem. Soc.*, **69**, 2068 (1947); **72**, 626 (1950).

(9) La méthode de HLSP signifie l'abréviation de celle de Heitler-London-Slater-Pauling.

(10) La méthode de HMM est ainsi celle de Hund-Mulliken-Hückel.

(11) ce bulletin, **23**, 168 (1950).

devient à peu près 3 kcal., qui est environ 8% de celle de benzène.

C'est entendu que le C.O.T. n'a guère le caractère aromatique en considérant du point de vue de l'énergie de résonance ainsi les autres propriétés physico-chimiques. Les spectres d'absorption du C.O.T. et du $C_{10}H_{10}$ sont semblables l'un et l'autre et on en conclut que les deux composés ont aussi la structure pareille. Nous continuons encore à étudier les propriétés du $C_{10}H_{10}$ et nous avons l'intention de publier bientôt le résultat de nos recherches.

Résumé

(1) Nous avons mesuré les spectres d'absorption du C.O.T. et du $C_{10}H_{10}$ à l'état gazeux et en solution.

(2) Deux bandes d'absorption se trouvent dans la région ultraviolette et elles ne donnent pas de structure fine.

(3) Les deux bandes du $C_{10}H_{10}$ correspondent à celles du C.O.T., mais celles-là sont

plus bathochromiques et, en même temps, plus hyperchromiques que celles-ci.

(4) L'effet de dissolvant du C.O.T. par l'alcool éthylique est le plus grand parmi tous les dissolvants employés.

(5) Le coefficient d'absorption du C.O.T. à la longueur d'onde à $280 m\mu$ croît un peu lorsqu'on y ajoute l'iode.

En terminant ce compte-rendu, nous avons à exprimer nos sincères remerciements au professeur S. Murahashi et au Dr. N. Hagiwara à l'Institut de Recherche scientifique et industrielle de l'Université d'Osaka, pour nous avoir offert les matières utilisées dans nos recherches actuelles, au Dr. S. Shida qui nous a bien encouragé pendant nos expériences, et, en même temps, au ministère de l'Instruction publique qui nous a aidés en se chargeant des frais de nos recherches.

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On the Mono-molecular Layer of α -Aminolauric Acid Polymer

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(Received March 17, 1951)

Introduction

The researches which have been made on the monolayers of various high polymers, natural and synthetic, for the past twenty years gave many valuable suggestions on the chemical structures of these polymers, above all, of natural proteins.

This short paper describes the results of surface pressure and potential measurements on films of α -aminolauric acid polymer which was synthesized as a protein-like high polymer. This polymer was chosen because it contains nonpolar lauric acid residue only as the side chain and electrical properties of the film are mainly ascribed to that of its polypeptide portions.

Experiment

Force-area relations were measured with a Langmuir-Adam surface balance of which sensitivity is 0.3 dyne. The surface potential was measured simultaneously with a dynamic electro-

meter.⁽¹⁾ The brass tray used was heavily coated with paraffine. α -Aminolauric acid polymer was synthesized in the laboratory of Dr. H. Tani and Dr. J. Noguchi by the method of N-carbonic acid anhydride of amino acid. The molecular weight determined by the osmotic pressure measurement was 172,000, and the mean polymerization degree was 870.⁽²⁾ It was spread on the water surface from benzene solution. Various pH solutions, and ammonium sulfate solutions were used as the substrates. All experiments were done at room temperature which was never above 15° or below 10°.

Results

Fig. 1 gives the results on distilled water, on *N*/100 HCl solution, and on *N*/100 NaOH solution. Full curves show the surface pressure, *F*, and the broken lines show the surface

(1) Cf., Rosenfeld and Hoskins, *Rev. Sci. Inst.*, **16**, 343 (1945).

(2) H. Tani and J. Noguchi, *Jour. High Polymers, Japan*, **8**, 51 (1951).

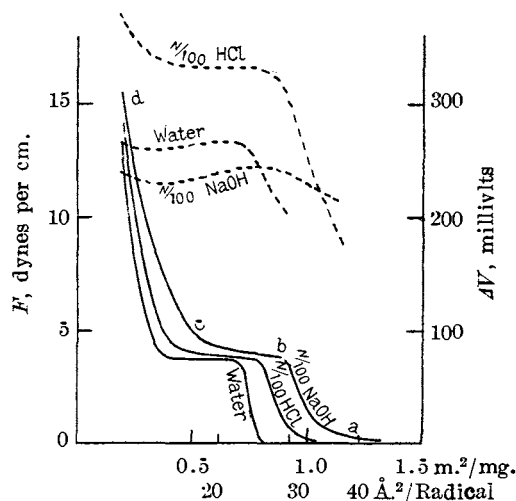


Fig. 1.—Various pH solutions.

potential change, ΔV , due to the films.

The whole shape of the curve resembles that of the transition curve shown by fatty acids. Each of the surface pressure area curves consists of three portions, a-b, b-c, and c-d. As the films on dilute solutions are highly compressible in the region, b-c, the curves are almost completely flat. The surface potential values fluctuate at large areas, but are stabilized at the concentration at which the surface pressure appeared (point a). On further compression lauric acid residues rise out of water surface and the surface potential increases rapidly up to a value at point b. It may be considered that in the highly compressible state, b-c, some transitions occur in the polypeptide main chain to form more compact structure. The nearly constant value of the surface potential in this region means that the compact form has a smaller normal dipole moment. The area decreased further, the surface pressure increases rapidly (point c). This sharp rise in surface pressure with compression indicates that at this point all the lauric acid residues are out of water and are packed closely as

possible. The cross sectional area of a lauric acid radical is about $20 \text{ \AA}^2$ or less at zero compression. The effect of the hydroxyl ions on the spreading of the polypeptide is greater than that of the hydrogen ions. The values of the vertical component of the dipole moment per radical at point b are given below,

on distilled water	2.0×10^{-19} e.s.u. per radical
on N/100 HCl	2.8 "
on N/100 NaOH	2.3 "

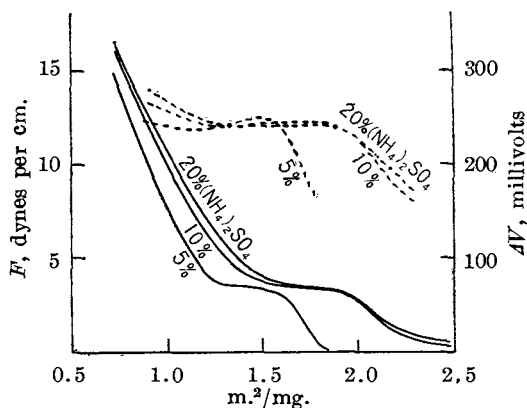


Fig. 2.—Salt solutions.

Fig. 2 exhibits the effect of salt concentrations of the substrate on the spreading. It seems probable that the large areas on the substrates of the increased concentrations are due to the adsorption of the salt ions.

The authors are grateful to Prof. B. Tamamushi for his kind guidance, and besides, to Dr. H. Tani and Dr. J. Noguchi for the provision of the polymer sample used in this work. A part of the expense of this study was defrayed from the Scientific Research Grant of the Ministry of Education.

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On the Possibility of Concentrating Colloid by Means of Freezing at the Sedimentation Equilibrium State Attained in a Centrifugal Field

By Tominosuke KATSURAI

(Received April 10, 1951)

In this note a suggestion has been made that the freezing of a colloid at the sedimentation equilibrium state attained in a centrifugal field could possibly be utilized as a means to concentrate the colloid. The argument is confined to the case in which the dispersion medium is water, and in which the concentration and molecular weight of the colloid, as well as the concentration of the electrolyte present in the colloid, are small.

The colloid is put into a cell and subjected to centrifuging (Fig. 1). After the sedimentation equilibrium has been reached, the temperature is lowered and the colloid in the cell

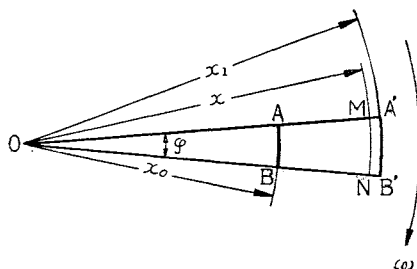


Fig. 1.

is frozen. Centrifuging is then stopped and the frozen colloid is taken out of the cell and the part near the bottom is removed. This is put to stand at a temperature slightly above zero and the frozen colloid is brought back to a sol which has a concentration greater than the initial one. Starting from the ample quantity of the colloid and by repeating the procedure, it is possible to get a colloid of very high concentration, if the colloid does not change by being subjected to the freezing-thawing treatment.

There are two factors which might influence the course of freezing of the colloid. They are hydrostatic pressure and concentration gradient. We know that the freezing point of water is lowered under pressure. The hydrostatic pressure of the colloid is the smallest at the top of cell AB and increases with x . Thus, when the temperature is lowered in equilibrium, ice formation will start at the top

and then proceeds gradually along Ox . The fact that ice is lighter than water will also favor the tendency. In a dilute solution, the freezing point lowering is proportional to concentration. From this fact we understand that the freezing point of the colloid is the highest at the top AB and that it becomes lower with the increase of x . Thus, both the hydrostatic pressure and the concentration gradient favor the ice formation from the top AB toward the bottom A'B', acting in the tendency to enhance the concentration gradient.

How far the colloid is concentrated by this procedure can be estimated as follows: Let us consider the colloid in AA'B'B. The thickness of cell is taken as unity. The concentration gradient in the sedimentation equilibrium is given by

$$\frac{c}{c_0} = \frac{\alpha(x_1^2 - x_0^2)}{e^{\alpha x_1^2} - e^{\alpha x_0^2}} \cdot e^{\alpha x^2}, \quad (1)$$

where c =concentration of colloid, c_0 =initial concentration of colloid, x =distance from the axis of rotation, $x_0=OA$, $x_1=OA'$, φ =sector angle, s =sedimentation constant of colloid, D =diffusion constant of colloid, ω =angular velocity, and $\alpha = \frac{s\omega^2}{2D}$.

If we could take out the colloid contained in the part MA'B'N near the bottom of cell without disturbing the concentration gradient, then we have a colloid having a concentration greater than c_0 . As a measure of the increase of the concentration, we make use of the local average concentration, a function of x , defined by

$$\bar{c}(x) = \frac{\text{total amount of colloid in MA'B'N}}{\text{volume of MA'B'N}},$$

(1) S. Oka, *Proc. Phys.-Math. Soc. Japan*, **18**, 522 (1936). This formula was derived as the solution of a special case ($\partial c / \partial t = 0$) of Lamm's differential equation of ultracentrifuging. A formula essentially the same, but without explicit use of sedimentation constant and diffusion constant, was given by Rinde before the publication of Lamm's equation. (Cf. H. Rinde, Dissertation, p. 176 (Upsala, 1928)). Oka's equation is used herewith for the sake of convenience.

$$\bar{c} = \frac{\int_0^\varphi \int_{x_1}^x c x dx d\varphi}{\frac{1}{2} \varphi (x_1^2 - x^2)} \quad (2)$$

This gives the average concentration of the colloid in MA'B'N at sedimentation equilibrium, and the ratio $\bar{c}/c_0$ gives the relative increase of the concentration. By means of (1), we obtain

$$\frac{\bar{c}}{c_0} = \frac{x_1^2 - x_0^2}{e^{\alpha x_1^2} - e^{\alpha x_0^2}} \cdot \frac{e^{\alpha x_1^2} - e^{\alpha x^2}}{x_1^2 - x^2} \quad (3)$$

We see from this that

$$[\bar{c}]_{x=x_0} = c_0, \quad \lim_{x \rightarrow x_1} [\bar{c}] = [c]_{x=x_1}$$

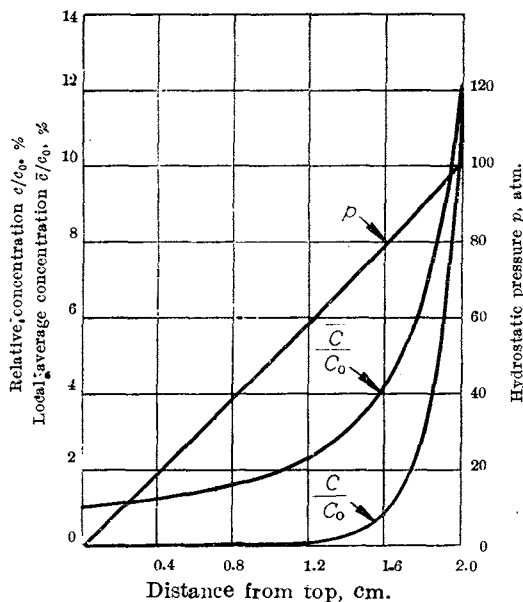


Fig. 2.

and $\bar{c} > c$ for $x_1 > x > x_0$.

For the sake of illustration, an example is given. Put $M=10,000$, $V=0.75$, $\rho=1.00$, $x_0=5.0$ cm., $x_1=7.0$ cm., and r.p.m.=30,000 or $\omega=3,140$, where M =molecular weight, V =partial specific volume, and ρ =density. In order to use the formula (3), it is necessary to know the value of s/D . We find this by means of the sedimentation velocity formula

$$\frac{s}{D} = \frac{M(1-V\rho)}{RT}$$

where R and T have their usual meanings. Using the above data and assuming that $T=288$ we have $s/D=1.044 \times 10^{-7}$. The results obtained by using this value are given in Fig. 2.

The hydrostatic pressure p in the cell is given as a function of x by the following relation

$$p = \frac{\rho \omega^2}{3} \left(\frac{x^3 - x_0^3}{x} \right) \quad (4)$$

The values of p calculated by this formula is also given in Fig. 2. From the Clausius-Clapeyron equation we understand that for the ice at 0° , the rate of freezing point lowering is -0.0076° per atmosphere. We see from Fig. 2 that the difference of freezing points at AB and A'B' is about 0.8° corresponding to the hydrostatic pressure difference 101 Atm.

In conclusion, the author wishes to express his cordial thanks to Professor Ole Lamm of Kungl. Tekniska Högskolan, Stockholm for his valuable remarks.

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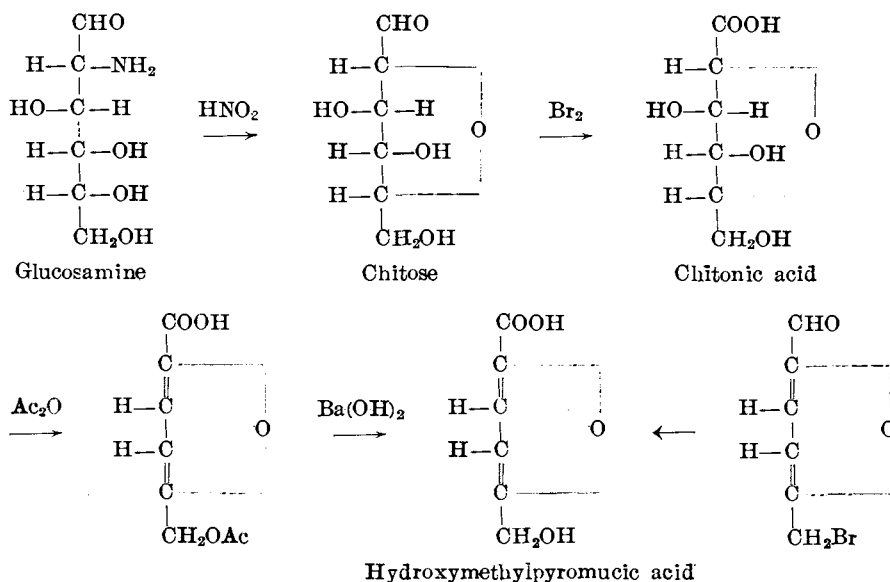
Studies on Amino-hexoses. II. The Mechanism of the Formation of So-called Chitose from Glucosamine

By Yoshio MATSUSHIMA

(Received September 18, 1950)

The reaction of nitrous acid upon glucosamine (2-amino-2-desoxyglucose) does not proceed, as expected from our "common" knowledge, to the production of glucose or mannose but to the production of so-called chitose. Fischer and Tiemann⁽¹⁾ obtained an acid which they called chitonic acid as its calcium salt by the bromine oxidation of the sugar-like substance which was formed from glucosamine by the action of nitrous acid and named by them chitose. Later, Fischer and Andreae⁽²⁾ treated chitonic acid with acetic anhydride and sodium acetate and obtained hydroxymethyl-pyromucic acid, the constitution of which was confirmed by Haworth, Hirst and Nicholson⁽³⁾ through its preparation from ω -bromo-5-methyl-furfural. Fischer and Andreae⁽²⁾ proposed the 2,5-anhydro-hexose structure for chitose from the elementary composition of chitonic acid and the reactions mentioned above which can be summarized as follows:

The "abnormal" behavior of glucosamine toward nitrous acid caused several workers to repeat the Fischer's experiment and the complicated results have been reported. Armbrecht⁽⁴⁾ believed that he obtained a hexosazone which was different from glucosazone, but the formation of osazone must be impossible if chitose has the structure mentioned above. Zechmeister and Toth⁽⁵⁾ reported the formation of glucose and they attributed the non-fermentability of the deamination mixture to the co-existence of some inhibitory substance. Schorigin and Makarowa-Semljanskaya⁽⁶⁾ approved of the Fischer's result and obtained the crystalline diphenylhydrazone of chitose. The complexity of the results let the authors of the text-books of sugar chemistry state that "Unsere bisherigen Kenntnisse von der chitose sind recht lueckenhaft. Auch Zweifel an der Einheitlichkeit des Produktes erscheinen berechtigt,"⁽⁷⁾ or "Die Chemie der Chitose bedarf jedoch noch einer eingehenden Bearbeitung."⁽⁸⁾



(1) E. Fischer and F. Tiemann, *Ber.*, **27**, 138 (1894).

(2) E. Fischer and F. Andreae, *Ber.*, **36**, 2587 (1903).

(3) W. N. Haworth, E. L. Hirst and V. S. Nicholson, *J. Chem. Soc.*, **1927**, 1513.

(4) W. Armbrecht, *Biochem. Z.*, **95**, 108 (1919).

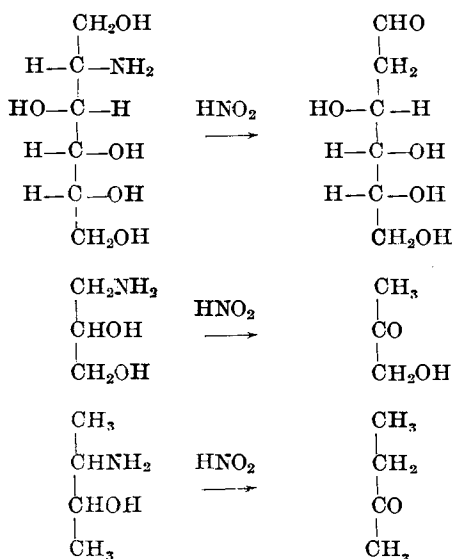
(5) L. Zechmeister and G. Toth, *Ber.*, **66**, 522 (1933).

(6) P. Schorigin and N. N. Makarowa-Semljanskaya, *Ber.*, **68**, 965 (1935).

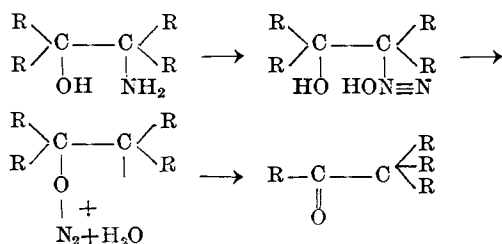
(7) Tollens-Elsner, "Kurzes Handbuch der Kohlenhydrate", 1935, S. 521.

(8) F. Michael, "Chemie der Zucker und Polysaccharide," 1939, S. 161.

However, the author's deamination experiment on glucosaminol, the hydrogenated product of glucosamine, and on some model substances, together with the search into literatures enabled him to put a reasonable interpretation upon the formation of chitose from glucosamine. The author found that glucosaminol, when treated with nitrous acid, did not produce any trace of sorbitol nor mannitol. The reaction mixture exhibited a reducing action upon Fehling's reagent and crystalline diphenylhydrazone was isolated from it. This was identified with the diphenylhydrazone of 2-desoxy-glucose. The experiments on two model substances proceeded equally on the same line with glucosaminol. Thus, 1-amino-propane-diol-(2,3) produced acetol and 2-amino-butanol-(3) produced methylethylketone when treated with nitrous acid.



McKenzie⁽⁹⁾,⁽¹⁰⁾ first observed the "abnormal" reaction of nitrous acid upon α -hydroxylamines and named the reaction "semi-pina-colic deamination" and explained the reaction by the following scheme.



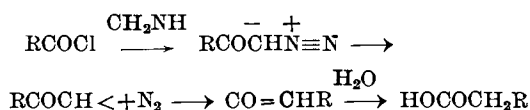
(9) A. McKenzie, *J. Chem. Soc.*, **123**, 79 (1923).

(10) A. McKenzie, *J. Chem. Soc.*, **125**, 814 (1924); cf. A. McKenzie and W. S. Dennler, *J. Chem. Soc.*, **125**, 2105 (1924); A. McKenzie and A. K. Mills, *Ber.*, **62**, 284 (1929); A. McKenzie and A. D. Wood, *Ber.*, **71**, 358 (1938).

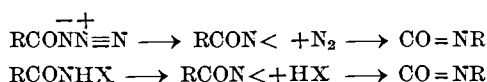
Several workers⁽¹¹⁾ have been engaged in the works of this line and the mobility of radicals has been discussed.

On the other hand, the "abnormal" reaction of nitrous acid upon common amines has been observed for a long time. Meyer and Forster⁽¹²⁾ reported the production of iso-propyl alcohol beside *n*-propyl alcohol when *n*-propyl amine was deaminated with nitrous acid. Freund and Schoenfeld⁽¹³⁾ observed the production of olefinic hydrocarbon $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}_6\text{H}_{13}$ and tertiary alcohol $(\text{CH}_3)_2\text{C}(\text{OH})\text{C}_6\text{H}_{13}$ from the amine $\text{NH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{C}_6\text{H}_{13}$. According to Levy and Gallais⁽¹⁴⁾ $\text{Ph}_2\text{CHCH}_2\text{NH}_2$ gives stilben $\text{PhCH}=\text{CHPh}$. Enlargement of the ring is reported by Wallach⁽¹⁵⁾ and Ruzicka⁽¹⁶⁾ when amino-methyl cyclo-paraffin is treated with nitrous acid.

The author's interpretation of these "abnormal" reactions originates in the Arndt-Eistert's⁽¹⁷⁾ synthesis of carboxylic acid homologues:



The reaction mechanism has an analogy in the Curtius' degradation of acid azide or in the Hofmann's degradation of acid amide.



In these reactions the intermediate bivalent radicals cause the rearrangements of atomic groups. The reactions of amines with nitrous acid can also be interpreted in the light of the same reaction mechanisms which are summarized as follows (the upper schema of p. 146).

McKenzie⁽⁹⁾ has already pointed out the similarity between glucosamine and α -hydroxylamines in respect of "unusual" behavior toward nitrous acid but he could not interpret explicitly the formation of 2,5-anhydro-ring in chitose. The author offers the following mechanism for the formation of chitose.

- (11) M. Tiffeneau and J. Lévy, *Compt. rend.*, **183**, 969 (1926); *C. A.*, **21**, 908 (1927); M. Migita, *This Bulletin*, **3**, 308 (1928); S. Kanoo and T. Yaguchi, *J. Pharmac. Soc. Japan*, **48**, 232 (1928); A. K. Mills, *J. Chem. Soc.*, **1934**, 1565; M. Tiffeneau, J. Lévy and E. Détz, *Bull. Soc. Chim.*, **2**, 1871 (1935); *C. A.*, **30**, 1781 (1936).
- (12) V. Meyer and F. Forster, *Ber.*, **9**, 535 (1876).
- (13) M. Freund and F. Schoenfeld, *Ber.*, **24**, 3350 (1891).
- (14) J. Lévy and P. Gallais, *Bull. Soc. Chim.*, **43**, 862 (1928); *C. A.*, **22**, 4504 (1928).
- (15) O. Wallach, *Ann.*, **353**, 325 (1907).
- (16) L. Ruzicka, *Helv.*, **9**, 399 (1926).
- (17) F. Arndt and B. Eistert, *Ber.*, **68**, 200 (1935).

10 g. of the hydrochloride is dissolved in 10 cc. of water and 5 g. of diethyl amine is added slowly. After adding 150 cc. of alcohol, the rubbing of the wall accelerates the growth of crystals. The colorless crystals of the free base thus obtained are quite free from chlorine and melt at 131-132°. The yield amounts to 75% of theory.

Deamination of Glucosaminol.—6.0 g. of glucosaminol (free base) dissolved in 50 cc. of water is added with 3 g. of sodium nitrite dissolved in 50 cc. of water and then with 3 cc. of acetic acid. Evolution of nitrogen gas ceases after over-night standing at room temperatures. The reaction mixture is concentrated *in vacuo* and is added with 2 g. of diphenylhydrazine dissolved in 5 cc. of alcohol. After an over-night standing the rubbing of the wall accelerates crystallization. The crystals thus obtained weigh 2.6 g. and melt at 175-177°. 0.2 g. of the same substance is recovered from the mother liquor. The substance which melts at 178-179° after being recrystallized twice from 96% alcohol shows no melting point depression when mixed with the diphenylhydrazone of 2-desoxyglucose which is prepared from D-glucal following the method of Bergmann, Schotte and Lechinsky.⁽²¹⁾ Analyses give the following results:

Found: C, 65.56; H, 6.74.
Calcd. for $C_{15}H_{22}O_4N_2$: C, 65.44; H, 6.71.

Preparation of 1-Amino-propane-diol and 2-Amino-butanol-(3). (a) 1-Amino-propane-diol was prepared following the method of Knorr⁽²²⁾ taking account of the report of Hirata.⁽²³⁾ The substance boiling at 140-141°/9 mm. in redistillation is colorless viscous liquid which has no reducing action toward Fehling's reagent or ammoniacal silver solution.

(b) 2-Amino-butanol-(3) was prepared following the method of Strauss⁽²⁴⁾ which was somewhat modified.

Diacetyl monoxime is reduced with sodium amalgam under cooling with ice and salt in acid conditions. The reaction mixture is made alkaline and extracted with ether in a automatic apparatus for 5 days. The substance boiling at 53.5-55.5°/7 mm. in redistillation is colorless viscous liquid which has a pyridine-like odor. The yield is 2.3 g. from 5 g. of diacetyl monoxime.

Deamination of 1-Amino-propane-diol and 2-Amino-butanol-(3). (a) 10 g. of 1-amino-propane-diol is dissolved in 50 cc. of water and the solution of 8.5 g. sodium nitrite in 10 cc. water is added. 25 cc. of 6 N-sulfuric acid is dropped into the mixture under stirring and ice-water cooling. After letting it stand for 4.5 hours at room temperatures hydrogen gas is passed until no trace of nitrous acid remains. Van Slyke amino deter-

mination carried out with a portion of the reaction mixture reveals that 2.8 g. of the starting amino-alcohol remains intact. The reaction mixture which exhibits now a strong reducing action upon Fehling's reagent or upon ammoniacal silver solution is neutralized with barium carbonate and the filtrate from barium sulfate is divided into two equal portions. One is treated with phenylhydrazine acetate and the other with semicarbazide. Precipitation takes place immediately in each case and the yield of raw phenylosazone of acetol melting at 137° with decomposition is 2.28 g. and that of semicarbazone melting at 197.5° with decomposition is 1.09 g. The yield of both derivatives of acetol corresponds to about 20% of the starting amino-alcohol consumed. The osazone melts at 146.5-147° with decomposition when once recrystallized from alcohol. The analyses give the following results:

Found: C, 71.75; H, 6.47; N, 22.42.
Calcd. for: $C_{15}H_{16}N_4$ C, 71.40; H, 6.39; N, 22.21.

The semicarbazone melts at 197-198° with decomposition when once recrystallized from water. The analyses give the following results:

Found: C, 36.54; H, 7.21; N, 32.56.
Calcd. for: $C_4H_9O_2N_3$ C, 36.66; H, 6.91; N, 32.04.

(b) 1.06 g. of 2-amino-butanol-(3) is dissolved in 10 cc. of water and the solution of 1.4 g. of sodium nitrite in 15 cc. of water is added. 3 cc. of acetic acid is dropped at room temperatures into the mixture under stirring. After an over-night standing the mixture is neutralized with sodium hydroxide to a pH value of 5 and distilled to about 80% of the whole. The distillate upon treatment with dimedone solution gives a precipitate which may, be isobutylaldomedone⁽²⁵⁾ but can not be identified owing to the small amount of the material. The mixture is again distilled and the distillate is now added with acetic solution of *p*-nitrophenylhydrazine. Precipitation takes place immediately. The yellow crystals thus formed weigh 0.88 g. and melt at 90-100°. After being recrystallized three times the specimen melts at 124-124.5° alone or at 125-126° with the authentic specimen of *p*-nitrophenylhydrazone of methyl ethyl ketone which melts at 127.5-128°. Analyses give the following results:

Found: N, 20.37.
Calcd. for $C_{10}H_{15}C_2N_3$: N, 20.28.

The author expresses his gratitudes for the guidance of Prof. Dr. S. Akabori and for the assistance from Mr. K. Okawa and Mr. T. Ikenaka.

Science Department, Osaka University, Osaka

(21) M. Bergmann, H. Schotte and W. Lechinsky, *Ber.*, **55**, 165 (1922).

(22) L. Knorr and E. Knorr, *Ber.*, **32**, 750 (1899).

(23) Y. Hirata, K. Inukai and T. Tsujituchi, *J. Chem. Soc. Japan*, **69**, 59 (1948).

(24) F. Strauss, *Ber.*, **33**, 2827 (1900).

(25) S. Akabori, *J. Chem. Soc. Japan*, **59**, 1192 (1938).

Equilibrium of the $\text{CO}_2\text{-NH}_3\text{-Urea-H}_2\text{O}$ System under High Temperature and Pressure. I. Equilibrium Pressure of Reaction in Urea-Synthesis from Ammonia and Carbon Dioxide

By Schohachi KAWASUMI

(Received December 18, 1950)

Introduction

In general, it is said that a content in a reaction vessel for the synthesis of urea from ammonia and carbon dioxide under high temperature and pressure is separated into two phases of melted solution and vapor.⁽¹⁾ But no one, so far as I know, has succeeded in analyzing plainly the equilibrium between the two phases in spite of the importance of industrial production of urea.

The writer has studied the equilibrium between the two phases of the $\text{CO}_2\text{-NH}_3\text{-Urea-H}_2\text{O}$ system under high temperature and pressure.

The relations between the temperature and the equilibrium pressure of the reaction have been studied by several investigators.⁽¹⁻⁴⁾ The reported values as shown in Fig. 1 are divergent, while the experimental values⁽⁵⁾ of the decomposition pressure of ammonium carbamate in the temperature range 10° to 80° are relatively fixed.

This paper covers a study of the equilibrium pressure of the reaction, in which loading mol ratio of carbon dioxide to ammonia is one by two, at the temperature range 130° to 170° , that is to say, in the absence of an excess of either reactant.

The experimental results showed that the equilibrium pressure depends upon the loading density or ratio of the weights of the materials to the total volume of the reaction vessel at a given temperature. From this experimental facts the writer discusses the relations among the temperature, the equilibrium pressure and the loading density.

Experiment

The apparatus used for pressure measurements

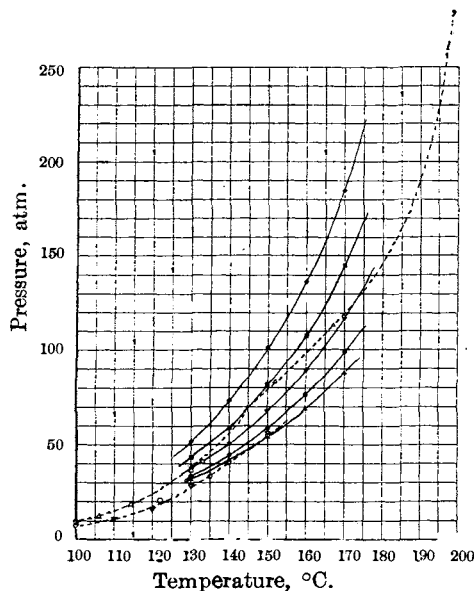


Fig. 1.—Pressure-temp. curves of the $\text{CO}_2\text{-NH}_3\text{-Urea-H}_2\text{O}$ system. Loading density g./cc. of the present measurement: $\blacklozenge$, 1.0; $\blacksquare$, 0.8; $\blacktriangledown$, 0.6; $\bullet$, 0.4; $\blacktriangle$, 0.2. Results given by other investigators: $\triangle$, Briner⁽²⁾; $\square$, Fichter and Becker⁽³⁾; $\circ$, Matignon and Fréjacques⁽¹⁾; $\triangledown$, Tokuoka⁽⁴⁾.

is shown in Fig. 2. The reaction vessel is made of steel with lead-lining and capacity is approximately 800 cc. For measuring pressure, the mercury trap of 20 cc. volume was fixed between the reaction vessel and the Bourdon pressure gauge to prevent condensation of ammonium carbamate in it. The reaction vessel and the mercury trap were both dipped in a thermoregulated oil bath and heated at a given temperature for 20 to 24 hours. The container was loaded with crystalline ammonium carbamate or equi-molal mixture of urea and water.

Ammonium carbamate was prepared from refined gaseous carbon dioxide and ammonia in a glass vessel at ordinary temperature and pressure.

The same equilibrium pressure was obtained from the carbamate side of the reaction and also from the urea-water side on the same basis of initial loading density. Therefore, the equilibrium

(1) Matignon and Fréjacques, *Compt. rend.*, **171**, 1003 (1920); *Bull. soc. chim.*, **31**, 394 (1922).

(2) Briner, *J. chim. phys.*, **4**, 266 (1906).

(3) Fichter and Becker, *Ber.*, **44**, 3473 (1911).

(4) Tokuoka, *J. Agr. Chem. Soc. Japan*, **11**, 174 (1935).

(5) Egan, J. E. Potts and G. D. Potts, *Ind. Eng. Chem.*, **38**, 454 (1946).

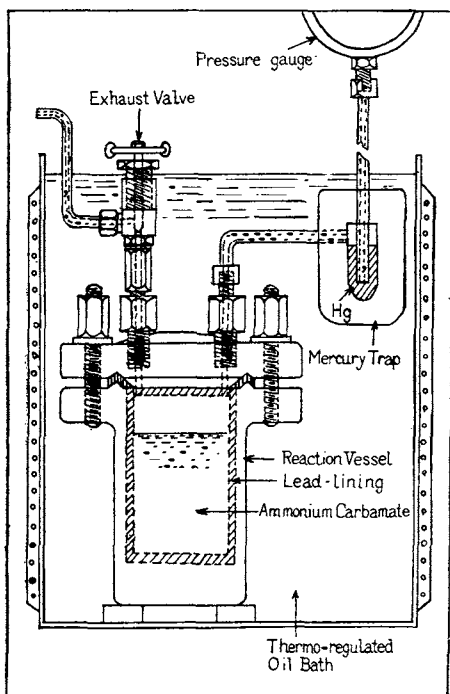


Fig. 2.—Apparatus for measuring the equilibrium pressure of the $\text{CO}_2\text{-NH}_3\text{-urea-H}_2\text{O}$ system. I.

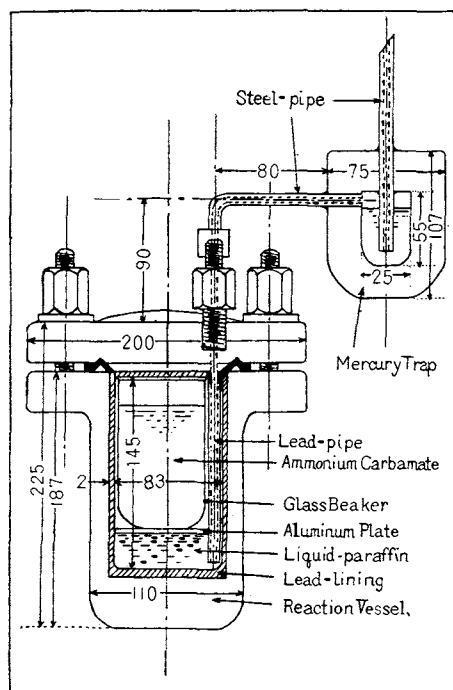


Fig. 3.—Apparatus for measuring the equilibrium pressure of the $\text{CO}_2\text{-NH}_3\text{-urea-H}_2\text{O}$ system. II.

pressure is constant regardless of the kinds of starting materials at a given temperature and loading density.

In the preliminary experiments, the equilibrium pressure was measured after eliminating a small amount of residual air in the reaction vessel by a vacuum pump at ordinary temperature in the beginning of the experiment and then the last residual air together with carbamate decomposition gas at 100° . But in the other experiments in which these procedures were omitted, the same results were also obtained. Therefore, as the effect of residual air for the equilibrium pressure is very small, these procedures were omitted.

The writer measured the equilibrium pressure in the apparatus of Fig. 3 which is more corrosion-resistant than that of Fig. 2. The following device was made so that corrosive gas might not touch the mercury trap and the steel-pipe connecting between the former and the reaction vessel. Because both of the mercury trap and the steel trap have no lead-lining. The apparatus of Fig. 3 has a lead-pipe of inner diameter 3 mm. and length 14 cm., jointing to the cover of the reaction vessel and reaching almost to the bottom of the vessel where 60 cc. of liquid paraffin is charged. Ammonium carbamate is loaded in a glass beaker through an aluminum plate on the liquid paraffin. At a high temperature, carbamate decomposition gas compresses the liquid paraffin which arrives at the mercury-trap through the lead-pipe and steel-pipe. Therefore the gas in the apparatus touches only the glass

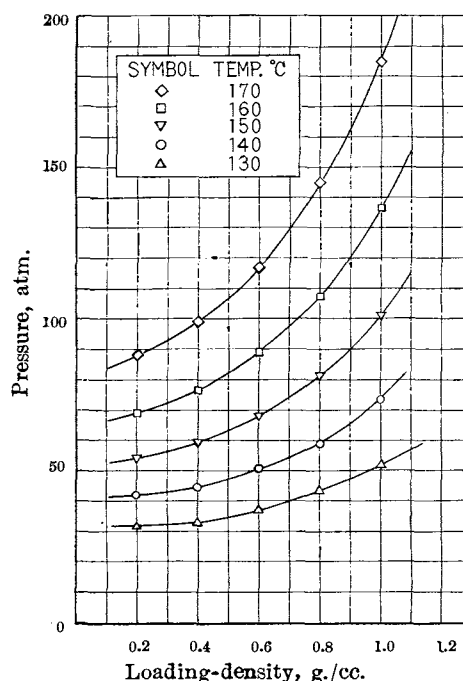


Fig. 4.—Equilibrium pressure-loading density curves of the $\text{CO}_2\text{-NH}_3\text{-urea-H}_2\text{O}$ system.

and lead wall, aluminum plate and liquid paraffin, and no steel wall.

The experimental results of this apparatus were of the same values as those obtained in the experiments of the apparatus of Fig. 2. Therefore, the effect of corrosion of carbamate decomposition gas for the equilibrium pressure is negligible. The writer usually used the apparatus of Fig. 2.

Experimental Results

Experimental results on the relation of the loading density and the equilibrium pressure over the temperature range 130° to 170° are shown in Figs. 1 and 4. At a given temperature the equilibrium pressure increases with the loading density. Table 1 gives the experimental equations which show the relation

Table 1
Experimental Equations for Equilibrium
Pressure-Temperature Relation of the
CO₂-NH₃-Urea-H₂O System

Loading density, g./cc.	Experimental equation $P = \text{atm.}, T = \text{absolute temp. } ^\circ\text{K.}$
0.20	$\log P = \frac{-1960}{T} + 6.366$
0.40	$\log P = \frac{-2139}{T} + 6.825$
0.60	$\log P = \frac{-2237}{T} + 7.117$
0.80	$\log P = \frac{-2369}{T} + 7.503$
1.00	$\log P = \frac{-2444}{T} + 7.781$

Table 2
Extrapolated Values of Equilibrium
Pressure at 180°, 200° and 250°C.

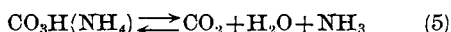
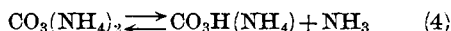
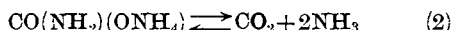
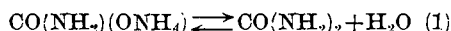
Loading density, g./cc.	Equilibrium pressure, atm.		
	180°C.	200°C.	250°C.
0.20	109	167	415
0.40	127	201	543
0.60	151	244	692
0.80	188	313	940
1.00	243	411	1280

between the temperature and the equilibrium pressure. Extrapolated values which were calculated at 180°, 200° and 250° from these equations are given in Table 2.

Discussion of Results

Matignon and Fréjacques⁽¹⁾ concluded already in 1920 that the system was bivariant, observing that the system consists of a vapor phase and a single homogeneous liquid phase,

and assuming the following five reactions in the system.



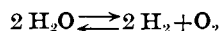
They conjectured that the equilibrium pressure was a function of ratio of volume of the reaction vessel to initial content of carbamate in it at a given temperature.

Nevertheless, they could not only show these facts in their own experiments, but also their explanation that the system is bivariant is a mistake because the equation (5) is deduced from the other equations (2), (3) and (4).

In general, diversity of equilibrium pressure is a character proper to "the thermal dissociation compounds" such as CO₂-NH₃-H₂O system.⁽⁶⁾

Supposing an equilibrium system of the thermal dissociation compound is charged in a sealed vessel with changeable volume by the movement of a piston, an isothermal increase of the volume induces the vaporisation of a part of the liquid phase. And if the volume decreases isothermally, a part of the vapor is condensed. In both cases, the total pressure of the system and the compositions of the liquid and gas phases undergo some change, although the total composition of the system remains as it is.

For example, pure water has a constant vapor pressure at a given temperature. If the water vapor decomposes into hydrogen and oxygen as the following equation at the temperature below the critical point,



hydrogen and oxygen would respectively dissolve into the liquid water with different solubility. Therefore, mol ratio of oxygen to hydrogen in the gas phase is not one by two and it will depend upon a ratio of initial content of water to volume of the vessel. At the same time the vapor pressure is indefinite and it will depend upon weight-volume ratio at the temperature.

By the above-mentioned qualitative explanation we can understand the diversity of the equilibrium pressure. In this paper the experimental results under the condition that

(6) "Gmelins Handbuch der Anorganischen Chemie," 23, Ammonium, p. 327, Verlag Chemie, G.m.b. H., Berlin, 1936.

loading mol ratio of carbon dioxide to ammonia is one by two have been described. In the next papers the writer will intend to report on the equilibrium pressure under such condition as loading mol ratio is less than one by two, that is, loading ammonia is in excess to carbon dioxide and the compositions of the liquid and gas phases quantitatively measured at various conditions of the loading density and the equilibrium pressure.

Summary

(1) In the study of the equilibrium pressure of the $\text{CO}_2\text{-NH}_3\text{-Urea-H}_2\text{O}$ system, it was experimentally found that the equilibrium pressure of the system is a function of loading density of reactants in the reaction vessel at a given temperature.

(2) The experimental equations that show the relation between temperature and equilibrium pressure were studied at various loading densities, under conditions that loading mol ratio of carbon dioxide to ammonia was one by two, and at the temperature range 130° to 170° .

(3) It was verified that the diversity of the equilibrium pressure of the system is reasonable.

The writer wishes to express appreciation for the kind guidance and the advice received from Prof. Shinjiro Kodama of Kyoto University and for the encouragement received from Dr. Kenji Fujimura, the chief of the Research Department, throughout this work.

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The Iodometric Determination of Propargyl Alcohol

By Kazumi YAMAMOTO, Minoru YOSHIMURA and Manzo TANAKA

(Received January 19, 1951)

Introduction

Our studies were conducted to estimate the quantities of propargyl alcohol in the reaction products which are formed by the reaction of formaldehyde and acetylene in accordance with the so-called "Reppe's alkynol synthesis".

As propargyl alcohol has the active methyne group, some of the well known analytical methods for the acetylenic compounds were employed. They did not give any satisfactory results, presumably either for the reason of the method itself being imperfect or by the interfering action of formaldehyde which usually remains in the product.

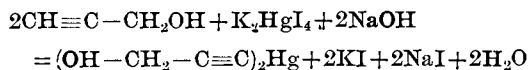
Our new method gave good results, especially, in the presence of formaldehyde too.

The Outline of the Several Methods Already Known:—(A) Argentometry of propargyl alcohol is not suitable in the case when formaldehyde is present as indicated by Hanna and Sigga.⁽¹⁾

(B) The methods^{2,3)} in which propargyl

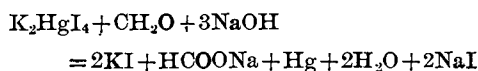
alcohol is precipitated as Cu-compound and then determined indirectly, are also not suitable, because the Cu-compound of propargyl alcohol precipitated with Ilosvay's reagent⁽⁴⁾ is not merely $\text{Cu}-\text{C}\equiv\text{C}-\text{CH}_2\text{OH}$ but the mixture with $\text{Cu}(\text{C}\equiv\text{C}-\text{CH}_2\text{OH})_2$, in proportion to the quantities of the reagent added.

(C) Potassium mercuric iodide method.⁽¹⁾ This method was recently proposed by Hanna and Sigga and gave good result for pure propargyl alcohol. The determination of propargyl alcohol is based on the following reaction.



We have observed, however, that this method is not applicable too, in the presence of formaldehyde of more than 0.5%.

According to our experiments, the reaction between formaldehyde and potassium mercuric iodide is expressed as follows:—



(1) Hanna and Sigga, *Anal. Chem.*, **21**, 1469 (1949).

(2) Hein and Meyer, *Z. Anal. Chem.*, **72**, 30 (1927).

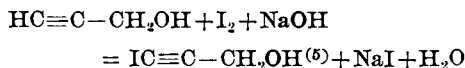
(3) Willstätter, *Ber.*, **53**, 936 (1920).

(4) Ilosvay, *Ber.*, **32**, 2697 (1910).

In case both propargyl alcohol and formaldehyde are present, however, the stoichiometric relation between formaldehyde and potassium mercuric iodide indicates considerable deviation.

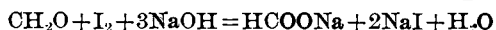
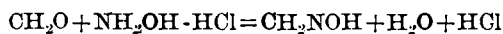
Our New Method

We observed that one mole of propargyl alcohol reacts with one mole of iodine quantitatively in alkaline solution and this reaction proceeds as follows:—



So, the excess of iodine may be backtitrated with standard thiosulfate solution after acidification. The result obtained has agreed well with the one by Hanna's method as shown in the following tables.

If the sample contains formaldehyde, which also reacts with iodine quantitatively as already known, the quantity of propargyl alcohol can be calculated by subtracting the amount of iodine corresponding to formaldehyde from the total of iodine consumed. The former is calculated from the quantity of hydrochloric acid determined in oximetry of formaldehyde in another run of the same sample.



Reagents to be used:—

- ca. 1*N* Sodium hydroxide solution,
- ca. 1*N* Sulfuric acid solution,
- ca. *N*/10 Iodine solution,
- N*/10 Sodium thiosulfate solution,
- ca. *N*/10 Hydroxylamine hydrochloride solution,
- N*/10 Sodium hydroxide solution

Indicators:—Starch solution, Methyl orange.

Procedure of analysis:—The sample containing 0.02 to 0.06 g. of propargyl alcohol is accurately taken and diluted to 10 cc. with water in conical beaker of 300 cc. capacity, then pipetted in by shaking 25 cc. of *N* NaOH solution and 25 cc. of *N*/10 iodine.

After letting it stand for about 10 minutes, 35 cc. of *N* sulfuric acid is added, thus liberated excessive iodine is titrated with *N*/10 sodium thiosulfate as usual. Let us assume the volume of thiosulfate required as *a* cc.

Separately, blank run is held. Let us assume the volume of thiosulfate required in the blank run as *b* cc.

So the quantity of propargyl alcohol (P.A.) is calculated as follows:—

$$\text{P. A.} = 0.005606 \text{ g.} \times \frac{b-a}{2}. \quad (1)$$

In case when formaldehyde is present, first, $(b-a)$ cc. of thiosulfate is determined as above. Using the same sample the quantity of formaldehyde is separately determined with hydroxylamine hydrochloride as usual.

Let us, then, assume the volume of *N*/10 sodium hydroxide required for neutralizing hydrochloric acid liberated, as *c* cc. So the quantity of propargyl alcohol is calculated as follows:—

$$\text{P. A.} = 0.005606 \text{ g.} \times \frac{(b-a) - 2c}{2} \quad (2)$$

The results obtained are shown in Tables 1 and 2.

Table 1

Result of Analysis of Pure Propargyl Alcohol

P. A. weighed, g.	Our method calculated by Eq. (1), g.	Hanna's method, g.
0.1018	0.1016	0.1014
0.05070	0.0506	0.05063
0.01018	0.01015	0.01014

Table 2

Result of Analysis of P. A. Containing CH_2O

Sample weighed g.	CH_2O by oximetry g.	P. A. calculated by Eq. (2), g.
(P. A. 0.06198 CH_2O *) 0.0018	0.0018	0.06199
(P. A. 0.06198 CH_2O *) 0.0180	0.0180	0.06196
(P. A. 0.06198 CH_2O *) 0.1703	0.1702	0.06200

* These values are determined by usual iodometry. P.A. and CH_2O were weighed separately and mixed before determination.

We have applied this method to the determination of methyl-(2)-butyne-(3)-ol-(2) which is prepared from acetylene and acetone, as well.

The result obtained was as follows:—

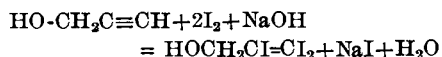
Sample taken	Our method	Hanna's method
0.05312 g.	0.05310 g.	0.05299 g.

Remarks:—Our method indicates some deviation in result if the amount of formaldehyde exceeds three times of the amount of propargyl alcohol.

The effect of butyne-(2)-diol-(1.4) on the result is negligible. If the concentration of the sample and reagents are too high or the temperature is much higher than room temperature, the

(5) We synthesized this compound in the same reaction and identified.

result obtained often indicates high value which is due to the formation of 3,3,2-triiodo allyl alcohol.



This method suggests that it can be applied to the determination of the acetylenic derivatives of type of $\text{RC}\equiv\text{CH}$.

Conclusions

(1) It is impossible to determine propargyl alcohol in the reaction products which are formed by the reaction of acetylene and formaldehyde, by the already known methods.

(2) In order to determine propargyl alcohol

under such conditions we invented new analytical method which is based on iodometry of propargyl alcohol.

Our study was conducted under the guidance of and with the encouragement from Dr. K. Yoshikawa, and we were given instructive advice by Dr. S. Murahashi, Prof. of Osaka University, as to the mechanism of the reaction between propargyl alcohol and iodine. Upon taking this opportunity we wish to extend our thanks to them.

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Concentration of N^{15} by Chemical Exchange Reaction Method

Asao SUGIMOTO, Ryohei NAKANE and Tsunao WATANABE

(Received January 31, 1951)

Introduction

For the purpose of the utilization of concentrated N^{15} as tracer works, we have been studying the concentration of N^{15} during these three years, and we are now able to concentrate the heavy nitrogen isotope up to nearly 10 atomic percent. The experimental results will be reported here briefly.

The method of the concentration of N^{15} was quite the same as that of Urey and others,⁽¹⁾ namely the chemical exchange reaction between ammonia gas and ammonium ion in the packed concentrating column.

Experimental Apparatus

The experimental apparatus consisted of two stages and their configurations were as shown in Fig. 1. The principal parts of the apparatus were as follows:

(1) **Concentrating column.**—The concentrating columns used in this work were made of glass tubes and total heights and inner diameters of the columns were 8 m. and 2.2 cm. for the 1st stage respectively and 6 m. and 1.0 cm. for the 2nd stage.

(1) H. C. Urey, J. R. Huffman, H. G. Thode and M. Fox, *J. Chem. Phys.*, **5**, 853 (1937); H. G. Thode and H. C. Urey, *J. Chem. Phys.*, **7**, 34 (1939).

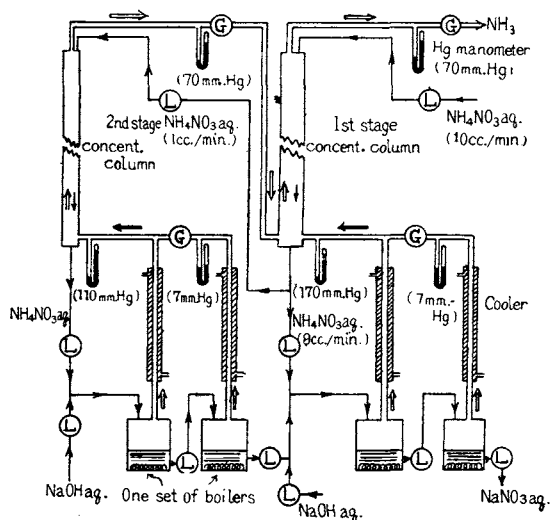


Fig. 1.

L: Liquid Pump. G: Gas Pump.

Each column was packed with the following: Fenske type (one turn helix) made of thin aluminum wire (0.3 mm. in diameter). The diameters of the helices were 2.4 mm. for the case of the 1st stage and 2.0 mm. for the case of the 2nd stage.

They were cleaned and boiled in water solution of Na_2CO_3 . By this treatment, the surfaces of them were changed to gamma crystals

of Al_2O_3 .⁽²⁾ These packing materials proved to be very satisfactory for the concentrating work as they were easy to produce on a large scale and also quite safe for the corrosion by the water solution of NH_4NO_3 and ammonia gas.

The space factors of the packing materials in the columns were 16.7% for the 1st stage column and 19.2% for the 2nd one.

(2) **Boilers.**—For each stage two sets of boilers were used. Each set was composed of five boilers made of copper tubes 10 cm. in diameter, four of which were 50 cm. in length and were placed horizontally while one was 20 cm. in height and was placed vertically. The five boilers were connected in series, the vertical one being placed at the end. Each boiler was heated with a 400 watt alumina heater. Water vapour was removed from the flow of ammonia gas at cold traps placed before each gas pump. The outsides of traps were cooled by methylalcohol-water mixture of about -15° circulating from a tank of a methyl-chloride refrigerating machine by a circulating pump. By introducing an auxiliary gas pump between two sets of boilers of each stage, we could reduce the residual amount of ammonium ions in the solution of NaNO_3 which would be drained from the last boiler of the stage less than one hundred thousandth ($1/100,000$) of the initial amount fed at the top of the column.

To keep the liquid levels in the boilers constant, we attached to the last boiler of each set a liquid level regulator as shown in Fig. 2. The liquid-contact electrodes were made of thin platinum foils. The magnetic valves were constructed especially for this purpose and were operated by the compression of rubber tubes by the action of electromagnets.

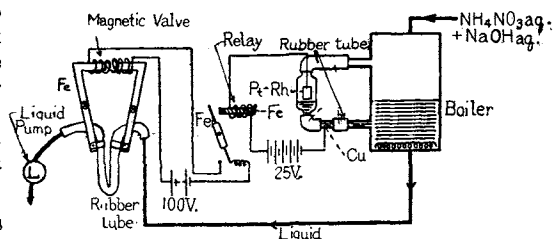


Fig. 2.

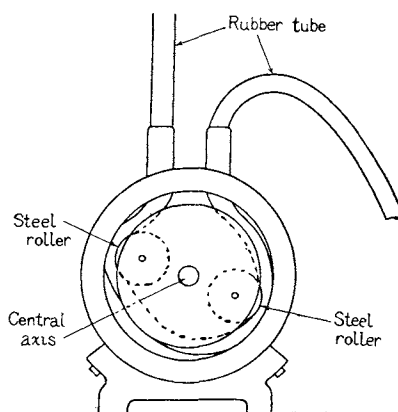


Fig. 3.

(3) **Liquid pump.**—For the transport of the chemical solutions (NH_4NO_3 , NaCH_3 , NaNO_3), we constructed a special type of liquid pump, the working mechanism of which can be easily seen in Fig. 3. By changing the velocity of rotation

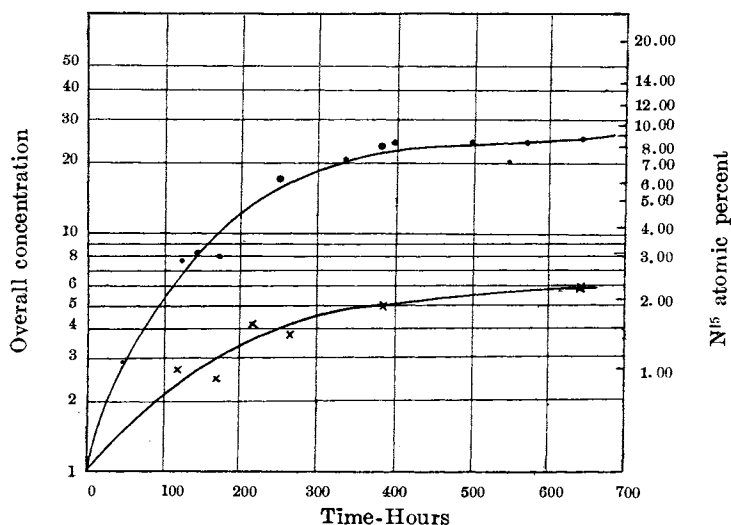


Fig. 4.—●, Concn. at the bottom of the second stage column;
x, Concn. at the bottom of the first stage column.

(2) We are greatly indebted to Miyata Laboratory of this institute for this surface treatment of the packing

materials.

of the central axis, and inner diameter of the rubber tube, we could change the speed of the transport of liquid from 0.01 cc./min. to 30 cc./min. by a single pump. As for the lubricant between the steel rollers and the rubber tube, we used glycerine which proved to be very satisfactory.

(4) **Chemicals.**—As for the solution of the ammonium ion we used 60% solution of NH_4NO_3 , to which 1% of methylalcohol was added. The feeding velocities of the ammonium nitrate solution were 10 cc./min. for the 1st column and 1 cc./min. for the 2nd column. As for the solution of NaOH , 30% solution of commercial caustic soda was used.

Experimental Results

We had operated the apparatus mentioned above from June 21 to July 19, nearly 670 hrs. The pressure at the top of the column of each stage was kept at 70 mm. Hg and the pressure drops in the columns were 10 mm. Hg per meter for 1st stage and 6 mm. Hg per meter for the 2nd one.

The changing rate of the concentration of N^{15} at the bottom of the column of each stage

was shown in Fig. 4. From 420 hrs. we began to produce samples of concentrated N^{15} in the form of $(\text{NH}_4)_2\text{SO}_4$ by sending bubbles of ammonia gas from the bottom of the 2nd stage column through H_2SO_4 . Thus we could get totally 20 g. of $(\text{NH}_4)_2\text{SO}_4$ during this work. The N^{15} contents of the samples varied from 8 to 9.3 atomic percent. The overall concentration factor of the two stages was 27 and that of the 1st stage only was 5.9.

In conclusion we express our thanks to the late Dr. Yoshio Nishina, the President of this Institute, for his kind encouragement throughout this work. We are also greatly indebted to the Ministry of Agriculture and Forestry for grants without which this work could not have been accomplished. We also wish to thank Messrs. Sadao Matsuo, Shyohei Isomura, Ryuzo Shibata, Shohichi Motonaga, Kozo Morishita for their assistance in connection with this experiment.

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Adsorption of Proteins from Aqueous Solution on the Films of Stearate and Lipids⁽¹⁾

By Taro TACHIBANA,⁽²⁾ Kiyoshige FUKUDA and Kozo HAMAGUCHI⁽³⁾

(Received March 20, 1951)

A metal slide covered with a barium stearate multilayer film, which was rendered hydrophilic by treating with thorium nitrate solution, is highly polar and can adsorb proteins from their solution. A slide prepared in this way is dipped into a protein solution. The following washing and drying bring an increase in thickness which can be measured optically. We have studied, by such a procedure,⁽⁴⁾ the adsorption of proteins. Some interesting phenomena observed in the investigation are briefly

described below. The detailed description may be given elsewhere.

1. Adsorption of egg albumin from its aqueous solution was studied on the surface of stearate film conditioned with thorium nitrate. The effect of concentration of the solution and the time allotted for adsorption have been measured.

Preliminary experiments have led to the results that the adsorption was completed within five minutes at room temperature and the maximum thickness was 50 Å. which was deposited from the aqueous solution of the concentration over 0.01 percent. The adsorption was irreversible.

As far as the stearate film was left dipping in solution, the thickness of adsorbed layer never exceeded 50 Å. However, after taking

(1) Read before the Special Meeting of the Chemical Society of Japan, Tokyo on Nov. 11th, 1949.

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(3) Present address, The Institute of Scientific and Industrial Research, Osaka University, Sakai, Osaka.

(4) I. Langmuir and V. J. Schaefer, *J. Am. Chem. Soc.*, **59**, 1406, 1672 (1937).

out the film from solution with the following washing and drying, the second dipping permitted the further increase of the thickness of adsorbed layer though the rate was much slower than in the case of the first dipping, *i. e.*, the increment was about 10 Å. thick at one hour after the beginning of the second adsorption. Thus, the repetition of dipping and drying always enhanced the adsorption. This seems to indicate that drying caused a certain change in the structure of adsorbed layer. Adsorbed layer of protein was found to decrease in thickness by bringing contact with 8 molal solution of urea. For instance, by this treatment the adsorbed layer decreased from 44 to 22 Å. in thickness for 16 hours, where it attained at minimal thickness.

By the way, it may be noted that the adsorption of egg albumin on unconditioned surface produced 20 Å. thick for 24 hours at 0°.

2. Likewise, experiments were performed with horse serum proteins. As shown in Table 1, it resulted that serum albumin was adsorbed on hydrophilic surface alone, while serum globulin was equally adsorbed from saline solution on both hydrophilic and hydrophobic surfaces. Serum globulin was not fractionated, so that which of the fractions was responsible for the phenomena was not established. Table 1 shows that salt also suppresses the adsorption of serum albumin.

3. A peculiar phenomenon was observed in dipping a slide having stearate multilayer film into rabbit serum. The maximal thickness of adsorbed layer, 50 Å., was obtained on the conditioned surface of stearate film, whereas with unconditioned stearate film the decrease of thickness of stearate film occurred at the rate of 15 Å. per one hour. This may be a case of solubilization and suggest a method of measuring the solubilizing power of serum towards a fatty acid.

Table 1

Adsorption of Horse Serum Protein from Solution onto Barium Stearate Film Conditioned or not with Thorium Nitrate.

Protein solution	The thickness of adsorbed layer on	
	Conditioned surface, Å.	Unconditioned surface, Å.
Serum albumin in aq. solution, 0.5%	36	5
Serum albumin in physiologically saline solution, 0.5%	28	0
Serum globulin in physiologically saline solution, 1.5%	68	71

Each figure represents an average of several determinations. Error is within 3Å.

4. Furthermore, experiments were made of the adsorption of serum protein on a single monolayer of lipids⁽⁵⁾ transferred onto conditioned stearate film at compression of 15 dynes. Such a slide was dipped into human serum for ten minutes at 10°. The adsorption produced the thickness of 50-60 Å. on cardiolipin monolayer, 25-35 Å. on lecithin monolayer. These results may indicate the adsorptive power of respective lipids to serum protein.

The authors express their sincere thanks to Prof. Jitsusaburo Sameshima for his kind advice and encouragement. The expense of this work has been defrayed from the Scientific Research Encouragement Grant from the Ministry of Education.

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(5) Samples were kindly provided by Department of Serology, Faculty of Medicine, the University of Tokyo.

Some Higher Alkyl Naphthenates as Lubricating Oil for Fine Instruments

By Tsutomu KUWATA,⁽¹⁾ Shizuo NOGUCHI⁽²⁾ and Hiroyasu ANDO⁽²⁾

(Received April 20, 1951)

Lower alkyl naphthenates, such as methyl or ethyl esters, have been known in detail, but as to the esters of higher fatty alcohols having more than eight carbon atoms no description has been found in the literature.

The present authors synthesized several higher alkyl esters of naphthenic acids and found that these new esters have suitable properties as lubricating oil for several fine instruments.

Synthesis of Higher Alkyl Naphthenates

Higher fatty alcohols used in the experiment are listed in Table 1. Refined naphthenic acids free from neutral oils, phenols, and other impurities are used for the study of characteristic properties of esters, and crude naphthenic acids contaminated with neutral oils, phenols, resinous substances and other impurities are employed for the estimation of commercial qualities of esters.

1. Refined naphthenic acids ($R_1\text{COOH}$) derived from Niitu light machine oil distillates are light yellowish viscous liquid and have the following properties: b. p. 180-225°/9 mm.Hg (uncor.); d_4^{25} 1.0025; n_D^{25} 1.4896; acid value 223.6; av. mol. wt. calcd. 250.9.

2. Refined naphthenic acids ($R_{II}\text{COOH}$) produced in the refining of the same distillates are yellowish viscous liquid and have the following properties: b. p. 182-229°/9 mm.Hg (uncor.); d_4^{25} 0.9992; acid value 220.6; av. mol. wt. calcd. 254.3.

3. Crude naphthenic acids ($R_{III}\text{COOH}$) obtained by the distillation of the crude petroleum acids imported from abroad have approximately the following composition: Pure naphthenic acids (acid value, 227.1) 76%; phenols, neutral oils and other impurities 23%. The acids are brownish viscous liquid and have the following properties: b. p. 155-247°/9 mm.Hg (uncor.); d_4^{25} 0.9882; n_D^{25} 1.4957; acid value 192.6. Higher fractions (above 200°/5 mm.Hg) of the neutral oils contained

Table 1
Properties of Higher Fatty Alcohols Used

Alcohols	Materials	B. p. °C. (mm.Hg uncor.)	d_4^{25}	n_D^{25}	Hydro- xyl value	Remarks
2-Ethylhexyl alcohol	Synthetic	182-183	0.8346	1.4316	—	—
<i>n</i> -Octyl alcohol	Reduction of coconut oil	191-196	0.8225	1.4298	429.8	B. p. (mainly) 193°
Decyl alcohol		120-125 (15)	0.8299	1.4356	353.8	{ B. p. (mainly) 122- 123°/15 mm.Hg
Lauryl alcohol		143-148 (15)	—	—	295.0	M. p. 23.5-25.5°
Lauryl alcohol (industrial)		130-165 (15)	0.8273	1.4377	224.2	{ Solid. point 5.5°; Purity calcd. from H. V. 74.5%
Cetyl alcohol	Spermaceti	188-190 (15)	—	—	233.0	M. p. 49.0-50.5°
Oleyl alcohol	Sperm liquid alcohol	205-210 (13)	0.8505	1.4630	209.8	Iodine value 91.5
Sperm alcohol	Sperm oil	165-205 (13)	—	—	214.6	{ I.V. 45.2; av. mol. wt. calcd. from H. V. 261.4
Sperm liquid alcohol	*	80-260 (13)	0.8495	1.4604	204.5	{ I.V. 83.2; av. mol. wt. calcd. from H. V. 274.3

* Sperm liquid alcohol was prepared from sperm alcohol by separating the solidified substance in acetone solution at -3~-7°; yield, 45.5% of sperm alcohol.

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in the crude naphthenic acid amounted to 3.4% (in weight) and it is considered to be most probable that naphthenic esters prepared from the crude naphthenic acids contain the corresponding amount of hydrocarbon oil as impurity.

Procedure.—The mixture of higher fatty alcohols, excess naphthenic acids, moderate quantity of xylene and conc. sulfuric acid is boiled in a flask fitted with reflux condenser and accessory which is widely used for measuring the water content in organic substance. When the volume of water distilled is constant, reactions are considered to be completed. The reaction products are washed with 0.5 *N* sodium hydroxide and then with distilled water and dried over sodium sulfate. After removing the solvent, the reaction products are distilled under reduced pressure in the presence of 1% anhydrous sodium carbonate or no additive. The data obtained are given in Table 2.

From these it is notable that under these experimental conditions esterification of naphthenic acids is carried out with satisfactory result. In the purification of the esters it is desirable to distil them under pressure as low as possible in order to avoid the increase of acid value.

General Properties of Higher Alkyl Naphthenates

The general properties of naphthenates are shown in Table 3. The increase of the carbon number of side chain attached to the carboxyl group reduces density, refractive index,

and increases viscosity, and improves viscosity-temperature characteristics as evidenced by high value of kinematic viscosity index. The reaction of the esters is always neutral except those prepared from the crude naphthenic acids distilled with no additive. Corrosion test is good. Esters have the odor resembling to mineral oil, and not the characteristic unpleasant odor of naphthenic acids or lower alkyl naphthenates. The higher alkyl naphthenates are pale yellowish liquid, and the color of the oil may be greatly improved by the redistillation.

As may be seen from the fact that the esters prepared from crude naphthenic acids have properties as good as those from refined naphthenic acids, small amount of neutral oils included within the esters have no unfavorable influence upon the esters. But it is wiser to use crude naphthenic acids from kerosene or gas oil fractions as the starting materials, because the presence of high boiling neutral oil is apt to give dark color to the esters.

The data cited in table 3 indicate that the esters are mostly characterized by little change in viscosity with temperature, low viscosity and viscosity ratio, adequately low volatility, high flash point, and reliable resistance to heating. They spread on metal or glass surface far less extent than hydrocarbon oils. Though

Table 2
Synthesis of Higher Alkyl Naphthenates

Names	Naphthenic acids		Alcohols, g. mol	Xy- lene, cc.	H ₂ SO ₄ , g.	Reac- tion time, hrs.	Reac- tion pro- ducts, g.	Distil.* method	Esters			
	Symbol	g. mol							B. p.	Main**	Ob- tained, g.	Yield, % to alcohols
									(°C./5 mm.)			
2-Ethylhexyl naphthenates	} R ₁₁ COOH	0.39	0.3	350	7	2	95.0	×	200- 240	200- 220	84.3	77
n-Octyl naphthenates		0.39	0.3	350	7	2	93.0	×	200- 245	210- 230	83.5	76
Decyl naphthenates	} R ₁₁ COOH	0.26	0.2	250	5	2	72.1	×	200- 255	220- 240	63.4	81
Lauryl naphthenates		0.39	0.3	400	8	2.5	117.0	0	210- 265	240- 260	99.1	78
Lauryl (industrial) naphthenates	} R ₁₁ COOH	0.11	0.1	150	3	2	41.5	×	200- 280	235- 260	32.8	78
Cetyl naphthenates		0.05	0.03	50	1	1.5	12.9	0	200- 278	260- 275	11.0	77
Oleyl naphthenates	} R ₁ COOH	0.05	0.03	50	1	1.5	13.5	0	200- 295	275- 290	11.7	78
Sperm naphthenates		0.05	0.03	50	1	1.5	13.6	0	200- 291	270- 290	11.4	77
Sperm liquid naphthenates	} R ₁₁ COOH	(35.0) 0.10	0.1	150	3	4	45.9	0	200- 300	285- 300	34.9	69

* 0, No Additive; ×, in presence of 1% anhydrous sodium carbonate.

** "Main" means the range of temperature in which more than 80% (in weight) of the esters are distilled.

Table 3

General Properties of Higher Alkyl Naphthenates

Esters	Color (un- ion)	d_4^{25}	n_D^{25}	Saponi- fication number	Acid value		Iodine value	Solid. point, °C.	Flash. point, °C.	*** Volatil- ity, %	Heating†		Kinematic viscosity (est)††					Visco- sity ratio (50°C.)	Kine- matic viscosity index
					Non treat- ing	After heat- ing					Ppt.	Color (union)	Non treating				After ht. 50°C.		
2-Ethylhexyl naphthenates }	1	0.9306	1.4745	140.5	1.1	1.1	0.5	-47	196	0.017	None	3 ¹ / ₄	29.85	13.38	21.47	3.74	13.52	1.00	43
n-Octyl naphthenates }	1 ¹ / ₂	0.9266	1.4721	144.8	0.9	1.2	0.8	-52	198	0.026	"	2 ¹ / ₂	21.82	10.70	16.14	3.44	10.70	1.00	95
Decyl naphthenates }	1 ¹ / ₂	0.9205	1.4719	120.7	2.7	2.9	1.2	-43	197	0.025	"	2 ¹ / ₂ -3	25.64	12.40	18.88	3.85	12.45	1.00	106
Lauryl naphthenates }	1	0.9139	1.4707	113.2	0.3	0.9	1.0	-45	210	0.012	"	2-2 ¹ / ₂	30.15	14.15	23.36	4.53	15.15	1.07	122
Lauryl (industrial) * naphthenates }	1 ¹ / ₂	0.9152	1.4747	111.8	0.0	<0.1	2.9	-45	207	0.028	"	2 ¹ / ₂ -3	31.92	14.97	23.31	4.46	15.13	1.01	116
Cetyl naphthenates }	1-1 ¹ / ₂	0.9077	1.4605	105.8	2.2	2.3	2.4	-10	215	0.026	"	1-1 ¹ / ₂	42.36	17.65	30.49	5.66	20.46	1.11	136
Oleyl naphthenates }	1 ¹ / ₂	0.9087	1.4653	100.5	2.7	2.8	36.6	-40	193	0.016	"	1 ¹ / ₂	45.38	21.11	32.84	6.10	22.78	1.03	138
Sperm naphthenates }	1 ¹ / ₂ -2	0.9071	1.4633	105.4	1.6	1.8	20.2	-16	220	0.005	"	1 ¹ / ₂ -2	47.03	21.63	33.96	6.24	22.93	1.06	138
Sperm liquid* naphthenates }	1 ¹ / ₄	0.9064	1.4733	100.9	0.0	<0.1	41.9	-32	198	0.023	"	3	38.33	18.12	28.07	5.40	18.73	1.03	138

* The distillate was washed with alkali solution in order to remove the acidic substances produced by thermal decomposition of crude naphthenates.

** Determined with Pensky-Martens closed tester.

*** Per cent loss of weight in 5 hr. at 98° in a convection type oven.

† Observed after 6 hr. at 140° in a convection type oven.

†† Determined with modified type of Ostwald viscometer.

cetyl and sperm naphthenates have high solid points, esters of higher saturated alcohol having not more than twelve carbon atoms have low solid points below -40° . On comparing the two isomers, 2-ethylhexyl and *n*-octyl esters, the former has higher boiling point, higher viscosity, and smaller viscosity index than the latter. The higher solid point of the former may be accounted for low temperature viscosity relationship.

It seems unavoidable that acid value of the distillate slightly increases during distillation under pressure as low as 5mm. In order to obtain fractions of lower acid value it may be necessary to distil the esters under high vacuum as far as possible. The presence of small quantities of anhydrous sodium carbonate may decrease acid value, though not to a satisfactory extent.

Considering from these properties, the esters of naphthenic acids above mentioned are almost comparable in lubricating quality to the lubricants hitherto known with the exception of

cetyl esters. Some esters, lauryl naphthenates may be expected to be available for the lubrication of watch, clock, and other delicate machinery of fine instruments.

Conclusion

2-Ethylhexyl, *n*-octyl, decyl, lauryl, cetyl, oleyl and sperm esters of pure naphthenic acids and lauryl (industrial) and sperm liquid esters of crude naphthenic acids are synthesized.

As the result of experiments it was found that higher fatty alkyl esters of naphthenic acids possess the most excellent qualities as lubricating fluids for delicate machinery of fine instruments; *i.e.*, pale yellowish color, low viscosity, low evaporation rate, low solid point, high flash point, high kinematic viscosity index, high thermal stability, and slow spreading velocity on metal or on glass surface.

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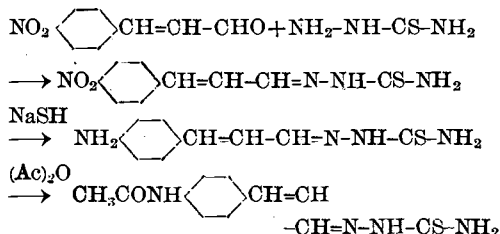
LETTER

Synthesis of *p*-Acetylamino- cinnamaldehyde Thiosemicarba- zone

By Tamio NISHIMURA

(Received May 7, 1951)

This paper reports the synthesis of a new antituberculous substance, *p*-acetylaminocinnamaldehyde thiosemicarbazone having activity in concentration of 1.3 γ/ml. (Aoyama B strain, Sauton medium). The reactions are given in the scheme:



A mixture of 8.9 g. of *p*-nitrocinnamaldehyde, 4.6 g. of thiosemicarbazide and 90 ml. of ethanol was heated by stirring on a steam bath for 20 minutes. After cooling, the solid product was filtered, washed with ethanol and dried, giving 11.9 g. (92%) of *p*-nitrocinnamaldehyde thiosemicarbazone (I), m. p. about 224°

(decomp.). *Anal.* Calcd. for $\text{C}_{10}\text{H}_{10}\text{O}_2\text{SN}$: N, 22.38. Found: N, 22.24.

After saturation of a mixture of 20 ml. of ethanol and 8 ml. of 2 *N* aqueous sodium hydroxide solution with hydrogen sulfide, 2.5 g. of (I) was added to the mixture in one portion. This mixture was heated at 50° for ten minutes, while crystals began to separate. After heating for further three minutes at 75° and after cooling, crystals were filtered, washed first with ethanol, then with water and again with ethanol, giving 1.6 g. (73%) of *p*-aminocinnamaldehyde thiosemicarbazone (II), m. p. 207° (decomp.). *Anal.* Calcd. for $\text{C}_{10}\text{H}_{12}\text{N}_4\text{S}$: C, 54.53; H, 5.50. Found: C, 54.29; H, 5.27.

To 1.1 g. of (II) suspended in 50 ml. of ethanol was added 2 ml. of acetic anhydride and the mixture was stirred for five minutes. Crystals were filtered and washed with water, giving 2.5 g. (95%) of *p*-acetylaminocinnamaldehyde thiosemicarbazone (III), m. p. 225° (decomp.). *Anal.* Calcd. for $\text{C}_{12}\text{H}_{14}\text{OSN}_4$: C, 54.95; H, 5.38. Found: C, 54.89; H, 5.48.

The nitro and amino compounds (I and II) also proved to have antituberculous activity.

Biological evaluation of these substances was executed by Dr. T. Takebe. The author wishes to express his gratitude to Dr. T. Takebe for his favor.

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Dissolution Phenomenon of Some Optical Glass in an Acid

By Shoji TSUCHIHASHI

(Received April 2, 1949)

Introduction

Many studies have been made concerning the effect of acid on optical glass from the standpoint of the scientific research or the practical use. There are numerous reports^(1,2,3,4,5) on the relation between the amount of the alkali dissolved and the time of dissolution. In most of these experiments powdered glass was used and the alkali dissolved in an acid solution after immersing the sample in it was titrated. In such cases, as pointed out by Tieze⁽¹⁾, it happens frequently that the metal ions present near the surface may dissolve at first without being peeled off of the SiO_2 film formed on the surface sloughs, therefore the reaction velocity is hard to measure.

The author adopted the method of measuring the apparent velocity through the change of interference color which was caused by the thickness of the SiO_2 film formed after the escape of metal ions from glass. In this method the SiO_2 film is not peeled off, so it is very advantageous to the observation of the erosive action of an acid for the polished surface of glass.

Experimental Method

The apparatus is shown in Fig. 1. A polished sample of optical glass, b, supported by a Terex

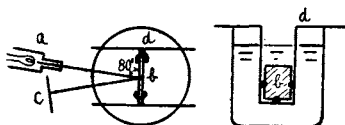


Fig. 1.—Experimental apparatus.

glass holder, d, was washed with alcohol, immersed for 1 minute in a 0.5 *N* solution of caustic soda, and washed again thoroughly with distilled water. Immediately after this treatment, it was immersed in a nitric acid solution kept at a constant temperature. After that, with much

attention to the change of the temperature, the reflection of the light radiated from the light source, a, was caught on a screen, c, and the change of the interference color with the time was observed at a desired temperature.

The change thus observed was examined from the relation between the interference color in the case of Newton's ring and the thickness of a film (SiO_2 film; $n=1.46$), and graphically shown in Fig. 2 as the relation between the thickness of a film and the time. A number of plates ($24 \times 20 \times 2$ mm. in size) of Flint glass (F-1, F-2, F-3, SF-2, KF-2 glass) were examined, each of which has been cut from the lump glass and polished under the same condition.

Their components are shown in Table 1.

Table 1
Composition of Glass

Glass	Component, %					
	SiO_2	PbO	Na_2O	K_2O	Al_2O_3	ZnO
F-1	45.0	45.1	1.5	7.7		
F-2	44.7	46.2	0.2	8.8	0.02	
F-3	45.6	43.4	1.7	8.6		
SF-2	40.99	51.1	0.6	6.9	0.04	
KF-2	66.8	11.6	16.0	0.1	1.5	3.8

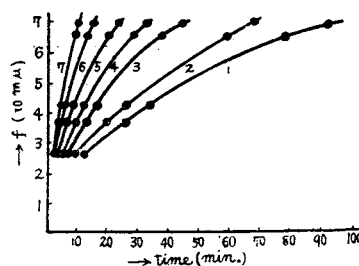


Fig. 2.—*f-t* curve of the F-2 glass:

1, 60°C.; 2, 63°C.; 3, 66.5°C.; 4, 70°C.; 5, 75°C.; 6, 80°C.; 7, 84.5°C.

Experimental Results and Discussion

(1) **On the Concentration Change of the Acid through the Experiment.**—The change of the concentration of the 1 *N* nitric acid was examined by the volumetric analysis, and it was almost negligible for the present investigation.

(2) **On the Reaction Velocity.**—When

(1) P. Tieze, *Sprechaal*, **61**, 809 (1928); *Glastech. Ber.*, **6**, 716 (1928-29).

(2) G. Keppeler, *Glastech. Ber.*, **12**, 366 (1934); *Chem. Centr. Bl.*, 2026 (1935).

(3) E. Berger, *Glastech. Ber.*, **14**, 351 (1936); **16**, 296 (1938).

(4) T. Moriya, *J. Soc. Chem. Ind. Japan*, **43**, 884, 886 (1940).

(5) S. Nagaeda, *J. Japan. Cer. Assoc.*, **49**, 140 (1941).

optical glass is immersed in an acid, the reflection from its surface gradually changes. This is ascribed to the formation of a film on the glass surface which differs from the base glass in the index of refraction and the film formed is a SiO_2 film, as clearly known from the studies of Blodgett and others^(6,7,8), so the refractive index of the film is considered to be 1.46.

In the case of ordinary soda-lime glass, the immersion in an acid solution does not cause the variation in the interference color, but alkali is dissolved in the solution. In the case of KF-2 glass, after showing a certain interference color, it becomes colorless. This indicates that the film remains without being peeled off to a certain thickness and then all was peeled off. In the case of F-2 glass, the interference color was gradually changed, which indicates that the SiO_2 film is not removed.

Therefore, it is phenomenologically inferred that PbO and K_2O present in the glass, reacting with nitric acid to be $\text{Pb}(\text{NO}_3)_2$ and KNO_3 , are removed and then the skeleton of SiO_2 remains with the water included.

The relation between the amount of reaction and time, as shown in Fig. 2, is generally parabolic. If the diffusion of something is supposed to be the factor for this reaction, the following equation is to be established.

$$\frac{df}{dt} = k \frac{1}{f} \dots\dots\dots (1)$$

where f is the thickness of the film. By integrating equation (1), it becomes (2),

$$f^2 = 2kt + k' \dots\dots\dots (2)$$

and the relation between f^2 and t (time) should be linear. From this point of view, the relation between f and t given in Fig. 2 was revised as that between f^2 and t , then it was represented as a straight line. This justifies the above presumption. It is concluded that the dissolution phenomenon of optical glass in an acid is parabolic at its initial stage, and its reaction velocity is dominated by the diffusion of some substance.

In Fig. 3 the relation between the reaction velocity k and the temperature is shown; the relation $\log k$ and $1/T$ is linear and there holds the following equation:

$$K = Ae^{-\frac{E}{RT}} \dots\dots\dots (3)$$

This may properly show that the reaction velocity is dominated with the diffusion of some substance.

(3) **Influence of the Additive Ion in the Solution.**—It is considered possible that the escaped ions from the glass may have some influence on the formation of this film.^(9,10) For the purpose of full discussion, we have traced the influence of the K^+ Pb^{++} on the SF-2 glass in the nitric acid. We have adopted the 100 cc. solution of 1 *N* nitric acid, in which 0.1 mg., 0.5 mg., 1 mg., 5 mg., 10 mg. of KNO_3 and $\text{Pb}(\text{NO}_3)_2$ were dissolved respectively at 50° and 80°.

It may be concluded from this experiment that the K^+ , Pb^{++} in the nitric acid give no influence on the reaction velocity described above.

(4) **Influence of Stirring on the Dissolution.**—When the solid dissolves in the liquid, it is well-known fact that the diffused layer, formed between the rubbing faces of the solid and the liquid, is very strong and does not come off easily, and that the diffusion of the ions or others through this layer generally determines the reaction velocity.

Dissolution phenomenon of the optical glass in an acid is not considered so simple as above mentioned, but it may be considered to contain that this phenomenon is found in one part of the diffused systems, then the possible existence of the diffused layer may be taken up for consideration.

For experimental convenience the author did not circulate the solution, on the other hand shaken up and down the test pieces of the optical glass (SF-2) in the solution. The distance of the movement in the solution was about 6 cm., and the number of times to move up and down 90 to 100 for one minute.

The observation of the reaction velocity was made by the optical method as similar to that mentioned above. The results showed that the reaction velocity becomes a little faster by the stirring but its amount is so small that the stirring gives no influence on the reaction velocity.

As it is unnecessary to consider the diffused layer which exists at the boundary between glass and liquid, it may be concluded that the diffusion which determines the reaction velocity is in the glass itself.

(5) **On the Peculiarity of the SiO_2 Film.**—As mentioned above, the author adopted

(6) K. B. Blodgett, *Phys. Rev.*, **55**, 391 (1939).

(7) I. Sawai, J. Tashiro and K. Umeya, *J. Japan. Cer. Assoc.*, **52**, 109, 198, 200 (1944).

(8) I. Sawai, J. Tashiro, K. Umeya, and S. Kozaki, *J. Japan. Cer. Assoc.*, **52**, 268 (1944).

(9) Geffeker, *Kolloid Z.*, **86**, 11 (1939).

(10) D. Hubbard and F. H. Hamilton, *J. Res. Nat. Bur. Stands.*, **27**, 143 (1941).

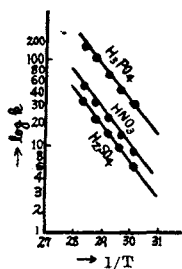


Fig. 3.—SF-2 glass.

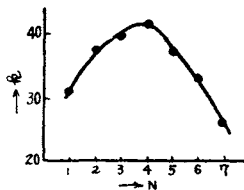


Fig. 4.—F-2 glass at 80°C.

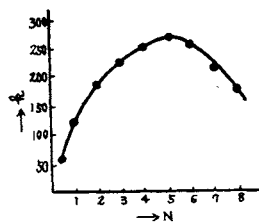


Fig. 5.—SF-2 glass at 80°C.

the method of measuring the apparent velocity through the change of interference color.

It means the safe existence of the skeleton of the SiO_2 retaining the binding force by hydrogen ions or water molecules which got into the hole formed after the escape of metal ions. The phenomenon in proof of this fact is that the interference color glides off into the one which is produced when the film seems to have decreased in thickness, if the glass is taken out into the air and decomposed by heat.⁽¹¹⁾

It is considered that the water included in SiO_2 skeleton run out by the the heat treatment and the film shrinks a little. In the case of KF-2 glass mentioned above, the intimate relations might be thought to exist between the inner constitution of the glass and the thickness of SiO_2 film capable of maintaining the SiO_2 linkage.

So it is surmised that the SiO_2 film is not peeled off but stays on the glass surface at the Flint glass, but the binding force acts in various ways in relation to the change of the glass component and inner constitution.

The author considered that the refractive index of the film is uniformly 1.46. But Schröder⁽¹²⁾ reported that the erosive film has not a simple refractive index as fused quartz, but some gradient along the depth of the film. He also reported that it has no objection to use the average refractive index $\bar{n}$. (actually it is a serious question what value is to be used for $\bar{n}$.)

When the initial stage of these reactions come into question, *i. e.*, the film is very thin, it may be considered that as if Na^+ , K^+ , Pb^{++} etc. are stayed in the SiO_2 film, and refractive index of the film grows larger corresponding to go into the inner part of the film. But this difference is very small, and it has no objection to think the refractive index of the film is almost 1.46.

(6) **Experiment in the Sulfuric Acid and Phosphoric Acid.**—The initial dissolution phenomenon in an acid with 1 *N* sulfuric acid and 1 *N* phosphoric acid besides 1 *N* nitric acid was studied, and it is found to proceed parabolically.

Fig. 3 shows the relation between $\log k$ and $1/T$ in the case of SF-2 glass. These linear lines only get loose in parallel and it is considered that the rate determining stage of this reaction is not caused by the diffusion of the anions (NO_3^- , SO_4^{--} , PO_4^{--}) in the glass.

(7) **The Relation between the Reaction Velocity Constant and the Concentration of the Solution.**—In the curve expressing the relation between the reaction velocity constant and the initial concentration of the solution there appears a maximum point in Fig. 4 and Fig. 5 in the case of F-2 and SF-2 glass and the position of the maximum points in two curves are not coincident.

This disparity of the maximum points is due to the amount of PbO contained in each optical glass, so it is considered that for the rate determining stage of this reaction the amount of PbO in the glass play an important part.

Conclusion (Reaction Mechanism)

It is surmised from the facts mentioned above that the mechanism of these reactions is as follows.

At first Na^+ , K^+ and Pb^{++} that existed combined with the tetrahedron of the SiO_2 in the glass are brought out, *i. e.*, diffused to the glass surface and thrown up into the solution leaving holes. Thus the skeleton layer of SiO_2 is formed. Then H^+ , H_3O^+ etc. enter into the holes of the skeleton layer and Na^+ , K^+ and Pb^{++} are diffused out further from the more inner part of the glass for the lack of the positive charge.

It is considered that the reaction is advanced by these courses, and that, therefore these reactions are the exchange reaction between

(11) S. Tsuchibashi, unpublished.

(12) H. Schröder, *Ann. Phys.* 39, 55 (1941).

Na^+ , K^+ , Pb^{++} and H^+ , H_3O^+ .

As mentioned above, the diffusion of the Pb^{++} carry out the important role in these steps.

It may also be considered that this mechanism is not unreasonable in consideration of the relation between the reaction velocity constant k (or diffused constant) and the component of the glass.

In conclusion the author wishes to express his thanks to the director of this institute Dr. K. Fuwa, and also to Professor S. Horiba (Kyoto University) for their stimulating interest in the author's work.

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Pyrolysis and Combustion of Cellulose in the Presence of Inorganic Salts

By Kenzi TAMARU

(Received March 2, 1951)

Introduction

Some chemicals which when applied to cellulose inhibit flaming of gases or combustion charcoal are called fire-resisting compounds, and several of them are, for example, ammonium sulphate and phosphate, aluminium sulphate and zinc chloride. Many investigations have been made on the action of the compounds since olden times.^{(1)~(6)}

The present author has studied on the process of carbonization of cellulose in the previous paper⁽⁷⁾ and reached the following conclusion. Generally speaking, by the carbonization of cellulose, charcoal is not produced by the continued collapse of cellulose structure, but the high molecules of cellulose are first depolymerised to low molecules by heat, a part of which evaporates increasingly as the rate of heat increases and the other part, being dehydrated, polymerizes to yield a high polymer, direct origin of charcoal. This polymer is degassed by heat, being cut its weak bindings and proceeding aromatization side by side in the structure. Such gases as carbon dioxide, carbon monoxide, methane or hydrogen are evolved from it, consequently producing the

"molecular roughness" or "Ultraporosität" in it. By further heating the gas evolution and the aromatization proceed and the "molecular roughness" increases till about 800°. However, it begins, in turn, to be eliminated by gradual breaking down of the skeleton of the polymer structure over 1000°, and by the severe treatment of heat the graphitization proceeds.

In the presence of some chemicals the process of carbonization of cellulose being affected, the change in flammability of cellulose in this case is possibly attributed to that in carbonization process.

In this paper, the carbonization and combustibility of cellulose in the presence of various salts are reported to consider the action of fire-resisting compounds.

Experimental

Effect of Inorganic Salts on the Pyrolysis of Cellulose:—The sample⁽⁸⁾ was treated in the 0.1 mol. solutions of various salts. About 0.5 g. of dry sample was put in the bottom of the quartz tube which was closed at one end. The tube was connected to a gas burette. After evacuating the air from the tube and the burette, the sample was thermally decomposed by inserting the bottom of the tube perpendicularly in an electric heater, the temperature of which was 480°. The gas evolved by the decomposition of the sample was conducted to the gas burette and after being heated for an hour, the gas was

(1) Gay Lussac, *Ann. chim. phys.*, **18**, 211 (1821).

(2) S. Tamaru, Y. Imai and T. Momma, *J. Chem. Soc. Japan*, **55**, 30 (1934).

(3) N. A. Richardson, *Chem. and Ind.*, **56**, 202 T (1937).

(4) R. W. Little, *American Chemical Society Monograph* No. 104 (1947).

(5) K. Tamaru, *J. Chem. Soc. Japan*, **69**, 20 (1948).

(6) American Chemical Society Symposium on "Flame Retarding of Textiles," *Ind. Eng. Chem.*, March, 1950.

(7) K. Tamaru, *J. Chem. Soc. Japan*, **69**, 21 (1948).

(8) Toyo Filter Paper No. 41, which contains no inorganic salt, was used as the sample.

Table 1

Salt	Total gas volume, cc./g.	CO ₂ , %	CO, %	CH ₄ , %	H ₂ , %	Others, %	R ₁ , %	R ₂ , %	V, %
Without salt	144	48	34	17	0	1	6	31	24
H ₃ BO ₃	120	44	43	11	2	1	13	20	33
NH ₄ Cl	101	44	31	15	8	2	29	2	51
(NH ₄) ₂ SO ₄	132	45	35	19	0	0	33	0	66
(NH ₄) ₂ HPO ₄	89	42	43	9	2	4	39	0	79
NH ₄ -molibdate	148	51	29	14	6	0	34	4	57
(NH ₄) ₂ PtCl ₆	149	42	24	18	17	0	—	9	45
LiCl	151	49	29	18	0	5	25	13	61
KCl	178	45	32	21	0	2	29	11	60
KBr	128	53	26	16	1	3	24	17	57
KI	109	53	23	15	7	3	28	18	56
KClO ₃	155	48	35	13	3	1	17	22	62
K ₂ SO ₄	192	44	29	25	0	2	19	19	50
KNO ₃	239	45	29	16	11	0	29	5	71
KH ₂ PO ₄	123	46	39	15	0	0	31	10	58
K ₂ CO ₃	242	42	23	26	6	3	31	1	75
KCN	234	42	33	25	0	0	35	0	76
KCNS	237	43	29	21	6	2	30	0	73
K ₄ Fe(CN) ₆	266	38	23	15	24	0	55	1	71
K ₃ Fe(CN) ₆	276	40	20	14	25	0	47	0	69
K ₂ SiO ₃	234	43	30	22	4	2	35	0	78
K ₂ Cr ₂ O ₇	240	49	16	23	10	3	39	0	55
NaOH	223	46	34	20	0	0	28	1	79
NaCl	165	50	28	20	0	2	20	12	56
Na ₂ SO ₄	177	46	34	18	0	1	18	17	45
Na ₂ S ₂ O ₃	219	51	32	17	0	0	31	0	84
Na ₂ CO ₃	210	45	36	19	0	1	29	1	82
Na ₂ B ₄ O ₇	132	51	32	16	1	1	43	3	73
MgCl ₂	124	50	32	16	0	1	28	2	59
CaCl ₂	143	54	22	21	2	3	42	2	62
BaCl ₂	128	51	31	17	0	1	20	15	49
AlCl ₃	129	43	40	17	0	1	22	14	41
Al ₂ (SO ₄) ₃	140	46	43	8	2	1	39	1	76
Rb-alum	146	51	33	14	1	1	21	13	47
CrCl ₃	146	45	29	16	9	2	29	9	57
MnCl ₂	124	49	32	15	3	2	32	7	47
MnSO ₄	164	49	31	15	5	1	21	18	34
FeCl ₂	90	48	32	12	6	2	18	23	53
FeSO ₄	146	52	26	15	6	2	27	9	52
FeCl ₃	118	46	28	13	11	3	33	5	69
CoCl ₂	120	29	37	15	15	4	45	2	65
NiCl ₂	161	33	32	16	16	4	29	12	49
CuCl ₂	118	42	32	13	12	2	20	17	54
CuSO ₄	158	45	35	13	7	0	26	10	66
AgNO ₃	179	47	28	11	13	1	16	23	48
ZnSO ₄	146	43	37	7	12	1	25	6	51
CdCl ₂	143	43	16	15	20	6	31	8	56
HgCl	70	49	37	10	4	1	17	21	46
HgCl ₂	92	46	35	13	4	2	14	31	39
HgI ₂	46	49	36	10	5	1	14	46	48
SnCl ₂	151	41	21	11	24	2	41	2	55
Pb-acetate	214	46	25	21	8	1	34	1	41
PdCl ₂	218	25	46	15	13	1	16	24	78
CuSO ₄ *	131	52	35	8	3	2	—	—	62
CuSO ₄ **	154	45	35	14	6	1	35	2	—

* The experiment was carried out at 430°.

** The experiment was carried out under the pressure of one atmosphere of carbon dioxide.

Table 2
The Effect of Inorganic Salts on the
Combustion of Cellulose (1)

Salt	<i>t</i> , sec*.	Height of flame, cm.
Without Salt	35.0	3.2
H ₃ BO ₃	31.6	2.6
NH ₄ Cl**	35.0	2.7
(NH ₄) ₂ HPO ₄ **	35.8	2.2
(NH ₄) ₂ SO ₄ **	40.3	1.8
LiCl	33.7	2.8
KCl	28.8	3.4
KBr	26.4	4.2
KI	24.7	5.0
KClO ₃	20.2	4.8
K ₂ SO ₄	38.7	2.6
KNO ₃	29.8	2.4
KH ₂ PO ₄ **	47.3	1.3
KCNS	38.0	2.1
Na ₂ SO ₄	38.1	2.4
NaHSO ₄	25.1	4.2
Ca(OH) ₂	37.7	2.8
BaCl ₂	29.3	3.4
MnSO ₄	25.1	3.3
FeSO ₄	28.3	2.6
CuCl ₂	31.2	4.2
CuSO ₄	35.3	2.1
ZnSO ₄ **	26.3	3.3
CdCl ₂ **	28.5	3.0
HgCl ₂	30.7	3.3
Pb-acetate	37.7	2.4

* The time taken to spread the flame in the middle 12 cm. length of the sample.

** The sample remained as charcoal as it was after the flame had passed over.

pumped out and then analysed. Carbon dioxide, carbon monoxide and heavy hydrocarbons were determined by absorbing with potassium hydroxide solution, cuprous chloride solution and fuming sulphuric acid, respectively and after the removal of the above gases, hydrogen and methane were estimated by the explosion method.

The results are shown in Table 1. R_1 in the table denotes the charcoal yield and V_1 the approximate percentage of the gas evolved in the first three minutes and it shows the rough decomposition velocity. Organic vapour produced by the decomposition was condensed at the upper part of the tube out of the heater, then the liquid produced went down along the tube and carbonized at the entrance of the heater. The amount of chars thus produced is designated by R_2 in the table.

Effect of Inorganic Salts on the Combustion of Cellulose:—The effect of inorganic salts on the combustion of cellulose was measured by burning the filter paper which was treated by 0.1 mol solution of various salts. The sample was supported its both sides by the folded sheets

of glass plates respectively and was placed in such a way that the glass plates were parallel with the width of 1.5 cm.⁽⁹⁾ and its gradient was 1/7 to horizon. The sample was ignited at its lower end and the time taken to spread the flame 12 cm. length in the middle was measured. The height of the flame was also measured using a perpendicular graduated mirror. Every experiment was carried out under the same condition as possible and the results were obtained by taking an average of the repeated experiments.

The results are shown in Table 2. The samples treated by such salts as potassium carbonate, silicate, bichromate and ferrocyanide, borax, Na₂S₂O₃ and aluminium sulphate were non-flammable and when the sample was horizontally placed those of ammonium sulphate and phosphate were also incombustible.

Consideration

We will see in Table 1 that by the presence of inorganic salts, R_1 was increased, R_2 decreased, while the velocity of decomposition became faster.

The volume of the gas produced was much affected by the inorganic salts. For example, in the experiment of mercuric iodide it was 46 cc./(g. cellulose) and of potassium ferri-cyanide 276 cc./(g. cellulose). The former was approximately one third of that of the untreated cellulose and the latter, about two times of it. The volume of the gas was increased by palladium and alkaline salts and decreased by mercuric or mercurous salts. The alkaline salts increased the volume of the gas in the following order: lithium, sodium, potassium and rubidium salts. The difference of valency showed a different effect as shown in the case of Fe salts. As for the anions, the volume of the gas was increased by carbonate, hydroxide, cyanide, ferri- and ferrocyanides and nitrate. Moreover, among sulphate, chloride, bromide and iodide, the relation that, if the cation present is the same, the volume of the gas became smaller in the order described above was found out.

As to the composition of the gas, it did not show so much effect of the compounds, that is, about 45 to 50% was carbon dioxide and its 30% was carbon monoxide and the major part of the remainder was methane. But most salts of the transition metals showed an increased content of hydrogen relative to oxygen in the gas.

When the pyrolysis was carried out in the atmosphere of carbon dioxide, the result was approximately the same, except the increased

(9) If a larger width was taken the flame became higher and the velocity of combustion larger.

value of R_1 and decreased R_2 . This showed that the evaporation of the organic vapour was suppressed by the presence of carbon dioxide and that the gaseous products by the carbonization of the organic vapour and those of the cellulose were not so different in this case.

At the lower decomposition temperature, the volume of the gas was decreased and its composition became richer in oxygen, showing that oxygen was more easily decomposed than hydrogen by the carbonization.

As to the results of the combustion experiment, it will be seen in Table 2 that higher the flame, faster the combustion velocity, and the velocities in the order of decreasing rates were: iodide, bromide, chloride and sulphate.

Oxidizing agents, such as potassium nitrate and chlorate, showed a faster velocity of combustion. The effect of the hydrated water on the salts was not directly observed.

T. Tatibana⁽¹⁰⁾ studied on the effect of the inorganic compounds on the ignition temperature of cellulose. He measured the lowest temperature enough to set cellulose, which was treated by inorganic salts, on fire, when the sample was put in the furnace. The "ignition temperature," which he so called, corresponds to the temperature at which the sample begins to ignite without flame, and the "flaming temperature," to fire with flame.

H. Akamatsu and H. Hamada⁽¹¹⁾ measured the effect of the various inorganic salts on the ignition temperature of carbon black⁽¹²⁾, which contained 5% salts in it using a simple thermobalance. The results are shown in Table 3.

Now we come to consider the action of fire-proofing compounds, referring to the above-mentioned data. Some investigators suggested⁽²⁾ that the action of fire-roofing compounds is possibly to let the volume of the combustible gas evolved by the pyrolysis to decrease and render cellulose noninflammable. However, though potassium carbonate, for instance, showed a large increase in the amount of combustible gas and, more over, the velocity of pyrolysis was large, it is practically one of the fire-resisting compounds. On the other hand, mercuric chloride showed only a small amount of combustible gas and had a slow decomposition velocity and, nevertheless, it is not a fire-resisting compound.

This contrast shows that the fire-resisting action is not mainly responsible to the amount

Table 3
The Effect of Inorganic Salts on the Ignition Temperature of Carbon Black

Salt	Ignition temp., °C.	Salt	Ignition temp., °C.
Without salt	491	Rochelle salt	359
LiCl	394	KAl(SO ₄) ₂	469
Li ₂ CO ₃	413	CuCl ₂	318
NaOH	330	CuSO ₄	370
NaCl	414	AgNO ₃	413
NaNO ₃	349	MgCl ₂	457
Na ₂ SO ₄	445	MgSO ₄	480
Na ₂ CO ₃	355	CaCl ₂	400
KOH	296	SrCl ₂	416
KCl	408	BaCl ₂	424
KBr	428	ZnSO ₄	451
KI	388	CdSO ₄	452
KCN	339	AlCl ₃	483
KONS	419	Al ₂ (SO ₄) ₃	466
KNO ₃	346	SnCl ₂	451
KClO ₃	397	Pb-acetate	333
K ₂ SO ₄	443	CrCl ₃	412
K ₂ CO ₃	323	MnSO ₄	450
K ₂ Cr ₂ O ₇	344	FeCl ₃	401
K ₄ Fe(CN) ₆	336	CoCl ₂	390
K ₃ Fe(CN) ₆	350	NiCl ₂	420

of the combustible gas, but suggests that the organic vapour, which was carbonized to produce R_2 , plays an important rôle in the combustion, as potassium carbonate produced no R_2 , while mercuric chloride produced an appreciable amount of it, and, furthermore, the fire-retarding compounds generally produced no or little R_2 and those which yielded a considerable amount of R_2 are not to be fire-resisting compounds as we see in the table. Thus the organic vapour might be considered, so to say, as a kindling material, when cellulose burns⁽⁵⁾.

The general process of combustion of cellulose is thought to its preceding thermal decomposition and successive ignition of the combustible materials, such as chars, combustible gases and vapours, and of these materials organic vapour is thought to be the most easily combustible.

Thus the inorganic salts are generally classified according to their effects on the combustion of cellulose as follows:

(I) Those that produce no or little organic vapour by the pyrolysis.

(A) Those that do not lower the ignition temperature of chars appreciably.

Al₂(SO₄)₃, (NH₄)₂SO₄, (NH₄)₂HPO₄, ZnCl₂, etc. (fire-resisting compounds)

(B) Those that appreciably lower the ignition temperature of chars.

NaOH, K₂CO₃, K₂Cr₂O₇, etc.

(10) Tatibana, *J. Chem. Soc., Japan*, **63**, 924 (1942).

(11) H. Akamatsu and H. Hamada, *J. Chem. Soc. Japan*, **66**, 8 (1942).

(12) This sample was made by the Mitsubishi Kasei Co. Ltd.

(II) Those that produce a considerable amount of organic vapour by the pyrolysis.

(A) Those that produce a large quantity of organic vapour.

H_3BO_3 , without salt.

(B) Others.

KCl , HgCl_2 , BaCl_2 , etc.

The salts in the first group, which produce no or little organic vapour, do not or hardly make cellulose to set flames under normal condition and potassium carbonate, silicate and ferrocyanide, sodium thiosulphate and aluminium sulphate and so on belong to this group.

But some salts in the group which lower considerably the ignition temperature of chars, as shown in Table 3, set cellulose on fire without flame, setting the produced chars on fire. Consequently the salts in the first group and those which do not lower the ignition temperature of chars appreciably, such as aluminium sulphate, ammonium sulphate and phosphate are to become the fire-retarding salts. And it is to be noted that no or little organic vapour associates to much charcoal yield and thus small quantity of heat evolved at the flames.

In the results of Tatibana⁽¹⁰⁾ aluminium sulphate, ammonium sulphate and phosphate have no "ignition temperature," suggesting that the charcoal yielded is not to be set on fire without the aid of the organic vapour, while such salts as potassium carbonate and sodium hydroxide show a lower temperature of ignition probably due to their lowering action of ignition temperature of chars.

In the case of the salts that produce a considerable amount of organic vapours by pyrolysis, cellulose burns in various ways according to the amounts and combustibilities of chars, gases and vapours. But when the organic vapours are so much as in the case of boric acid and untreated cellulose, the kindling material being so much, cellulose is not to be set on fire without flame and thus have no "ignition temperature" as shown by Tachibana⁽¹⁰⁾.

The action of such salts as zinc sulphate, cadmium chloride, ammonium sulphate and phosphate by which cellulose remained as charcoal after the flame had passed over, is to be explained by their comparatively small amount of organic vapour and less lowering action of ignition temperature of chars.

Thus we see that the actions of various inorganic salts are explained from two major factors: the yield of the tarry product and the catalytic action in the combustion of charcoal. Of course, other factors such as the formation of glaze, evolution of inert gas, and absorption of heat by the salts also play a part but only to a minor extent compared with the two major factors.

The chief effect of the fire-resisting compounds upon the above-mentioned carbonization process of cellulose is possibly considered that they promote the polymerization rate by catalysis or ready dehydration from cellulose, consequently, producing little organic vapour.

Summary

(1) The effects of the various inorganic salts on the thermal decomposition of cellulose were investigated.

(2) The combustion of cellulose in the presence of various inorganic salts was measured.

(3) It was suggested that the organic vapour produced by the pyrolysis plays an important rôle in the combustion of cellulose and that the major action of the fire-resisting compounds is to prohibit the yield of this vapour.

(4) The effect of the inorganic salts on the combustion of cellulose were classified and were explained from the two major factors: the yield of organic vapour and the lowering action of ignition temperature of the charcoal.

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Studies on Dielectric Behavior of Bound Water in Timber in the High Frequency Region

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Introduction

It has been well-known up to this time that the dielectric properties of timber remarkably depend upon the water contained. Recently, a new industry of utilizing the high frequency electric waves as a heat source for drying timbers or for gluing wood pieces together was developed in this country,⁽¹⁾ and many factors involved in the process were examined, *e. g.*, the amount of water contained, the temperature of the treatment and the wave-length of electric wave to be employed. Indeed, it is often regarded important as well as interesting to investigate why the water contained in timber has such a predominant effect upon its dielectric properties.

In the present paper, the author has intended to report the dielectric behavior of timber in the high frequency region and its possible interpretation of the results. Special attentions were paid to the measurements of the microwave region, where remarkable dielectric dispersion and absorption are expected to occur. And in comparing the dielectric behavior of pure water and that of bound water in timber, we hoped to obtain some useful informations about the state of the latter.

Experimental Method

The measurements of complex dielectric constants were carried out

- 1) at 3×10^3 M. C. by the free wave method^(2,3)
- 2) *ditto* by the wave guide method^(4,5)
- 3) at 300 M. C. by the impedance bridge method⁽⁶⁾
- 4) in the region of 0.2—15 M. C. by the dynatron method⁽⁷⁾

(1) "Theory and Application of High Frequency Phenomena," ed. by Asami (1950), Research Institute of Applied Electricity, Hokkaido University.

(2) Yasumi, This Bulletin, 24, 53 (1951).

(3) This measurement was made with the help of Mr. K. Nukazawa, Research Institute of Applied Electricity, Hokkaido University.

(4) Matsumoto and Suzuki, Bull. Technology (Hokkaido University) 1, 138 (1949).

(5) This measurement was carried out in the collaboration with Prof. Suzuki of the Department of Electric Engineering, Faculty of Technology, *ditto*.

(6) Morita, J. Inst. Elec. Eng. (Japan), 65, 59 (1946).

(7) Nishi and Sakamoto, *ibid.*, 59, 699 (1940).

- 5) d. c. conductivity by the usual galvanometer method.

The timbers of the species *tilia* (product in Hokkaido) were chosen as the experimental materials. The wood pieces to be tested were prepared in three different ways, *i. e.*, (a) cut perpendicular to the wood vessels, (b) to the medullary rays and (c) parallel to the both. The samples which were dried for several hours in a drought at the temperature of 100° were assumed as the standard material for zero-water-content. They were dried in a bath and then put into a vessel, the humidity of which was kept constant by the use of H_2SO_4 solution. The amount of absorbed water was determined with a chemical balance.

Experimental Results

The measurements of dielectric constant and loss factor were made in the region of 0.2-3000 M. C. for the samples of various water-contents (from 0 to 14 % at 300 and 3000 M. C.; from 0 to 20 % in the region of 0.2—15 M. C.). The results were shown in Figs. 1-6, where ϵ' denotes dielectric constant, ϵ'' loss factor, σ

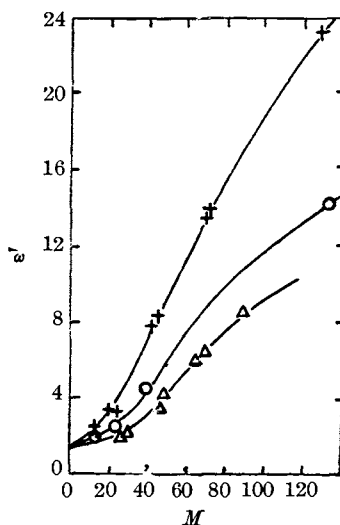


Fig. 1.—Dielectric constant at 3000 M. C. (room temp.): x, the electric field $\parallel$ wood vessels; O, the electric field $\parallel$ medullary rays; Δ , the electric field $\perp$ wood vessels and $\perp$ rays.

conductivity, f frequency, ω angular frequency and M water-content (in weight percentage), respectively.

In Figs. 1 and 2, dielectric constants and loss-factors measured at 3000 M. C. are plotted against the moisture-content, while in Fig. 3 the results obtained at 300 M. C. are shown. In all these diagrams the variations in ϵ' and ϵ'' due to the inhomogeneity of the material are clearly observed.

In Figs. 4 and 5 are shown the results obtained for a wide range of frequencies—in

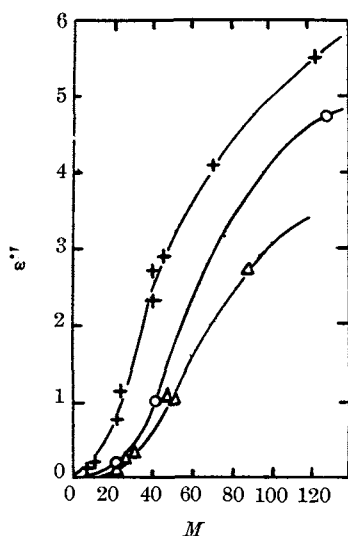


Fig. 2.—Loss factor at 3000 M. C. (room temp.) $\times$, $\circ$, $\triangle$, ditto.

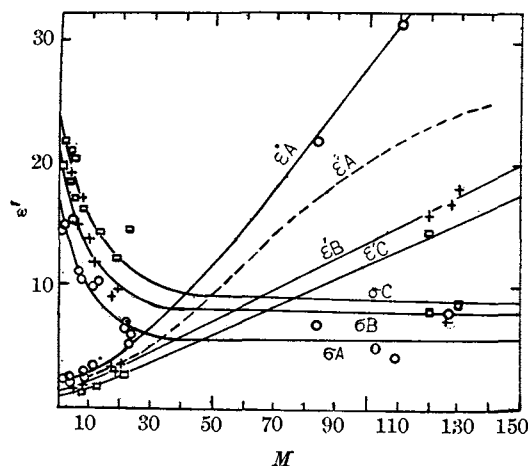


Fig. 3.—Dielectric constant and conductivity at 300 M. C. (full line) and at 3000 M. C. (broken line) (temp. $15^{\circ} \pm 2^{\circ}\text{C}.$): A, the electric field $\parallel$ the wood vessels; B, the electric field $\parallel$ the medullary rays; C, the electric field $\perp$ vessels and rays.

Fig. 5 the direct current measurement is also included. In Fig. 4 the increase in ϵ' with the increase of water-content is found to decrease with the increase in frequency. It is further to be noted that these increases in value of ϵ' are not marked in the range of 0 to 5 %. Moreover, it is interesting that the curves

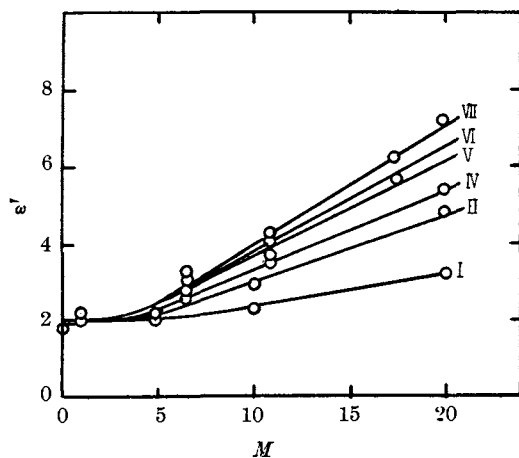


Fig. 4.—Dielectric constant and water-content ($15^{\circ}\text{C}.$): I, 3×10^9 cycles; II, 3×10^8 cycles; IV, 1.0×10^7 cycles; V, 3×10^6 cycles; VI, 1×10^6 cycles; VII, 0.4×10^6 cycles.

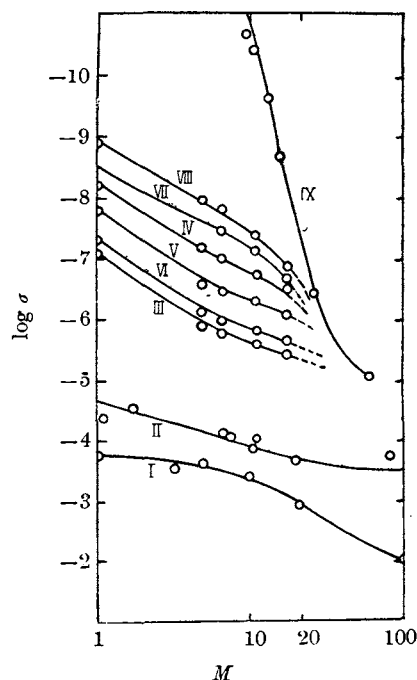


Fig. 5.—Conductivity and water-content ($15^{\circ}\text{C}.$): I, 3×10^9 cycles; II, 3×10^8 cycles; III, 15×10^6 cycles; IV, 10×10^6 cycles; V, 3×10^6 cycles; VI, 1×10^6 cycles; VII, 4×10^5 cycles; VIII, 2×10^5 cycles; IX, d. c.

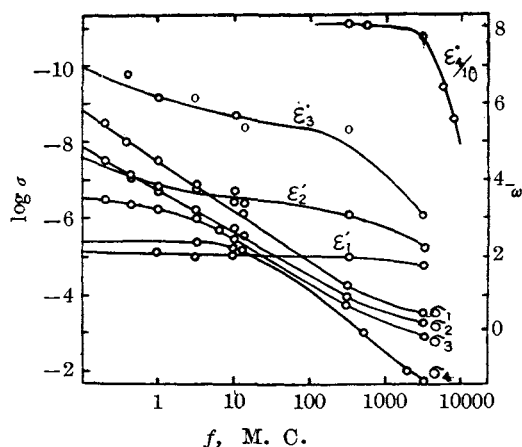


Fig. 6.—Dielectric constant and conductivity (15°C.).

ϵ'_1, σ_1	water-content	3.5%
ϵ'_2, σ_2	"	10%
ϵ'_3, σ_3	"	20%
ϵ'_4, σ_4	pure water	

of $\log \sigma$ versus M in Fig. 5 are similar to those of the dried carrot obtained by Dunlap and Makover⁽⁸⁾.

The values of ϵ' and $\log \sigma$ of the samples of the same water-content are plotted against the frequency in Fig. 6. The dielectric constants of the samples of the 10% and 20% water-contents decrease with the increase in frequency, while $\log \sigma$ generally increases with the increase of frequency. On closer examination, it appears that the inflection points of the curves for low-water-content shift to the side of lower frequency than those for high-water-content and that for pure water.

Discussion

To begin with the discussion, we must admit that our material of study, timber, is a very complicated substance to which no heterogeneous theory of dielectrics is quite applicable. Therefore we will not venture to give any complete explanation for the results observed but rather wish to present some useful notes connected with this topic. First of all, we will consider the dielectric behavior of pure water. (See the curves of ϵ'_4 and σ_4 in Fig. 6.) The relation between dielectric constant (or loss factor) and the frequency was treated theoretically by Debye⁽⁹⁾ on the basis of dipole rotation. If we assume the Onsager's inner field instead of the Clausius-Mosotti's relation which was adopted in the Debye's original

theory, the dielectric quantities will be expressed as follows:

$$\left. \begin{aligned} \epsilon' - i\epsilon'' &= \epsilon_{(\infty)} + \frac{\epsilon_0 - \epsilon_{(\infty)}}{1 + i\omega\tau} \\ \text{and} \quad \sigma &= \frac{\omega\epsilon''}{4\pi} \end{aligned} \right\} \quad (1)$$

where $\epsilon_{(0)}$ and $\epsilon_{(\infty)}$ are dielectric constants at $\omega = 0$, and $\omega = \infty$ respectively, τ is the relaxation time which differs from that of Debye by a constant factor.

We put the values $\epsilon_{(0)} = 81$, $\epsilon_{(\infty)} = 1.8$ and $\tau = 9.4 \times 10^{-12} \text{ sec}^{-1}$ (at 15°) into Eq. (1), and the calculated results are found to be in good accord with the experimental data for angular frequencies ω above 50 M. C.

As often pointed out, the following equation holds in the low frequency range.

$$\log \sigma = 2 \log f + \text{const.} \quad (2)$$

If the relation that $\omega < \frac{1}{\tau}$ is assumed, then Eq. (2) can easily be derived from Eq. (1). If water has an appreciable d. c. conductivity, σ_{ion} which arises from the movement of ions, σ is expressed as follows:

$$\sigma = \frac{(\epsilon_{(0)} - \epsilon_{(\infty)})}{4\pi} \cdot \frac{\omega^2 \tau}{1 + \omega^2 \tau^2} + \sigma_{\text{ion}} \quad (3)$$

(σ and σ_{ion} in e. s. u.)

The experimental values of σ in the region of frequencies less than 50 M. C. are found to agree with that of Eq. (3).

The dielectric constant of timber in general increases with the increase in water-content. Further, it is to be noted that the dispersion region of the dielectric constant of timber (10%—20% water-content) shifts to the side of the longer wave length than that of pure water⁽¹⁰⁾. This fact is an indication that the relaxation time of bound water in timber has a larger value than that of pure water. According to Debye, the relaxation time τ is related to internal viscosity η by the following equation.

$$\tau = \frac{4\pi\eta a^3}{kT} \quad (4)$$

where a is the radius of rotating molecule. If the internal viscosity η of bound water happens

(8) Dunlap and Makover, *J. Phys. Chem.*, **49**, 601 (1945).

(9) Debye, "Polare Molekeln," Leipzig, 1929, s. 108.

(10) The dielectric behavior of ethyl alcohol absorbed by silica gel was studied by Higuti and it was found that dielectric dispersion shifted to a longer wave length than that of pure ethyl alcohol. This is in complete agreement with our observation.

to be larger than that of pure water^(11,12), it will be natural to conclude that its relaxation time will exceed that of free water.

The experimental results for the wet timbers cannot, of course, be treated by Eq. (1). Trying to find a more general relation than that of Debye, Cole and Cole⁽¹³⁾ succeeded in proposing the following empirical relationship,

$$\epsilon' - i\epsilon'' = \epsilon_{(\infty)} + \frac{\epsilon_{(0)} - \epsilon_{(\infty)}}{1 + (i\omega\tau)^{1-\alpha}} \quad (5)$$

where τ is a most probable relaxation time and α is an empirical constant having a value between 0 and 1. The data for timbers are plotted in Fig. 7, as required by the relation of Cole and Cole (see Table 1).

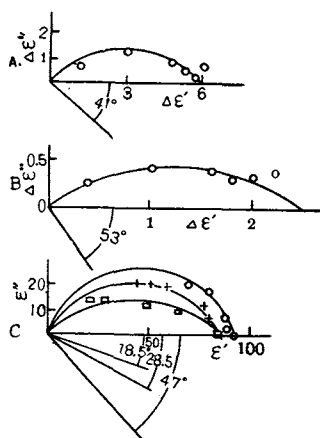


Fig. 7.—The Cole-Cole diagram.

Timber of A, 20%; B, 10% water-content.
C, cane sugar solutions: O, 30%; ×, 50%;
□, 65%.

Table 1

Water-content in the sample, %	τ , $\times 10^{-10}$ sec.	α
10	1.9	0.59
20	1.3	0.45

For the comparison's sake, the values for sucrose solution⁽¹⁴⁾ are also plotted in Fig. 7. The relation between the concentration and values of α in sucrose solution is similar to that of the water-content and α in the case of timber. Therefore, it may be concluded that the dielectric behaviors of wet timbers are represented by the two parameters, α and

τ , with the equal accuracy to the case of sugar solutions. The values of $\Delta\epsilon''$ measured at low frequency region do not lie on a semi-circular arc in Fig. 7, this departure from the curve being attributable to the conductivity of ion.

From earlier studies of bound water, it was suggested^(15,16) that the absorbed water in timber can be grouped into three classes. (1) Strongly bound water in the region of 0–5 % water-contents, (2) weakly bound water in the region of 5–30 % water-contents — so-called capillary absorbed water, (3) nearly free water in the region of more than 30 % water-content.

The relaxation time of strongly bound water may be considered to be very large that the dielectric constant should have a small value — this being revealed by Figs. 1, 3 and 4. The fact that the rate of increase in ϵ becomes constant in the range of the greater water-content, i. e., more than 30 %, suggests that the water of this range is nearly free in the timber.

Lastly we may add that Nukazawa and Takeda⁽¹⁷⁾ have examined also some of our microwave data by the use of the theories due to Maxwell, Wagner⁽¹⁸⁾, Sillars⁽¹⁹⁾ and Ozawa^(1,20) for the heterogeneous dielectrics. The results appeared to be in good accord with the assumption of bound water, since we found always remarkably large loss factor and smaller dielectric constant for component water at 3000 M. C.

Summary

1. Dielectric constants and loss factors of timber *tilia* containing various amounts of water have been measured in the region of frequencies of 0.2–3000 M. C.

2. The dielectric properties of these materials at the high frequency region are found to depend upon the rotation of dipoles of water, free and bound, in timber. The empirical relation proposed by Cole and Cole are utilized for the explanation.

3. Their dielectric properties at lower frequencies may be attributed to the other causes such as the movement of ions in the material.

The present research was undertaken when the author was a member of Research Institute of Applied Electricity, Hokkaido University

(11) Higasi, *Kagaku (Science)* **17**, 82, 83, 126, (1947).

(12) Higasi and Nukazawa, *Kagakuno-Kenkyu (Chemical Research)* **1**, 23, (1949).

(13) Cole and Cole, *J. Chem. Phys.*, **6**, 385 (1938).

(14) Slevogt, *Ann. Phys.*, (5) **36**, 141 (1936).

(15) Stamm, *Ind. Eng. Chem.*, **21**, 94 (1929).

(16) Stamm, *J. Phys. Chem.*, **39**, 121 (1934).

(17) Nukazawa and Takeda, *Kagaku (Science)*, **17**, 181 (1947).

(18) Wagner, *Elektrotech.*, **2**, 371 (1914).

(19) Sillars, *J. Inst. Elec. Eng.*, **80**, 378 (1937).

(20) Asami, Higasi and Ozawa, *Nature*, **165**, 195 (1950).

and he wishes to express his sincere thanks to Professor K. Higasi for his kind guidance. His thanks are also due to Mr. Nukazawa and Mr. Suzuki for their kind cooperation, and Dr. Yasumi for his help in translating the original

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Magnetic Property and Resonance Character of Cyclooctatetraene (C_8H_8)

By Shoji SHIDA and Saburo FUJII

(Received April 25, 1951)

Introduction

If cyclooctatetraene (C. O. T.) is assumed to have a regular eight-membered ring structure, it may be paramagnetic in the ground state. This has been theoretically suggested by E. Hückel⁽¹⁾ in his earlier quantum mechanical treatment and shown recently also by Y. Mori, I. Tanaka and S. Shida⁽²⁾ from the standpoint of the antisymmetrical molecular orbital theory including electron repulsions.

On the other hand, if it is not paramagnetic but diamagnetic on account of some reasons, it will have more or less diamagnetic anisotropy due to resonance in analogy with benzene and other aromatic molecules.

In the course of the study the following fact has come to be clear that R. C. Pink⁽³⁾ and W. Klemm⁽⁴⁾ had obtained -51.9×10^{-6} and -55.6×10^{-6} respectively as the molecular diamagnetic susceptibility of C. O. T. The difference between the above two values, which is beyond the usual experimental errors in susceptibility measurements, may be considered to be dependent upon impurities in the C. O. T. used by them, and their interpretations for the magnetic property seem to be different from ours so far as we can know from the available abstracts⁽⁵⁾ of their works.

Therefore it is worthwhile to report our new susceptibility measurements for purified C. O. T. and to describe our opinions for this mag-

netic property, especially for the relationship between the diamagnetic anisotropy and the resonance character, on the basis of its probable structures^{(6)~(11)}, its thermal data^{(12)~(14)} and the quantum mechanical calculations⁽²⁾,⁽¹⁵⁾ on its electronic levels.

Experimental

Our apparatus for magnetic susceptibility measurements is a Weiss-Föex type⁽¹⁶⁾ with several refinements and the main part is shown diagrammatically in Fig. 1.

This main part is doubly covered with glass plates to prevent it from air disturbance. Passing a constant direct current of 20 amperes through this magnet, the field strength between the pole-pieces, 17 mm. apart from each other, is about 10,000 gauss. According to the tests with several common substances this apparatus is proved to be useful with an error of 0.5 percent for determinations of mass susceptibilities of 10^{-6} order and able to detect its temperature dependence exceeding 0.5 percent over the temperature range 20° to 100°C.

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(8) E. P. Lippincott, R. C. Lord and R. S. MacDonald, *J. Chem. Phys.*, **16**, 548 (1948).

(9) H. S. Kaufman, I. Fankuchen and H. Mark, *J. Chem. Phys.*, **15**, 414 (1947).

(10) H. S. Kaufman, I. Fankuchen and H. Mark, *Nature*, **161**, 165 (1948).

(11) R. Hedberg and V. Schomaker, Annual Meeting of Am. Chem. Soc., 1949.

(12) E. T. Prosen, W. H. Johnson and F. D. Rossini, *J. Am. Chem. Soc.*, **69**, 2068 (1947).

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(14) D. W. Scott, M. E. Gross, G. D. Oliver and H. M. Huffman, *J. Am. Chem. Soc.*, **71**, 1634 (1949).

(15) I. Tanaka and S. Shida, *This Bulletin*, **23**, 54 (1950).

(16) G. Foex and R. Forrer, *J. phys.*, **7**, 180 (1926).

(1) E. Hückel, *Z. Physik*, **70**, 204 (1931); *J. de phys. et rad.*, **6**, 347 (1935).

(2) Y. Mori, I. Tanaka and S. Shida, *This Bulletin*, **23**, 168 (1950).

(3) R. C. Pink and A. R. Ubbelohde, (a) *Nature*, **160**, 502 (1947); (b) *Trans. Faraday Soc.*, **44**, 708 (1948); (c) *Chemical Abstracts*, **43**, 2479f (1949); (d) *ibid.*, **44**, 6212f (1950).

(4) W. Reppe, "Acetylene Chemistry," 1946.

(5) References 3a, 3c, 3d, and 4.

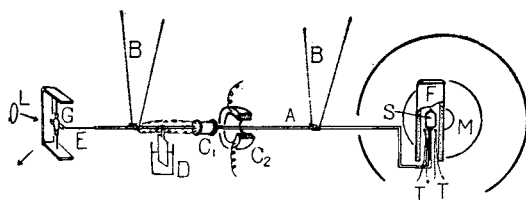


Fig. 1—Weiss-Föex Balance: A, quartz rod; B, fine copper wire; C₁, the 1-st coil; C₂, the 2-nd coil; D, oil damper; E, magnetized needle; F, electric furnace; G, mirror suspended by fine bronze ribbon (its back is pasted with polished thin steel plate); L, lens; M, magnet; S, sample vessel; T, thermocouple.

The C. O. T. used in the present measurement was obtained through the courtesy of Professor S. Murahashi and Dr. N. Hagiwara⁽¹⁷⁾, who prepared it with the catalytic polymerization of acetylene in autoclave and purified it by means of several fractional distillations under a low pressure of nitrogen. This substance is a transparent yellow liquid (m. p. -7.5° , b. p. 95.6° at 185 mm. Hg) and stored in an evacuated tube in the dark because it becomes turbid brown in a day if opened in air. Before each measurement this substance, not including any detectable amount of styrene, was distilled several times *in vacuo* and the last middle portion always used.

Our measured value of the mass susceptibility of this C. O. T. at 30° is

$$(-0.518 \pm 0.003) \times 10^{-6}$$

hence the molecular susceptibility

$$(-53.9 \pm 0.3) \times 10^{-6}$$

This value is between those obtained by W. Klemm and by R. C. Pink. In the measurement of the temperature dependence of susceptibility for this substance the experiment was carried out with the sample distilled in an evacuated small glass vessel for susceptibility measurement and the correction for the vessel was done under the condition of it being evacuated. The magnitude of force acting on the sample liquid in a non-homogeneous magnetic field depends sharply upon the volume and the position which are occupied by the sample between both pole-pieces. Therefore the magnitudes of force acting on the constant mass at various temperatures are, though slightly, detectably different from each other owing to the volume change with temperature of the sample liquid. The fact indicates that the relation between the magnetic force and the volume of sample is necessary to be determined in this experiment. The correction⁽¹⁸⁾ for the

effect described above was also taken into account in the present measurement.

According to these three measurements the temperature dependence of the mass susceptibility of C. O. T. could not be detected over the temperature range 30° to 80°C. with an experimental error of 0.5 percent.

Discussion

Though we cannot determine the reliable order for the three different values of the mass susceptibility of C. O. T. because the detailed reports on W. Klemm's and R. C. Pink's experiments cannot be obtained, this substance is now clearly proved to have a temperature independent diamagnetism and therefore the possibility of a spin paramagnetism, as suggested by E. Hückel, excluded. Our purpose for the measurement of the temperature dependence of this diamagnetism was to examine the possibility of a small energy difference between the diamagnetic ground state and the lowest triplet one as well as that of a mixture of diamagnetic and spin paramagnetic isomers, this latter one being assumed in the first report^(3a) by R. C. Pink and A. R. Ubbelohde. But our result does not support these possibilities.

Next it is important to consider the diamagnetic anisotropy of this molecule in comparison with aromatic and hetero-cyclic ones composed of conjugated double bonds, for the previous authors^{(3), (4)} did not pay any attention to this property. The diamagnetic anisotropy of ring-shaped molecules composed of conjugated double bonds is generally recognized to be induced by the free migration of resonating $p\pi$ electrons along the molecular network under an external magnetic field, and therefore it can be represented qualitatively with circulating electric currents along the molecular network. The molecular structure of C. O. T. has not yet been determined definitely, but the most probable one may be $D_{2d}^{(9)} \sim (11)$, while $D_{4d}^{(6), (7)}$ and $D_4^{(8)}$ are also recently reported by different authors.

Then, with these structures and the models shown in Fig. 2, the anisotropic parts to x and y directions may be nearly negligible because each component of the diamagnetic currents is canceled out vectorially by oneself from the above view-point.

According to this consideration the molecular susceptibilities to the both directions have to be equally $4/3$ times of that of benzene, *i. e.*, about -49.7×10^{-6} . Then, from the experimental mean molecular susceptibility -53.9×10^{-6} and the values to x and y directions, the

(17) The members of the Institute of Scientific and Industrial Research, University of Osaka.

(18) This correction was obtained by the use of toluene. The mass susceptibility of toluene has not a temperature dependence exceeding 0.5 percent over the temp. range 10° to 50° . (G. F. Boeker, *Phys. Rev.*, **43**, 756 (1933)).

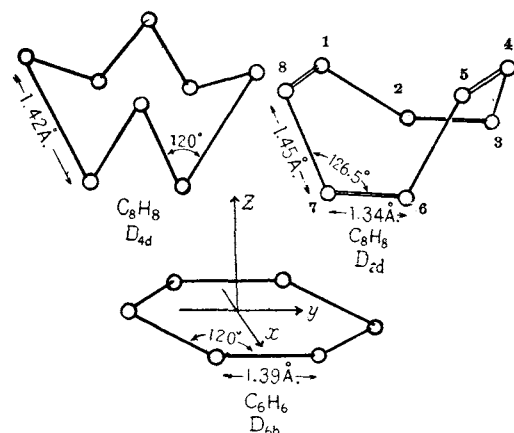
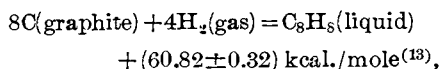


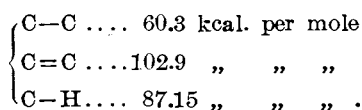
Fig. 2.

anisotropic part⁽¹⁹⁾ to z -direction is estimated as about -12.6×10^{-6} per mole, that is, about 23 percent of that of benzene. This estimated anisotropy is very small in spite of the fact that this molecule has eight $p\pi$ electrons and larger projected area on the xy plane than that of benzene.

On the other hand, the estimated resonance energy of this compound is also small and about 2.9 kcal. per mole, it being about 7 percent of that of benzene. It is calculated from the following thermal data determined recently;



the heat of vaporization of liquid C_8H_8 is 10.300 ± 0.075 kcal./mole⁽¹⁴⁾ and the bond energies⁽²⁰⁾



R. C. Pink and A. R. Ubbelohde^(3a) have obtained 25.4 kcal./mole for this resonance energy. The old value used by them for the heat of formation of this compound is considered to have some uncertainty and therefore their question that C. O. T. is magnetochemically aliphatic rather than aromatic in spite of its considerable resonance energy may not be fit. From these relationships between resonance energies and diamagnetic anisotropies of C. O. T. as well as aromatic and heterocyclic molecules composed of conjugated double bonds we can understand that the larger

anisotropy a molecule has, the more remarkable its resonance character is. This phenomenon can be explained qualitatively from the quantum mechanical view-point by the fact that these two properties are both directly related to the resonance integrals of $p\pi$ electrons.

According to the atomic and molecular orbital calculations^{(2), (15)} on the electronic levels of this molecule the exchange or resonance integrals between any adjacent carbon atoms in the case of D_{4d} and these between the 1-st and 2-nd carbon atoms in D_{2d} in Fig. 2 are smaller than those of benzene. Also the calculated resonance energy⁽²⁾ in the case of D_{2d} on the basis of the L-C-A-O approximation is 2.7 kcal./mole, it being consistent with the value estimated from thermochemical data.

Therefore the small anisotropy of this molecule can be also explained by the fact that the small resonance integral means the difficulty of free migration of $p\pi$ electrons along the molecular network under an external magnetic field. Then it is interesting to discuss this anisotropic part on the basis of Langevin's classical theory⁽²¹⁾ and the molecular orbital method by F. London.⁽²²⁾ The latter obtained an excellent agreement with experiments in the calculation of the anisotropies of aromatic molecules. According to P. Langevin the anisotropic part of a simple ring-shaped molecule with n migrating $p\pi$ electrons can be written

$$\Delta\chi_{\text{M}} = -\frac{Ne^2}{4\pi mc^2} \sum_{i=1}^n \bar{r}_i^2 \dots\dots\dots (1)$$

where N is the Avogadro number and $\bar{r}_i^2$ mean square radius of the i -th migrating $p\pi$ electron along the molecular ring.

In the cases of benzene, pyridine, furane, pyrrole, thiophene and cyclopentadiene, all of which have plane structures and relatively large resonance energies, the calculated anisotropies⁽²³⁾ from Eq. (1) are in agreement with the values estimated from the Pascal additivity law within the maximum error of about 10 percent. However, the calculated values for C. O. T. as D_{4d} and D_{2d} are -103.7×10^{-6} and -155.6×10^{-6} respectively, and obviously they are quite different from the value estimated by us, *i. e.*, -12.6×10^{-6} . Hence Langevin's theory may be applied only to the molecule with a plane structure and a remarkable resonance character.

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(20) J. T. Cotrell and L. E. Sutton, *J. Chem. Phys.*, **15**, 685 (1947).

(21) E. C. Stoner, "Magnetism and Matter," Methuen & Co. Ltd, London, 1934, p. 107.

(22) F. London, *J. de phys. et rad.*, **8**, 397 (1937).

(23) G. Hazato, *J. Chem. Soc. Japan*, **64**, 622 (1943).

Now we shall apply the London theory to this molecule to see what results we can get from this method. If the field perturbation is neglected, his theory is reduced to a simple type of the one-electron approximation, and then the ground electronic states calculated in this case are illustrated in Fig. 3.

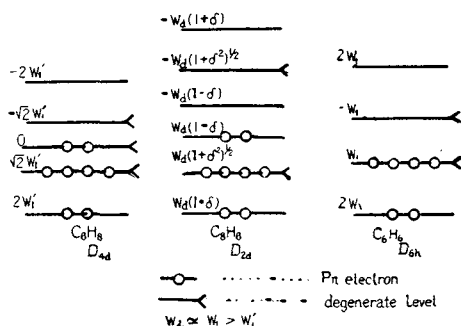


Fig. 3.

In Fig. 3 it is shown that both D_{2d} and D₄ structures are diamagnetic but D_{4d} should have a spin paramagnetism owing to a degenerate level occupied by only two electrons and so the calculation of the anisotropic part for D_{4d} may be meaningless. Therefore we shall calculate the anisotropy in the case of D_{2d}, and the present calculation follows, for the convenience's sake, the same notation and procedure as London's paper.

If $\left(\frac{x_k + x_l}{2} \pm \xi_{kl}, \frac{y_k + y_l}{2} \pm \eta_{kl}\right)$ are two xy -coordinates where the overlap between Pz wave functions in the k -th and the l -th carbon atoms is maximum, and we put

$$\theta_{kl} = \frac{\pi e}{hc} [(x_k - x_l)\eta_{kl} - (y_k - y_l)\xi_{kl}],$$

then the anisotropic part due to a $p\pi$ electron in the p -th energy state is expressed as follows:

$$\chi_p = - |W'_a| \times \left\{ \frac{(\theta_a^2 + \delta^2 \theta_s^2) + \left(\frac{\pi^2 e^2 S^2}{16 h^2 c^2} + \theta_a^2 + \theta_s^2\right) \delta \cos \frac{2\pi}{4} p}{\left(1 + 2\delta \cos \frac{2\pi}{4} p + \delta^2\right)^{1/2}} + \frac{\left(\frac{\pi^2 e^2 S^2}{16 h^2 c^2} + \theta_a^2 + \theta_s^2\right) \delta^2 \sin^2 \frac{2\pi}{4} p}{4 \left(1 + 2\delta \cos \frac{2\pi}{4} p + \delta^2\right)^{3/2}} \right\}, \dots (2)$$

where $\theta_{ii} = \theta_{s1}$, $\theta_s = \theta_{12}$, $\delta = W_s/W_a < 1$. S is the projected molecular area on the xy -plane and W_s , W_a are the resonance integral between

the 1-st and the 2-nd carbon atoms and the one between the 1-st and the 8-th carbon atoms respectively. Here the positions of carbon atoms are denoted as shown in Fig. 2.

Therefore the total anisotropic part to z -direction is

$$\begin{aligned} \Delta\chi_M &= 2(\chi_{-1} + \chi_0 + \chi_1 + \chi_2) \\ &= -4 |W_a| \left[\delta^2 \left(\frac{\pi e S}{2hc} \right)^2 \left\{ \frac{1}{(1 + \delta^2)^{3/2}} - \frac{1}{1 - \delta^2} \right\} \right. \\ &\quad \left. + \theta_a^2 + \frac{\theta_s^2 + \delta^2 \theta_s^2}{(1 + \delta^2)^{1/2}} \right], \dots (3) \end{aligned}$$

Using the numerical data measured by K. Hedberg and V. Shomaker⁽¹¹⁾ we obtain

$$S = 7.9(\text{\AA}^2), |\theta_a| = 0.32 \left(\frac{2\pi e}{hc} \right) (\text{\AA}^2) \text{ and } \theta_s = 0.$$

Then assuming $\delta = 0.4$ ⁽²⁾ we obtain

$$\Delta\chi_{C_6H_6, D_{2d}} = +0.26 |W_a| \left(\frac{2\pi e}{hc} \right)^2, \dots (4)$$

while for benzene

$$\Delta\chi_{C_6H_6, D_{6h}} = -5.75 |W_1| \left(\frac{2\pi e}{hc} \right)^2, \quad W_1 \simeq W_a.$$

Eq. (4) indicates the anisotropic part for D_{2d} being weak paramagnetic and furthermore Eq. (3) represents that the anisotropy becomes more paramagnetic as δ approaches to 1 over 0.4.

These results are obviously in contradiction with experiments and physical aspects. The calculated results in the case of D₄ are identical with that of D_{2d}, though the numerical values of W_a , δ , S , θ_a and θ_s are different from those in D_{2d}. Considering the above discussions both of Langevin's theory and London's method in the original form cannot explain the small diamagnetic anisotropy of C. O. T. quantitatively or even qualitatively. The question why the London's method cannot apply to this molecule with his original procedure is remained unsolved and under investigation.

Summary

We have obtained -53.9×10^{-6} at 30° as the molecular diamagnetic susceptibility of purified cyclooctatetraene, and its temperature dependence exceeding 0.5 percent over the temperature range 30° to 80° has not been detected. The diamagnetic anisotropy of this molecule has been estimated -12.6×10^{-6} per mole on some assumptions, and the resonance energy 2.9 kcal. per mole from the thermal data.

The relationship between the small anisotropy and the weak resonance character of this

molecule has been discussed and explained qualitatively on the basis of the quantum mechanical considerations. Langevin's theory and the original procedure of London's method have been found to be unsuitable for the explanation of this small anisotropy.

The authors wish to express their appreciation to Professor M. Tamura at the Kyoto University for his encouragement and to Mr. I. Tanaka for his helpful discussion during the course of this work. They are also grateful

to Professor O. Murahashi and Dr. N. Hagiwara at the Institute of Scientific and Industrial Research, University of Osaka, for their kind offer of cyclooctatetraene and for their helpful advice. The cost of this research was defrayed from the Scientific Research Encouragement Grant from the Ministry of Education, to which the authors' thanks are due.

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On the Action of Carriers in the Catalytic Hydrogenation of Acetylene by Palladium Catalyst

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Introduction

The author previously investigated⁽¹⁾ the hydrogenation of acetylene on Pd-alumina (1:100) catalyst by the static method. It was found that the hydrogenation of acetylene proceeds in two distinct steps at room temperature. The first step consists of the reduction and polymerization of acetylene, and the second step the hydrogenation of ethylene to ethane. The second step started after all acetylene was used up, accompanying a sudden increase in the rate of hydrogenation, and this phenomenon was explained by the strong adsorption of acetylene on the surface of the catalyst. Poisoning or retarding both steps of the hydrogenation simultaneously, it was suggested⁽²⁾ from the kinetical treatment of the reaction that the hydrogenation of acetylene occurs on the various "active regions" with different proportions from that of ethylene.

Palladium catalysts which was deposited on kieselguhr with various dispersities proceeded the hydrogenations of the two hydrocarbons with different relative rates. Hence, this fact was considered to suggest⁽³⁾ the difference of the dispersity of the catalyst to have connection with the appearance of the various "active

regions" of the catalyst surface with different ratios.

In this study experiments were carried out on the palladium catalyst deposited on the various carriers and the rôle of the carrier, along with the mechanism of the hydrogenation of acetylene, was considered.

Experimental

Palladium was deposited on the various carriers by the similar method with that of the previous experiments, that is, suspending the carriers in the palladium chloride solution, potassium hydroxide solution and formaldehyde were added to deposit the palladium on the carriers. Silica gel, french chalk, carbon black, active charcoal, quartz sand, Japanese acid clay, alumina and kieselguhr were used as carriers⁽⁴⁾ and the ratio of palladium to the carrier was 1/100 for each carrier.

The experiments were carried out by the static method and their procedure was the same as the previous experiment⁽¹⁾. The results of the several experiments at 30.0° are shown in Fig. 1. The

(4) The used carriers were as follows: Silica gel and Japanese acid clay were prepared by the Takeda Pure Chemicals Ltd. Osaka; French chalk by the Hirasawa Pharmaceutical Laboratory, Tokio; carbon black by the Nihon Kasei Co. Ltd.; active carbon (powder) by E. Merck, Darmstadt, and quartz sand by the Schering-Kahlbaum A. G. Berlin.

The granular active carbon was prepared from the charcoal impregnated by phosphoric acid and each granule was about 0.02 to 0.05 g. in weight.

(1) Kenzi Tamaru, This Bulletin, **23**, 64 (1950).

(2) Kenzi Tamaru, This Bulletin, **23**, 180 (1950).

(3) Kenzi Tamaru, This Bulletin, **23**, 184 (1950).

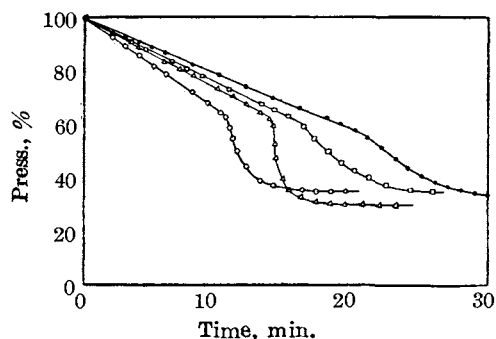


Fig. 1.—Hydrogenation of acetylene by Pd-catalyst on the various carriers at 30°.

	Total press., mm.-Hg	C ₂ H ₂ , %
—□—□—: Pd-French chalk (0.210 g.)	439	32.5
—●—●—: Pd-Japanese acid clay (0.165 g.)	474	36.1
—△—△—: Pd-active carbon (Merck) (0.519 g.)	402	33.7
—○—○—: Pd-carbon Black (0.545 g.)	422	35.0

change of the composition of the reactant with time was qualitatively similar with that in the experiments on Pd-alumina or Pd-kieselguhr catalyst in the preceding papers, and the hydrogenation of acetylene first proceeded linearly with time, and when acetylene was used up, the second step, or ethane formation, began with a faster rate.

When the granular active carbon was used as a carrier, the change of the total pressure of the reactant with time was very different from Fig. 1, as shown in Fig. 2 by the full line, and the

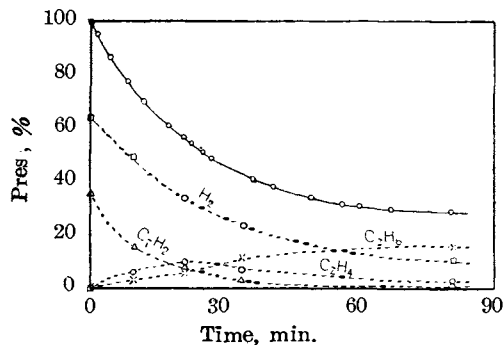


Fig. 2.—Hydrogenation of acetylene by Pd-granular active carbon at 30°: Catalyst, 0.425 g.; total press., 511 mm.-Hg; C₂H₂, 36.0%.

reaction rate was appreciably different according to the sizes of the granules. The change of the composition of the reactant was given by the broken lines in the figure. In this case no inhibition of the ethane formation by acetylene was observed and both hydrogenations of acet-

ylene and ethylene were simultaneously occurred, showing a typical successive reaction.

But when the catalyst was powdered in the mortar, the hydrogenation proceeded in a different way from the granular one, as shown in Fig. 3 by the full and the broken lines, that is, a new reflection point appeared, which is indicated by the arrows in the figure. The change of the composition of the reactant was shown by the dotted lines in Fig. 3 in the case of the initial

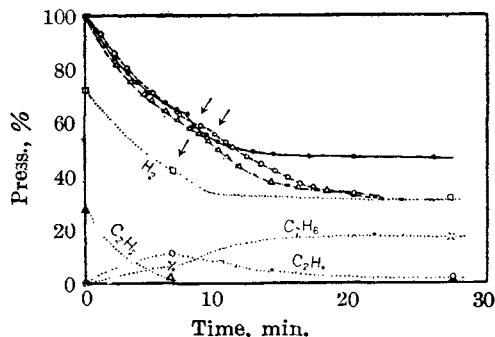


Fig. 3.—Hydrogenation of acetylene by Pd-powdered active carbon and Pd-silica gel at 30°.

	Total press., mm.-Hg	C ₂ H ₂ , %
--○---○--: Pd-powdered active carbon (0.248 g.)	495	36.7
—●—●—: Pd-powdered active carbon (0.096 g.)	514	27.6
—△—△—: Pd-silica gel (0.620 g.)	405	36.4

composition of 27.6% acetylene content. The ethane formation was already observed while acetylene was being hydrogenated and the reflection point corresponded to the moment that all acetylene was consumed.

The result of the Pd-silica gel catalyst is shown in Fig. 3 by the chain line and this is very similar to that of Pd-powdered active carbon catalyst. It was shown by gas analysis that the reflection point was the point that all acetylene was used up and that ethane formation was to be seen before the point, similarly with the case of Pd-powdered active carbon catalyst.

When quartz sand was used as a carrier the result was appreciably different from the other carriers, and ethane and ethylene formations proceeded simultaneously as shown in Fig. 4. When the initial composition was changed, the reaction proceeded, for example, as shown in Fig. 5 and no self-retardation of acetylene was observed in this case.

The hydrogenation rate of acetylene and ethylene by palladium on the various carriers were shown in Table 1, where the reduction rate of ethylene to ethane was obtained through the hydrogenation of ethylene without retardation of polymers and was given in the table by the reaction constant of the first order reaction.

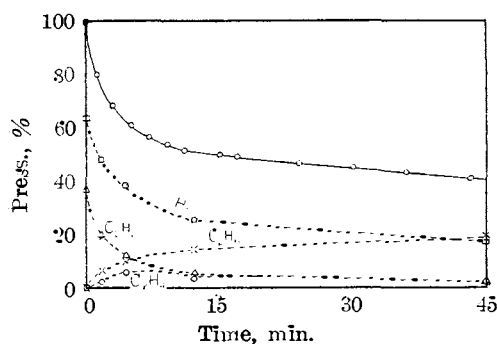


Fig. 4.—Hydrogenation of acetylene by Pd-quartz sand catalyst at 30°: Catalyst, 0.387 g.; total press., 521 mm.-Hg.; C₂H₂, 36.5%.

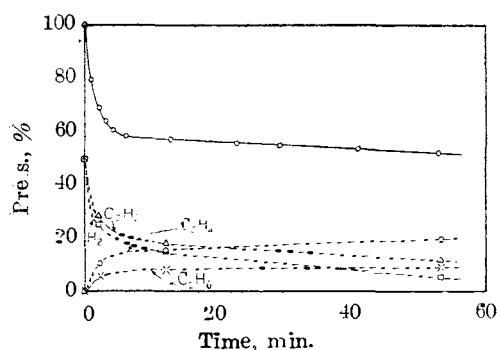


Fig. 5.—Hydrogenation of acetylene by Pd-quartz sand catalyst at 30°: Catalyst, 0.467 g.; total press., 550 mm.-Hg.; C₂H₂, 49.8%.

Table 1

The Hydrogenation Rates of Acetylene (V_1) and Ethylene (k_2) by Palladium on the Various Carriers

Carriers	V_1^* , %/10 min.	k_2
Alumina	21.0	20.0
Kieselguhr	25.0	24.6
Japanese acid clay	13.3	—
French chalk	11.9	8.0
Carbon black	6.6	6.0
Active carbon (Merck)	5.2	9.0
Powdered active carbon	28.1	—
Silica gel	11.8	—
Quartz sand	59.5	—

* The initial rate of hydrogenation of acetylene per gram catalyst when the total pressure of the reactant was 400 to 500 mm.-Hg and acetylene content approximately 35%.

From the dependence of the hydrogenation rate of acetylene upon temperature, the activation energies of the reaction on the various carriers were obtained as follows: carbon black 10, French chalk 11, quartz sand 11, powdered active carbon 11, kieselguhr 10, alumina 12 kcal. per mole.

Now we come to consider the experimental data mentioned above to study the functions of the carriers for the various cases.

Consideration

We have observed the various types of the reaction curves in the several figures. Now we shall consider how and why these different types of the reaction can occur by the palladium catalyst on the various carriers and study on the functions of carriers for individual cases.

In the preceding paper several functions of a carrier were referred and it was suggested from the kinetical treatment of the reaction that the dispersity of catalyst has connection with the appearance of various "active regions" of the catalyst surface.

As we see in Fig. 1, in the case of such carriers as carbon black, active carbon (Merck), French chalk and Japanese acid clay, the hydrogenation of acetylene proceeded in two distinct steps quite similarly to the case of kieselguhr or alumina and the hydrogenation of ethylene to ethane could not proceed while acetylene was present in the reactant, because of the strong adsorption of acetylene on the palladium surface.

If the carriers provide only a larger effective surface of the catalyst proper, the ratio of the hydrogenation rate of acetylene to that of ethylene is not to be altered by the carriers, though the rate of the hydrogenations may be changed by them. In fact, the ratio of the two hydrogenation rates changed according to the carriers as shown in Table 1. While the activation energies of the hydrogenation of acetylene showed approximately the same value for the carriers, it may be said from the kinetical treatment that the effective area of the various "active regions" of the catalyst will be changed by the kinds of carriers not only their area, but also the proportions of the individual "active regions."

As shown in Fig. 2, the hydrogenation of acetylene proceeded on the Pd-granular active carbon in a different way from such carriers as alumina or kieselguhr, and the hydrogenations of acetylene and ethylene occurred side by side, not proceeding in two distinct steps. Thus it was shown that the granular active carbon is not to be used as a carrier in practice for the selective hydrogenation of acetylene.

But when the catalyst was powdered in the mortar, the reflection point appeared, at which, as the gas analysis showed, all acetylene was consumed, while the ethane formation was already observed before the point. This fact

shows that the different type of the curve in Fig. 2 is not to be ascribed to the disappearance of the self-retardation of acetylene, but to the heap of the carrier. Hence, it is to be explained as follows: in the case of the granular carrier the rate of diffusion of the reactant or acetylene into the inner part of the granule is not so fast as the reaction rate at the part, the self-retardation of acetylene, therefore, is not to be seen there, being deficient in the gas, and proceeding the ethane formation, while acetylene is present in the bulk space. When the catalyst was powdered, the proportion of the inner part of the granule practically decreased and the ethane formation in the presence of acetylene could not proceed so much as the granular one, while the reflection point appeared somewhat later than the normal carriers. Hence, the self-retardation of acetylene was also to be observed by the experiments as shown in Fig. 3, and when the acetylene content in the initial composition of the reactant was increased, the reaction rate was appreciably retarded as in the case of such carriers as alumina and others.

In the case of Pd-silica gel catalyst the reaction curve was very similar with that of powdered active carbon, suggesting the similar mechanism of the hydrogenation. It is suggested, consequently, that from these reaction curves we can study the structural property of materials, using them as a carrier of this reaction.

When the quartz sand was used as a carrier, the hydrogenation proceeded in a different way from others. As shown in Fig. 4, the ethane and ethylene formations occurred simultaneously, showing no self-retardation of acetylene.

The Pd-quartz sand catalyst was, as it were, a mixture of palladium metal and quartz sand, because of the scanty adsorbability of the carrier and the experiments were not so reproducible as the other carriers, as the distribution of the palladium was not so homogeneous. But it was observed that the initial reaction rate was not so retarded by the increased content of acetylene in the reactant as shown in Fig. 5. The following explanation will possibly be given in this case: scanty adsorbability of the carrier resulted in the much deposited polymers on the surface of the catalyst proper. Hence, the adsorption rate of acetylene was retarded in such an extent that the rate became slower than that of the reaction rate on the catalyst surface. Thus, the effective surface of the catalyst being not covered by acetylene, both hydrogenations of acetylene and ethylene proceeded side by side, showing no self-retardation of acetylene. The

considerably fast rate of hydrogenation of acetylene on this catalyst, as given in Table 1, is also considered to support this explanation, as the scanty adsorbability of the carrier should result in the smaller area of the catalyst surface if acetylene covers the catalyst surface as in the other carriers.

Summary

Acetylene was hydrogenated by palladium deposited on such carriers as carbon black, active carbon (Merck), Japanese acid clay, French chalk, silica gel, granular active carbon, and quartz sand, and the functions of the carriers were considered for individual cases.

The catalysts deposited on the first four carriers catalyzed the hydrogenation in two distinct steps at 30° in the same manner as alumina and kieselguhr, that is, hydrogenation and polymerization of acetylene proceeded in the first step and then ethylene was reduced to ethane in the second step, showing a pronounced self-retardation of acetylene. It was suggested that the kind of carriers has connection with the appearance of various "active regions" with different ratios.

When the granular active carbon was used as a carrier, the hydrogenations of acetylene and ethylene proceeded not in two steps, but simultaneously. This phenomenon was explained by the slow diffusion velocity of acetylene into the inner part of the granule. Powdering the catalyst, the reflection point appeared in the hydrogenation curve and the curve was very similar to that of silica gel, suggesting a similar mechanism of the reaction.

When the quartz sand was used as a carrier, the hydrogenations of the two hydrocarbons occurred at the same time. This is explained by the retardation of the adsorption rate of acetylene by the deposited polymers to such an extent as the adsorption rate becomes to be rate-determining.

It was shown, therefore, that the granular active carbon and quartz sand are not to be used in practice for the selective hydrogenation of acetylene.

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Magnetic Properties of Condensed Aromatic Hydrocarbons with Four Benzene Nuclei. I. On the Diamagnetism of Chrysene

By Hidemasa HONDA and Kōji ŌUCHI

(Received April 28, 1951)

Introduction

The Pascal's additive law⁽¹⁾ of magnetic susceptibility is very well adopted to the aliphatic compounds but the values of molecular susceptibility of aromatic compounds in the treatment as well as the aliphatic compounds for the carbon and hydrogen atoms are diamagnetically smaller than the experimental values. Pascal assigned this excessive parts of diamagnetism to the respective carbon atoms that form the condensed nuclei. Taking into account the constitutive corrections the larger the condensibility of benzene nuclei is, the larger the difference between the calculated values by additive law and the experimental ones becomes.

On the other hand, F. London⁽²⁾ calculated the ratios of the diamagnetic anisotropies of various condensed aromatic compounds to that of benzene by a quantum mechanical procedure, based on Hückel's molecular orbital treatment, extending to the case of the presence of a magnetic field and obtained an excellent agreement with experiment.

In general, the diamagnetism of condensed aromatic hydrocarbons becomes larger with the increase of hexagon number, but it will be expected that the diamagnetic susceptibilities of condensed aromatic hydrocarbons with the same number of hexagon are changed by the form of molecule. Accordingly, the London's theory is applied to the theoretical calculation of the anisotropic part in the condensed aromatic hydrocarbons with four benzene nuclei and the experimental values are compared.

Form of Chrysene Molecule

The X-ray analysis of chrysene crystal has been made by Iball⁽³⁾. The crystal belongs to

the space group C_{2h}^6 (12/C) or C_3^4 (1C). The dimensions of the unit cell are $a=6.59$, $b=7.84$, $c=14.17$ Å, $\beta=108.5^\circ$, and it contains 4 molecules. The crystal density 1.27, melting point 250°C ., boiling point 448°C ., molecular weight 228, and the form of molecule is plane and consists of regular hexagons with interatomic distances of 1.41 Å.

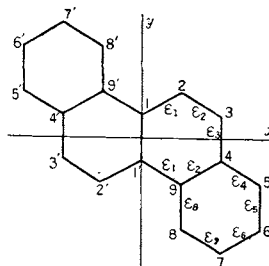


Fig. 1.

Theoretical Calculation

The present calculation follows the same notation and procedure as London's paper.⁽⁴⁾ London's secular equation is as follows:

$$|\eta_{kl} \exp(2\pi i f_{kl}) - x \delta_{kl}| = 0, \quad (1)$$

where $\eta_{kl} = \begin{cases} 1 & \text{if } k \text{ is a neighbor of } l \\ 0 & \text{if } k \text{ is not a neighbor of } l \end{cases}$
 $\delta_{kl} = \begin{cases} 1 & \text{if } k=l \\ 0 & \text{if } k \neq l, \end{cases}$

$$f_{kl} = \frac{e}{2hc} H(x_k y_l - x_l y_k), \quad (2)$$

$$\exp(2\pi i f_{kl}) = W_{kl} / W_1, \quad (3)$$

$$\text{and} \quad x = \frac{E^{(1)} - W_0}{W_1} \quad (4)$$

In Eq. (2), H is the field strength, x_k etc. are the coordinates and f_{kl} can be considered as a numerical value proportional to the magnetic flux through the area of the triangle

(1) Cf., for instance, P. W. Selwood, "Magnetochemistry", New York, 1943.

(2) F. London, *J. de Physique*, **8**, 397 (1937).

(3) J. Iball and J. M. Robertson, *Nature*, **132**, 750 (1933); J. Iball, *Proc. Roy. Soc. (London)*, **A 146**, 140 (1934).

(4) F. London, *J. de Physique*, **8**, 397 (1937).

formed by the neighbors k, l and the origin, arbitrarily chosen in the plane of the molecule. In Eq. (3), W_{kl} represents the exchange integral in the presence of magnetic field and W_1 is the ordinary exchange integral of the nearest neighbors of the orbital theory in the absence of magnetic field. In Eq. (4), $E^{(1)}$ is the ordinary first order perturbation energy and W_0 is the Coulomb integral independent of the magnetic field.

Following the above conditions and the model shown in Fig. 1, the following secular determinant of chrysene molecule can be gained.

$$\begin{vmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 1' & 2' & 3' & 4' & 5' & 6' & 7' & 8' & 9' \\ 1 & -x\varepsilon_1 & & & & & & & & & & & & & & & & \varepsilon_1^* \\ 2 & \varepsilon_1^* - x\varepsilon_2 & & & & & & & & & & & & & & & & \\ 3 & & \varepsilon_2^* - x\varepsilon_3 & & & & & & & & & & & & & & & \\ 4 & & & \varepsilon_3^* - x\varepsilon_4 & & & & & & & & & & & & & & \\ 5 & & & & \varepsilon_4^* - x\varepsilon_5 & & & & & & & & & & & & & \\ 6 & & & & & \varepsilon_5^* - x\varepsilon_6 & & & & & & & & & & & & \\ 7 & & & & & & \varepsilon_6^* - x\varepsilon_7 & & & & & & & & & & & \\ 8 & & & & & & & \varepsilon_7^* - x\varepsilon_8 & & & & & & & & & & \\ 9 & & & & & & & & \varepsilon_8 - x\varepsilon_1 & & & & & & & & & \\ 1' & 1 & & & & & & & & \varepsilon_1^* - x\varepsilon_1 & & & & & & & & \\ 2' & & & & & & & & & & \varepsilon_1^* - x\varepsilon_2 & & & & & & & \\ 3' & & & & & & & & & & & \varepsilon_2^* - x\varepsilon_3 & & & & & & \\ 4' & & & & & & & & & & & & \varepsilon_3^* - x\varepsilon_4 & & & & & \varepsilon_2 \\ 5' & & & & & & & & & & & & & \varepsilon_4^* - x\varepsilon_5 & & & & \\ 6' & & & & & & & & & & & & & & \varepsilon_5^* - x\varepsilon_6 & & & \\ 7' & & & & & & & & & & & & & & & \varepsilon_6^* - x\varepsilon_7 & & \\ 8' & & & & & & & & & & & & & & & & \varepsilon_7^* - x\varepsilon_8 & \\ 9' & & & & & & & & & & & & & & & & & \varepsilon_8 - x \end{vmatrix} = 0, \quad (5)$$

where $\varepsilon_k = \exp(2\pi i f_{k,k+1})$ and

and $\varepsilon_k^* = \exp(-2\pi i f_{k,k+1})$.

For convenience' sake, ε_k is preferred to ε_k^* in case of the clockwise rotation about the origin.

This secular determinant can be transformed to the type as follows:

$$\begin{vmatrix} \Delta_1 & 0 \\ 0 & \Delta_2 \end{vmatrix} = 0.$$

Therefore Eq. (5) can be separated into the solution of two determinants, namely

$$\Delta_1 = \begin{vmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 \\ 1 & (1-x)\varepsilon_1 & & & & & & & \varepsilon_1^* \\ 2 & \varepsilon_1^* - x\varepsilon_2 & & & & & & & \\ 3 & & \varepsilon_2^* - x\varepsilon_3 & & & & & & \\ 4 & & & \varepsilon_3^* - x\varepsilon_4 & & & & & \varepsilon_2 \\ 5 & & & & \varepsilon_4^* - x\varepsilon_5 & & & & \\ 6 & & & & & \varepsilon_5^* - x\varepsilon_6 & & & \\ 7 & & & & & & \varepsilon_6^* - x\varepsilon_7 & & \\ 8 & & & & & & & \varepsilon_7^* - x\varepsilon_8 & \\ 9 & \varepsilon_1 & & & & & & & \varepsilon_8 - x \end{vmatrix} = 0$$

and

$$\Delta_2 = \begin{vmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 \\ 1 & (-1-x)\varepsilon_1 & & & & & & & -\varepsilon_1^* \\ 2 & \varepsilon_1^* & -x\varepsilon_2 & & & & & & \\ 3 & & \varepsilon_2^* - x\varepsilon_3 & & & & & & \\ 4 & & & \varepsilon_3^* - x\varepsilon_4 & & & & & \varepsilon_2 \\ 5 & & & & \varepsilon_4^* - x\varepsilon_5 & & & & \\ 6 & & & & & \varepsilon_5^* - x\varepsilon_6 & & & \\ 7 & & & & & & \varepsilon_6^* - x\varepsilon_7 & & \\ 8 & & & & & & & \varepsilon_7^* - x\varepsilon_8 & \\ 9 & -\varepsilon_1 & & & & & & & \varepsilon_8 - x \end{vmatrix} = 0.$$

Expanding Δ_1 and Δ_2 , and after substitution of ε by f , we have

$$\begin{aligned} \Delta_1 = & x^9 - x^8 - 10x^7 + 8x^6 + 32x^5 - 21x^4 - 39x^3 \\ & + 22x^2 + 15x - 8 + (x^4 + x^3 - 4x^2 - 2x \\ & + 6)(2\pi f)^2 = 0 \end{aligned} \quad (6)$$

$$\begin{aligned} \Delta_2 = & x^9 + x^8 - 10x^7 - 8x^6 + 32x^5 + 21x^4 - 39x^3 \\ & - 22x^2 + 15x + 8 - (x^4 - x^3 - 4x^2 + 2x \\ & + 6)(2\pi f)^2 = 0, \end{aligned} \quad (7)$$

where $f = (e/hc) \cdot H \cdot S_B$, (8)

S_B = the area of each hexagon.

Since Eqs. (6) and (7) have the form:

$$F_1(x) + F_2(x) \cdot (2\pi f)^2 = 0 \quad (9)$$

and f is very small, the second term may be considered as a correction. Accordingly, let x' be a root of $F_1(x) = 0$ and

$$x = x' + x''(2\pi f)^2 \quad (10)$$

be a root of Eq. (9), x'' will be expressed approximately by

$$x'' = \frac{F_2(x')}{F_1'(x')} \quad (11)$$

according to Newton's equation. In Eq. (11),

F_1' represents the first differential of F_1 with regard to x .

Now we need nine roots of lower energy levels in eighteen roots of Eqs. (6) and (7). These values are shown in Table 1.

Table 1

$-x'$	x''
2.49904	+0.03965
2.16651	-0.00899
1.70076	-0.12892
1.53977	+0.06547
1.28577	+0.16687
1.21644	-0.29292
0.87532	+0.35968
0.79233	-0.58089
0.52013	+0.62639
$\Sigma; +0.24638$	

Substituting the values of x in Eq. (4), $E^{(1)}$ is given and a susceptibility contribution of a π -electron becomes

$$\chi_p = - \left(\frac{\partial^2 E^{(1)}}{\partial H^2} \right)_{H \rightarrow 0} \quad (12)$$

From (4), (8), (10), (12) and numerical value of $\Sigma(x'')$ we obtain the diamagnetic anisotropy of chrysene as follows:

$$\begin{aligned} \Delta\chi &= 2 \sum_{p=-\frac{N-2}{4}}^{\frac{N-2}{4}} \chi_p = -4 \Sigma(x'') |W_1| \left(\frac{2\pi e S_B}{hc} \right)^2 \\ &= 18 \Sigma(x'') \Delta\chi_{\text{Benz.}} \\ &= 4.43 \Delta\chi_{\text{Benz.}} \end{aligned} \quad (13)$$

where $\Delta\chi_{\text{Benz.}}$ is the anisotropic contribution of π -electrons in benzene.

Magnetic Measurements and Discussion

The principal diamagnetic anisotropies along the three principal axes of chrysene single crystal have been measured by K. Lonsdale and K. S. Krishnan.⁽⁶⁾ These values are as follows:

$$\begin{aligned} K_1 &= -88.0 \times 10^{-6}, \quad K_2 = -83.3 \times 10^{-6}, \\ K_3 &= -310.8 \times 10^{-6}, \end{aligned}$$

then the anisotropic part per mole becomes

$$\Delta\chi = 4.17 \cdot \Delta\chi_{\text{Benz.}} \quad (14)$$

We measured the mass susceptibility of powdered chrysene by the modified Gouy's method⁽⁹⁾ and chose the purified water as standard. This chrysene specimen had been extracted from coal-tar and purified by several recrystallizations and sublimations. The results obtained as follows:

$$\chi_g = -0.731 \times 10^{-6}, \quad \chi_M = -166.67 \times 10^{-6},$$

where χ_g and χ_M denote the mass and mole susceptibilities respectively. Accordingly, we can deduce $\Delta\chi$ as follows:

$$\Delta\chi = 4.10 \cdot \Delta\chi_{\text{Benz.}}, \quad (15)$$

using the modification of Pascal's additive law.⁽⁷⁾

This result (Eq. (15)) coincides closely with that of relation (Eq. (14)), and the result calculated according to London's theory (Eq. (13)) shows a relatively good agreement with the experiments.

The difference of K_1 and K_2 in chrysene is small but, in general, it is expected that the larger the discrepancy of molecular form from the circle is, the larger this difference becomes. Accordingly, the relative diamagnetic anisotropies to benzene under the assumption of $K_1 = K_2$ will become uncertainly, then it may be doubtful to compare the values of experimental relative anisotropy to the theoretical values. These questions have to be discussed further in detail.

In this experiment, the electromagnet was lent to the authors by the Glass Research Institute, Tohoku University, and they wish to express their sincere thanks to Prof. Hitoshi Tominaga and Prof. Genjiro Hazato, for their kind permission and advice.

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Kawaguchi, Saitama Pref.

(6) K. Lonsdale and K. S. Krishnan, *Proc. Roy. Soc. (London)*, A **156**, 597 (1936); K. Lonsdale, *Proc. Roy. Soc. (London)*, A **159**, 149 (1937).

(9) Cf., for example, P. W. Selwood, "Magnetochemistry," New York (1943); G. Hazato and K. Aida, *Rep. Glass Research Institute, Tohoku Univ.*, No. 3 (1949).

(7) G. Hazato, *J. Chem. Soc. Japan*, **64**, 483 (1943); H. Shiba and G. Hazato, *This Bulletin*, **22**, 92 (1949).

Heterogeneous Hydrolytic Degradation of Cellulose

By Kei MATSUZAKI and Hiroshi SOBUE

(Received May 1, 1951)

Introduction

As it is well-known, cellulose is a chain molecule consisted of glucosidic anhydrides linked together through 1- and 4-positions. Recently, E. Husemann⁽¹⁾ investigated hydrolysis of purified ramie in 0.5 *M* KHSO₄ solution for 2-1200 hours at 60°. Chain length distribution of the nitrates of both slightly and extremely hydrolyzed products indicated a uniform splitting of the glucosidic bonds, but the chain length distribution of intermediately hydrolyzed products showed an increase in uniformity especially in the products of a degree of polymerization (D. P.) of 400-500. He concluded that wood cellulose as well as cotton and ramie cellulose has weak bonds at intervals of about 500 glucose units which split 5000 times faster than the usual glucosidic bonds. G. V. Schulz⁽²⁾ also stated the same conclusion and the others supported him. Since 1946, E. Pacsu⁽³⁾ suggested the presence of hemiacetal bonds at intervals of 260 glucose units which split on mild hydrolysis faster than the usual glucosidic bonds. E. Heuser,⁽⁴⁾ according to his unpublished work, also found that a uniform splitting took place upon hydrolysis of cotton cellulose in H₃PO₄, but of Aspen wood cellulose, molecules of a chain length of about 500 glucose units were accumulated, as Schulz *et al.* recognized.

If cellulose has such acid-weak bonds in its linkages, and cellulosic materials are submitted to acid treatments such as sulphite cooking, acetylation or nitration, the chain length distribution of the samples treated should be different from the case where uniform splitting takes place. We showed, in our previous work,⁽⁵⁾ that the fractional precipitation of cellulose nitrate with acetone-ligroin gave superior results to that of fractional solution with acetone-ethanol or ethyl acetate-ethanol,

or fractional precipitation with acetone-water. The distribution becomes broad and it seems that high-molecular as well as low-molecular fractions are considerably separated enough. We applied this fractional procedure to purified cotton, wood cellulose and their hydrolyzed products and attempted to prove the presence of the weak bonds and investigated heterogeneous hydrolysis of cellulose as a model experiment of cooking.

Experimental Procedures and Results

Samples studied were purified surgery cotton and red pine (*Pinus densiflora* S. *et* Z.) pulp for viscose rayon grade. 4 g. of conditioned samples were weighed and imbibed in 300 cc. of 3.5 *N* HCl for 4-120 hours at 30°. At the end of each specified hydrolysis period, they were taken out, washed thoroughly, dried in air and then dried under vacuum in CaCl₂ desiccator. Table 1 shows

Table 1

Results of Heterogeneous Hydrolysis of Cotton and Wood Pulp in 3.5 *N* HCl at 30°

Time	Purified Cotton Residue, %	D. P.	Wood Pulp Residue, %	D. P.
0	—	1080	—	950
4	99.7	889	—	—
24	99.1	466	98.8	488
48	—	—	98.7	400
72	98.9	318	98.5	343
120	98.7	282	98.3	321

the weight loss and D. P. change of the samples by these mild hydrolysis. In spite of the large changes in D. P. the weight loss is very little, because of recrystallization⁽⁶⁾ of splitted, disorganized and strained chains. Then these degraded samples were nitrated with the acid mixtures of HNO₃, H₃PO₄ and P₂O₅ (60:35:5) for 6 hours at 0°. The nitrates were washed with water for 24 hours and stabilized with methanol refluxing for 30 minutes. About 2 % of methanol soluble products were obtained. As nitrogen content and viscosity of the stabilized products increased with this treatment, the methanol

(1) E. Husemann, *Makromol. Chem.*, **1**, 140 (1947); E. Husemann and M. Goecke, *ibid.*, **2**, 293 (1948); **4** 194 (1949).

(2) G. V. Schulz and G. Sing, *J. Polymer Sci.*, **3**, 385 (1948).

(3) P. C. Mehta and E. Pacsu, *Textile Research J.*, **18**, 387 (1948).

(4) E. Heuser, *Tappl. Monograph Series No. 6*, 8-74 (1948).

(5) K. Matsuzaki and H. Sobue, *J. Chem. Soc. Japan., Ind. Chem. Sec.*, **54**, 289 (1951).

(6) O. A. Battista, *Ind. Eng. Chem.*, **42**, 507 (1950); J. A. Howsmon, *Textile Research J.*, **19**, 162 (1949).

soluble products would probably have low nitrogen content and low D. P. Also, almost all of combined H_3PO_4 is removed by this treatment. Acetone solution (1%) of the stabilized nitrates was then fractionally precipitated with ligroin and the weight and D. P. of each fraction were determined. The results are tabulated in Tables 2-9.

As a number of samples have high molecular weight, high-molecular fractions were at first precipitated, dissolved in acetone again and re-fractionated. Integral chain length distribution curves were plotted and by graphical differentiation differential chain length distribution curves

were also plotted. The curves are illustrated in Figs. 1-4.

Since two main fractions were separately fractionated for a number of samples, integral and differential distribution curves should be obtained from the summation of the curves for the two main fractions. But, as the procedure which enables to obtain continuous integral curves from the step-wise experimental data contains an arbitrary factor, we plotted integral curves for these samples simply rearranging all fractions in the order of D. P. without plotting the curves for the two main fractions separately.

Table 2

Fractionation of Nitrate of Purified Cotton.
Sample 5.002 g., Yield 97.3 %.
av. D. P. 1080, N 12.86 %⁽⁷⁾

High-molecular Fractions			Low-molecular Fractions		
Fraction	Weight %	D. P.	Fraction	Weight %	D. P.
1	2.20	500	1	2.91	90
2	0.78	910	2	1.31	140
3	12.76	935	3	2.68	230
4	1.80	1085	4	5.37	335
5	5.88	1160	5	3.54	495
6	2.32	1255	6	3.31	595
7	8.24	1465	7	2.58	680
8	2.60	1580	8	12.44	750
9	11.20	1605	9	3.19	1205
10	7.43	1740	total	37.33	
11	7.43	1950			
total	62.64				

Table 3

Fractionation of Nitrate of 4-hrs. Hydrolyzed Purified Cotton. Sample 5.004 g., Yield 96.3 %, av. D. P. 889, N 13.09 %

High-molecular Fractions			Low-molecular Fractions		
Fraction	Weight %	D. P.	Fraction	Weight %	D. P.
1	2.10	290	1	4.53	95
2	1.15	340	2	5.25	160
3	0.72	410	3	2.66	215
4	1.18	535	4	6.30	275
5	8.50	560	5	5.42	360
6	4.90	790	6	4.39	445
7	16.36	850	7	5.67	480
8	1.99	885	8	13.05	630
9	4.28	1050	9	3.38	820
10	1.52	1075	10	2.69	1005
11	3.96	1330	total	53.34	
total	46.66				

(7) Details of the fractional procedures are given in the following issue: *The Science of Forest Products*, 5, 53 (1950).

Table 4

Fractionation of Nitrate of 24-hrs. Hydrolyzed Purified Cotton. Sample 3.030 g., Yield 97.2 %, av. D. P. 466, N 12.96 %

Fraction	Weight %	D. P.
1	6.17	75
2	1.65	160
3	3.99	170
4	3.76	190
5	3.91	210
6	10.57	280
7	3.70	345
8	0.74	345
9	7.07	365
10	15.71	430
11	5.76	490
12	12.36	675
13	19.88	750
14	4.73	885

Table 5

Fractionation of Nitrate of 72-hrs. Hydrolyzed Purified Cotton. Sample 3.051 g., Yield 97.2 %, av. D. P. 318, N 13.1 %

Fraction	Weight %	D. P.
1	10.58	55
2	1.17	110
3	5.74	130
4	4.32	155
5	7.41	200
6	1.56	230
7	13.70	245
8	1.81	300
9	3.35	315
10	5.93	330
11	13.41	340
12	6.41	430
13	17.80	535
14	6.81	630

Table 6

Fractionation of Nitrate of 120-hrs. Hydrolyzed Purified Cotton. Sample 3.048 g., Yield 96.3 %, av. D. P. 282, N 12.93 %

Fraction	Weight %	D. P.
1	9.76	45
2	1.28	115
3	7.71	130
4	3.62	155
5	5.94	175
6	1.27	215
7	13.83	235
8	1.43	290
9	2.59	300
10	5.42	305
11	17.13	320
12	6.24	400
13	15.26	480
14	8.53	620

Table 7

Fractionation of Nitrate of Wood Pulp. Sample 5.056 g., Yield 95.3 %, av. D. P. 950, N 12.9 %

Fraction	Weight %	D. P.
1	4.84	2360
2	8.11	2020
3	4.17	1910
4	9.16	1720
5	5.15	1630
6	9.82	1170
7	8.67	1010
8	2.11	690
9	15.77	545
10	1.74	425
11	2.92	335
12	5.44	295
13	10.77	170
14	11.36	45

Table 8

Fractionation of Nitrate of 48-hrs. Hydrolyzed Wood Pulp. Sample 2.869 g., Yield 95.0 %, av. D.P. 400, N 12.9%

High-molecular Fractions		
Fraction	Weight %	D. P.
1	6.77	1095
2	3.05	950
3	2.65	820
4	8.83	650

Low-molecular Fractions		
Fraction	Weight %	D. P.
1	0.97	940
2	9.03	555
3	6.60	480
4	16.50	370
5	16.63	305
6	9.71	170
7	8.18	80
8	5.07	80
9	2.51	40
10	3.50	—

Table 9

Fractionation of Nitrate of 120-hrs. Hydrolyzed Wood Pulp. Sample 2.805 g., Yield 95.8 %, av. D.P. 321, N 12.9 %

High-molecular Fractions		
Fraction	Weight %	D. P.
1	2.05	920
2	3.88	735
3	6.51	530

Low-molecular Fractions		
Fraction	Weight %	D. P.
1	0.77	720
2	6.92	415
3	5.03	385
4	12.63	300
5	22.07	270
6	7.13	230
7	7.27	140
8	7.15	105
9	18.59	30

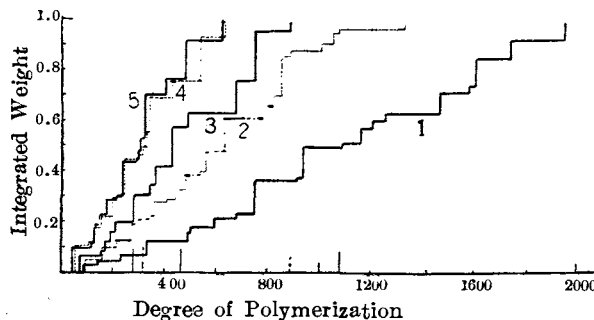


Fig. 1.—Integral chain length-weight distribution curves of hydrolyzed cotton (3.5 N HCl, 30°): 1, original; 2, 4 hrs. hydrolyzed; 3, 24 hrs. hydrolyzed, 4, 72 hrs. hydrolyzed, 5, 120 hrs. hydrolyzed

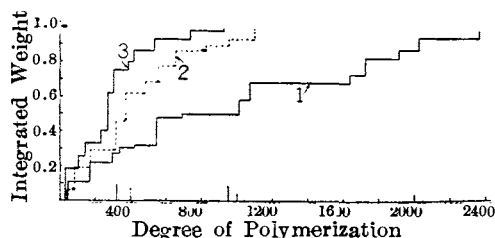


Fig. 2.—Integral chain length-weight distribution curves of hydrolyzed wood pulp (3.5 N HCl, 30°): 1, original; 2, 48 hrs. hydrolyzed; 3, 120 hrs. hydrolyzed.

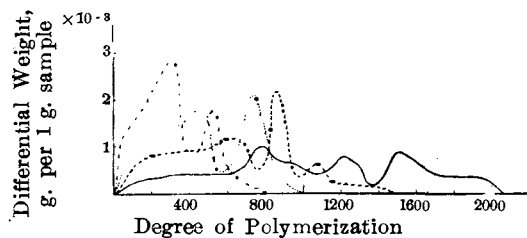


Fig. 3.—Differential chain length-weight distribution curves of hydrolyzed cotton: — original; ---- 4 hrs. hydrolyzed; 24 hrs. hydrolyzed, - . . . 120 hrs. hydrolyzed.

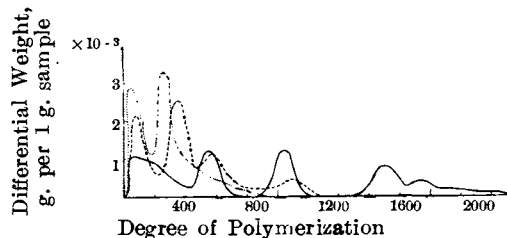


Fig. 4.—Differential chain length-weight distribution curves of hydrolyzed wood pulp: — original; ---- 4 hrs. hydrolyzed; 120 hrs. hydrolyzed.

Discussion

From Figs. 1-4, the difference between the chain length distributions of purified cotton and wood cellulose is evident, although these two samples have been degraded with several purification treatments. Wood cellulose has more low and high molecular weight fractions and more nonuniform distribution of chain length than purified cotton. The difference does not disappear even if the hydrolysis proceeds. The weight loss is little due to recrystallization and it is evident that the short recrystallized splitted chains are also included in the samples. These short chains of lower D. P. than 200 increase rapidly, as hydrolysis proceeds. Several maxima in the chain length distribution curves of purified cotton and pulp shifts to low molecular weight as the reaction proceeds. It seems as if these maxima are not so distinct as to give a positive proof of the presence of the weak bonds which would split 5000 times faster than the usual bonds and exist at regular intervals of 500 or 260 glucose units. If those acid-sensitive bonds exist in cellulose molecules, more rapid accumulation of chains of 500 or 260 glucose units would be expected. The heterogeneous degradation of cellulose can be explained well with its submicroscopic structure as follows.

In cotton and wood cellulose, crystalline

regions of relatively uniform length exist between amorphous regions. On hydrolysis, acid diffuses into the amorphous regions where the chains are splitted. Therefore the D. P. becomes lower and lower as the hydrolysis proceeds giving rise to several maxima in the differential distribution curves corresponding to several times the length of crystalline regions. Chain length of the crystalline regions at the beginning of the hydrolysis seems to be 200-300. Although the reason for the discrepancy between this value and that measured with x-ray method (120) is not yet clear, it is probable that the chain length of the crystalline regions grows long by the recrystallization of the splitted chains or acid-resistant crystalline regions may have different D. P. from that determined with x-ray method.

As previously mentioned, the nonuniformity of chain length distribution of wood pulp does not disappear upon hydrolysis. This indicates that the submicroscopic structure of wood pulp is not uniform. On one side, its amorphous regions are easily attacked with acid, but on the other, the crystalline regions or mesomorphous regions are more resistant to acid than that of cotton. This nonuniformity of crystalline structure of wood pulp would be closely related with the difference in chain

length distribution and reactivity of cotton when submitted to micellar reactions as hydrolysis, xanthation or acetylation.

Summary

Purified cotton and wood pulp were hydrolyzed in 3.5 *N* HCl for 4-120 hours at 30°. The hydrolyzed products were nitrated with the mixtures of H_3PO_4 - HNO_3 - P_2O_5 at 0° for 6 hours. Acetone solutions of the nitrates were fractionally precipitated with ligroin, and chain length distribution curves were plotted. These curves show no positive proof of the presence of the weak bonds which split 5000 times faster than the usual glucosidic bonds. These are well explained with the submicroscopic structure of cellulose.

The authors express thanks to Kazuo Kosuge and Takeo Iwata for their earnest aids to the experiment. The expense of this work was defrayed from the Scientific Research Encouragement Grant of the Department of Education.

Department of Applied Chemistry, Faculty of Engineering, the University of Tokyo, Tokyo

The Absorption Spectra of Quinolino-quinolines

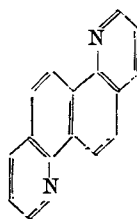
By Kazuo SHIBATA

(Received May 10, 1951)

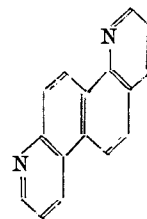
The recent advances in chemical physics have enabled us to interpret the electronic states and spectra of rather complicated molecules, although the theoretical treatments are more or less crude ones, which may be inevitable at the present stage of our knowledge. In this respect, the most well studied are aromatic hydrocarbons, while no pertinent investigations have hitherto been made with hetero-molecules, which is mainly due to the lack of spectroscopic data on these substances. The present report is concerned with the study of spectroscopic properties of quinolino-quinoline compounds, with a view to contributing fundamental data for theoretical elucidation of electronic states of heterocyclic compounds.

The compounds investigated were the fol-

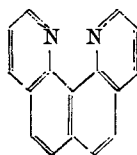
lowing four types of quinolino-quinolines;



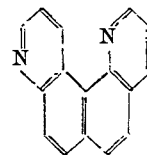
(I)



(II)



(III)



(IV)

Among these, the compounds (I) and (II) correspond to the hydrocarbon chrysene, and (III) and (IV) to 3,4-benzo-phenanthrene. The solvent used was ethanol and the measurement of absorption was made within the range of 2500 Å. to 4000 Å. by using the quartz-spectrograph QM-60 combined with the photomultiplier-tube 1P28.

It was found that the four compounds studied have the property in common of showing three main absorption bands, among which the band at the shortest wave-length is most intensive, while the other two have almost the same intensity. These three bands may be regarded as corresponding to the three bands of chrysene and 3,4-benzo-phenanthrene, respectively. The characteristic features of the absorption bands shown by quinolino-quinolines lie in the fact that, in the case of the compounds (I) and (II), the second band is split into two, while in the case of compounds (III) and (IV) the splitting occurs in the band at the longest wave-length. The absorption maxima observed are listed in Table 1, in which also the data for chrysene and 3,4-benzo-phenanthrene reported by Klevens and Platt⁽¹⁾ are given for comparison.

As may be seen from the table, the absorption spectra shown by the compounds (I) and (II) are very similar to each other, resembling

Table 1		(λ in Å. unit)	
Compounds	First band	Second band	Third band
Chrysene	2690	3310	3640
I	2640	2940, 3080	3490
II	2650	2930, 3060	3490
III	2640	3100	3460, 3610
IV	2690	3050	3460, 3660
3,4-benzo-phenanthrene	2810	3300	3740

on the whole the spectrum shown by chrysene, while those of compounds (III) and (IV) are similar to each other, both resembling the spectrum of 3,4-benzo-phenanthrene. It is, however, to be noticed that when compared with bands shown by the corresponding hydrocarbons, the bands shown by quinolino-quinolines are always shifted more or less to the side of shorter wave-lengths. At any rate, it may be concluded that the replacement by nitrogen of the carbon in a benzene ring entails far less change in the spectroscopic properties of aromatic compounds than does the change in the mode of combination of benzene nuclei.

The author wishes to express his thanks to Prof. E. Ochiai for giving the author his precious compounds for this research.

(1) H. B. Klevens and J. R. Platt, *J. Chem. Phys.*, **17**, 470 (1949).

The Absorption Bands of Benzene and Its Derivatives in Visible Region

By Kazuo SHIBATA, Hiroshi KUSHIDA and Seiyō MORI

(Received May 10, 1951)

Benzene is known to show four absorption bands at 1850 Å., 2070 Å., 2590 Å. and 3400 Å., the one at the shortest wave-length being the strongest. - According to the theory proposed by Goeppert-Mayer and Sklar⁽¹⁾, the molecule of benzene has one ground level ${}^1A_{1g}$ and six lower excited levels ${}^3B_{1u}$, ${}^3E_{1u}$, ${}^3B_{2u}$, ${}^1B_{2u}$, ${}^1B_{1u}$ and ${}^1E_{1u}$, with the energies increasing progressively in the given order. The strongest ab-

sorption band at 1850 Å. was attributed to the transition ${}^1A_{1g}-{}^1E_{1u}$, and the bands at 2070 Å. and 2590 Å. were ascribed to the transition ${}^1A_{1g}-{}^1B_{1u}$ and ${}^1A_{1g}-{}^1B_{2u}$, respectively. As to the band at 3400 Å., an interpretation was given in the paper of the authors named, but later it was assumed by Sklar⁽²⁾ to be due to the forbidden ${}^1A_{1g}-{}^3E_{1u}$ transition. This theory, however, cannot be regarded as being quite satisfactory, especially in so far as it restricts

(1) M. Goeppert-Mayer and A. L. Sklar, *J. Chem. Phys.*, **6**, 645 (1938).

(2) A. L. Sklar, *Rev. Mod. Phys.*, **14**, 232 (1942).

the considerations only to the transition to the triplet states. Indeed, it has been criticized by London,⁽³⁾ Mulliken⁽⁴⁾ and Shull⁽⁵⁾ from various points of view; but even when we take into account the opinions of these authors, we cannot explain why the singlet-triplet transition would not yield the corresponding absorption bands, which may lie in the visible region. Apart from these considerations, it seemed worth while to scrutinize the spectroscopic properties of benzene and its derivatives in the visible region. It was found that, besides the four bands hitherto known, benzene and some of its derivatives show a weak, but distinct, absorption band in the vicinity of 5200-5300 Å., which, strangely enough, has escaped observations by the earlier workers.

The measurements were made by photoelectric method, using a multiplier photo-tube RCA 931A. The samples were purified by the method described in "Organic Solvent"⁽⁶⁾ with the greatest possible care. The observations were made with a pure substance without using any solvent. The thickness of the liquid in the cell was 20 cm.

The maximum of the band shown by benzene was situated at 5200 Å. with the intensity of about 5×10^{-6} in molar extinction coefficient unit. The corresponding absorption was also found in toluene, monochlorobenzene and tetralin with the maximum at 5290 Å., 5250 Å.

and 5280 Å., respectively. In the cases of benzene, monochlorobenzene and tetralin, the curves of absorption spectrum showed a smooth protrusion in the said spectral region, while that of toluene was split into two crests. It may be reasonable to assume that these bands are due to the singlet-triplet transitions, although the numerical agreement, with the calculated energy difference found in earlier reports, is not satisfactory.

In addition to the new finding described above, it is of great interest to note that there is a nice simple rule governing the location of absorption bands observed in benzene. Namely, if we divide the wave-numbers (in cm^{-1} unit) corresponding to the absorption maxima with 9653 cm^{-1} , we obtain almost the round numbers 2, 3, 4 and 5, except for the band at 1850 Å. which gave the figure 5.6 (see Table 1). We

Table 1

λ in Å.	ν in cm^{-1}	$1/\nu \times 10^5$
1850	54054	5.600
2070	48356	5.009
2590	38612	4.000
3400	29412	3.047
5200	19231	1.992

are not in a position at present to give an explanation of this interesting rule, but it is doubtless that it involves a problem which awaits theoretical elucidation in the future.

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(3) A. London, *J. Chem. Phys.*, **13**, 396 (1945).

(4) R. S. Mulliken, *J. Chem. Phys.*, **16**, 118 (1948).

(5) Shull, *J. Chem. Phys.*, **17**, 296 (1949).

(6) A. Weissberger and E. Proskauer, "Organic Solvents."

A Remark on the Goeppert-Mayer and Sklar's Theory on the Excited States of Benzene

By Kazuo SHIBATA

(Received May 10, 1951)

Of the numerous theoretical procedures which have been proposed to elucidate the electronic states of benzene, the most outstanding is the so-called GMS-method (Goeppert-Mayer and Sklar's method), though it is in many respects open to criticism. Despite the effort of London⁽¹⁾

and Mulliken⁽²⁾ to improve the method, the fundamental deficiency of the theory still remains, especially as it concerns the singlet-triplet transitions. In a preceding paper we have reported that benzene shows an absorption band at 5200 Å, which has been overlooked by

(1) A. London, *J. Chem. Phys.*, **13**, 396 (1945).

(2) R. S. Mulliken, *J. Chem. Phys.*, **16**, 118 (1948).

earlier workers. The purpose of the present paper is to achieve, applying the principle of the GMS-method and taking duly into account the newly discovered absorption band, a more satisfactory agreement of the theory with experimental data. It may be stated in advance that our trial also proved to be far from successful, but its presentation here may be relevant, since it seems to have revealed the limit of applicability of the GMS-method.

To begin with, a correction had to be made in the values of integrals used by Goeppert-Mayer and Sklar⁽³⁾, which was taken from the Bartlett's table of molecular integrals. We calculated these values by using equations derived by Kotani⁽⁴⁾ and Parr and Crawford⁽⁵⁾, which gave results coinciding satisfactorily with each other. This agreement may indicate the validity of the recalculated values. Applying the corrected values, the energy differences between the ground level and the excited levels were calculated according to the GMS-method.

For the sake of simplicity, we shall omit here the procedures of calculation and only show the result in Table 1, in which the energy differences are given in e. v. unit.

Table 1

	${}^3B_{1U}$	${}^3E_{1U}$	${}^3B_{2U}$	${}^1B_{2U}$	${}^1B_{1U}$	E_{1U}
corrected values	0.7	1.3	1.9	3.8	4.3	6.6
uncorrected values	1.5	2.2	3.0	5.0	5.8	8.0

As is indicated by the figures in the table, our corrected values yielded results which are rather in worse agreement with experiments than in the case of the original calculation by Goeppert-Mayer and Sklar. Our calculation gives lower values for all energy levels, and especially so for the triplet states.

The most prominent characteristics of the calculation by GMS-method is that the energy levels can be calculated, though with rather crude approximation, almost absolutely; that is to say, with no parameters and empirical data except those concerning the C-C distance and the effective nuclear charge. Since, however, this method gives such a poor agreement with experiment as shown above, it seems worth while to introduce a parameter in the calculation in order to get better quantitative agreement with the experiment.

In the above calculation, the C-C distance was taken to be $r=1.39 \text{ \AA}$. which was based

on the experimental data on benzene. It is, therefore, unreasonable for us to take the value of the C-C distance as a parameter. On the other hand, the effective nuclear charge was chosen to be $Z=3.18$, a value which was obtained by Zener⁽⁶⁾ on the basis of a variational calculation minimizing the energy of the ground state of one carbon atom. There is, however, no evidence that the value of Z fitted for the atomic state must be the same as the value for the molecular state. It is to be supposed that the 2p electron cloud of a carbon atom is deformed in the benzene molecule on account of various kinds of interaction. Considering these points, it seems pertinent to take the effective nuclear charge as a parameter. Calculation was made taking the figures 2.28, 3.04, 3.18 and 3.80 as the value of Z . These values were chosen only for the sake of easiness of calculation. The result of the calculation is shown in Fig. 1, in which the height of energy levels is plotted against the values of Z , and the dotted lines show the height of energy levels determined from experiments.

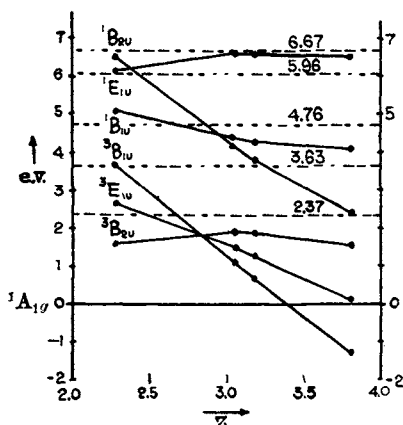


Fig. 1.

It is obvious from this figure that the increase of the value of Z causes the height of energy levels to be lowered, although the heights of ${}^1E_{1U}$ and ${}^3B_{2U}$ are not altered profoundly. The heights of excited levels at $Z=3.80$ are not reasonable, because they are too low; equally unreasonable is the result at $Z=2.28$, which does not agree with experiments even qualitatively. Contrary to our expectation, a comparatively better result was obtained at $Z=3.18$, the value that has been used in the original work of Goeppert-Mayer and Sklar. As will

(3) M. Goeppert-Mayer and A. L. Sklar, *J. Chem. Phys.*, **6**, 645 (1938).

(4) M. Kotani, *Proc. of the physico-mathematical Soc. of Japan*, 20, extra No. (1938); **22**, extra No. (1940).

(5) Parr and Crawford, *J. Chem. Phys.* **16**, 1049 (1948).

(6) Zener, *Phys. Rev.*, **36**, 51 (1930).

be seen from these results, our trials to get more satisfactory results than the already obtained one have, on the whole, proved to be quite unsuccessful. The failure we have experienced may show that for attaining satisfactory results we have to improve fundamentally the method of approximation itself.

The author wishes warmly, at this opportunity, to thank Prof. Kotani for his valuable advice and his kind interest in the course of this work.

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Some Rheological Measurements on Coal Tar Pitches⁽¹⁾

By Tsurutaro NAKAGAWA

(Received May 2, 1951)

Rheological properties of coal tar pitches in the softening range ($80^{\circ}\sim 110^{\circ}$) were studied from the following three points of view. (1) They are used as a binding material for the production of some carbonaceous matter, *e. g.*, carbon brush etc., and their practical quality is said to be partly related to the rheological properties of the binder. (2) Highly viscous substances usually behave as visco-elastic, *i. e.*, they have some elastic nature besides being viscous. Rheological anomalies of these substances may be ascribed to the visco-elastic effects. (3) Internal structure of some bituminous solid, *e. g.*, pitches, asphalts and coals, makes an interesting problem in the present stage of chemistry of coal. Analysis of rheological data may disclose some one of these points.

Experimental

As the experimental procedure for studying and analysing rheological behavior of tar pitches, the author took the method of measuring the visco-elastic properties of the material, using a newly constructed dynamic apparatus suitable for the study in the range of seconds~minutes of period, which should give information about the dynamic modulus and dynamic viscosity much different from those in the audiofrequency range, where much more work has been done.

Dynamic Method for Measuring Visco-elastic Properties. Method by the Phase Difference.⁽²⁾—Consider a modification of a

rotation viscometer (Fig. 1), and apply the sinusoidal torsional displacement,

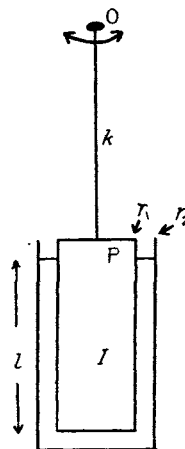


Fig. 1.

$$\Theta = \Theta_0 \sin \omega t,$$

at the top O of the torsion wire whose torsion constant is k dyne cm., so that the equation of motion of the inner cylinder P is

$$I\ddot{\theta} + R\dot{\theta} + E\theta = k(\Theta - \theta) \quad (1)$$

where $I\ddot{\theta}$ is the inertial resistance, and $R\dot{\theta}$ and $E\theta$ are the viscous and elastic resistance respectively of the visco-elastic body existing among the two cylinders, and $k(\Theta - \theta)$ is the external torque imposed on the inner cylinder. T. Kuyama⁽³⁾ suggested a method for studying

(1) Read before the 4th annual meeting of the Chemical Society of Japan on Apr. 8, 1951.

(2) Details of the method will appear in *J. Chem. Soc. Japan*, **72**, 759 (1951).

(3) T. Kuyama, *Kagaku (Science)*, **16**, 149 (1946).

the visco-elastic effect from the graphical analysis of the stress-strain hysteresis loop.

The author, in the present study, has used a modified scheme. (1) is rewritten as

$$\ddot{\theta} + 2\varepsilon\dot{\theta} + n_e^2\theta = L \sin \omega t \quad (1')$$

$$2\varepsilon \equiv R/I, \quad n_e^2 \equiv (k+E)/I, \quad L \equiv k\Theta_0/I \quad (1'a)$$

The stationary solution of (1') is

$$\theta = A \sin(\omega t - \phi) \equiv m\Theta_0 \sin(\omega t - \phi) \quad (2)$$

$$\text{where} \quad \tan \phi = 2\varepsilon\omega / (n_e^2 - \omega^2), \quad (2a)$$

and

$$m \equiv A/\Theta_0 = \frac{k}{I\sqrt{(n_e^2 - \omega^2)^2 + 4\varepsilon^2\omega^2}} \quad (2b).$$

As is plain from (2a) and (2b), it is possible to calculate R and E from the observed phase difference ϕ and the amplitude ratio m at the stationary state of the forced oscillation, by using the next relations

$$\left. \begin{aligned} R &= \frac{kT \sin \phi}{2\pi m} \\ E &= k \left(\frac{\cos \phi}{m} - 1 \right) + \frac{4\pi^2 I}{T^2} \end{aligned} \right\} \quad (3)$$

where T is the period ($\omega = 2\pi\nu = 2\pi/T$).

If R and E are determined, viscosity η poises and rigidity G dyne/cm.² of the substance are known from the following formulas^{(4) (5)}:

$$\left. \begin{aligned} \eta &= \frac{R}{4\pi l} \left(\frac{1}{r_1^2} - \frac{1}{r_2^2} \right) \equiv K_0 R \\ G &= \frac{E}{4\pi l} \left(\frac{1}{r_1^2} - \frac{1}{r_2^2} \right) \equiv K_0 E \end{aligned} \right\} \quad (4)$$

where l , r_1 , and r_2 are the lateral length of the immersed portion of the inner cylinder, radius of the inner and the outer cylinder respectively.

In the present measurement the experimental condition is as follows.

$$I = 8.76 \times 10^3 \text{ g. cm.}^2;$$

$$k = 1.12 \times 10^5 \text{ dyne cm. (piano wire of 1 mm. diameter, 72 cm. length);}$$

$$r_1 = 2.50 \text{ cm.; } r_2 = 3.70 \text{ cm.; } l, \text{ about 16 cm. in all cases;}$$

$$\Theta_0 = 8^\circ 45' (0.153 \text{ radians}), \text{ so that } A \text{ is less than that;}$$

$$T, 3 \text{ min. to 20 min.; temp., } 80 \sim 110^\circ \pm 0.1^\circ.$$

In the case of large T as in the present, the

term $4\pi^2 I/T^2$ in (3) can be omitted. Temperature control was done by the oil bath thermostat regulated in the ordinary manner. Thermal uniformity in the cylinder was so slowly reached for the large dimensions of the vessel that it was necessary to wait about two hours or more before measurement was begun. The sinusoidal motion was supplied by the mechanism of the crank-shaft principle. Deflections Θ and θ were read by the method of lamp-and-scale by means of the two small galvanometer mirrors attached to the upper disk and the lower cylinder. The phase angle ϕ is given by

$$\phi = \frac{\tau}{T} \times 2\pi \quad \text{radians}$$

where τ sec. is the measured time interval between the instant when O passes $\Theta = 0$ and the instant when P passes $\theta = 0$; $\Theta = 0$ and $\theta = 0$ corresponding to the middle point of the rotational oscillation. The torsion constant k was determined from the period T_0 of the free oscillation with a weight of the known moment of inertia I_0 by

$$k = 4\pi^2 I_0 / T_0^2.$$

It should of course be kept in mind that k changes with the length of the wire.

Coal Tar Pitches.—Pitches from coal tar of ordinary high temperature carbonization were subjected to test. Their origin and the conventional softening temperature are tabulated below (Table 1).

Table 1

Abbreviation	Origin	So-called softening point, °C.
Tar pitch N	Nisshin Kagaku Co.	80
O	Osaka Gas Co.	—
H	Hirohata Iron-Works	79
Y	Yahata Iron-Works	65

Results and Discussions

Frequency Dependence of η and G .—Figs. 2 and 3 show frequency dependence of viscosity η and rigidity G at various temperatures. As is read from the figures, no appreciable frequency effect upon η was observed. Elastic nature is very slight in this frequency range. G cannot be detected at higher temperatures, and becomes appreciable first at lower temperatures. Rheological property of tar pitch so is simply Newtonian for such comparatively

(4) E. Hatschek, "The Viscosity of Liquids," G. Bell and Sons, Ltd., London, 1928.

(5) Th. Schwedoff, *J. de Phys.* [2] 8, 341 (1889).

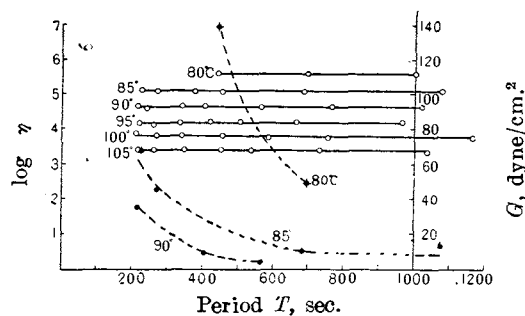


Fig. 2.—Frequency dependence of η and G of tar pitch H: — indicates the frequency dependence of η and ----, that of G .

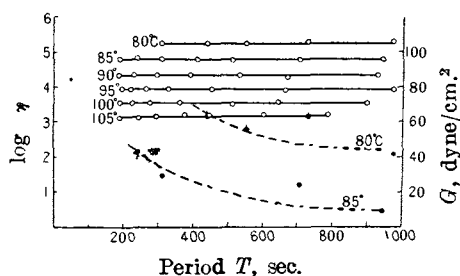


Fig. 3.—Frequency dependence of η and G of tar pitch Y: — indicates the frequency dependence of η and ----, that of G .

slow observation as in the present case. It is supposed that the time of mechanical relaxation is less or far less than several minutes in these temperatures, so that the mechanisms of elastic strain in the internal structure, if they exist, will decay into the mechanisms of viscous flow in our experimental condition of a long period. Elastic effect may on the other hand become remarkable if they are treated in the range of far larger frequency, *e. g.*, audiofrequency range⁽⁶⁾ for which our experimental device is not available.

From the rheological point of view, frequency dependence of the visco-elastic properties as has appeared in Figs. 2 and 3 will be interpreted as follows. Our whole experimental procedure and scheme of analysing the observed values depend on the assumption that the rheological properties of the material can be simply symbolized by the Voigt model (viscosity and elasticity in parallel) as is schematized in Fig. 4 b. If the material is truly of Voigt type in the rheological behavior, R and E , or η and G will appear as constant. But, on the other hand, if it is intrinsically of Maxwell type as in Fig. 4 a, the Voigt scheme analysis

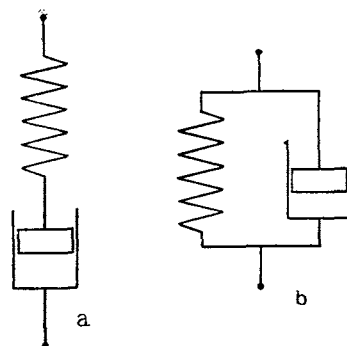


Fig. 4.

of it should lead to η and G variant with frequency or amplitude. Assume, now, that tar pitch is a simple Maxwellian body as the first approximation, then the Voigt type analysis of its rheological behavior should bring about the result that viscosity remains constant regardless of period, and that elasticity vanishes with the increase of period. This situation coincides with our observed data.

From the above-stated, it will be admitted that tar pitch is a Maxwellian body (viscosity and elasticity in series, *cf.* Fig. 4 a) with respect to the rheological behavior.

Temperature Dependence of Viscosity.—

As has been stated above, viscosity is constant in our frequency range. An arithmetical mean of viscosity data at the same temperature was taken as viscosity at the temperature, and was plotted against $1/T$ °K. in Fig. 5. η falls to

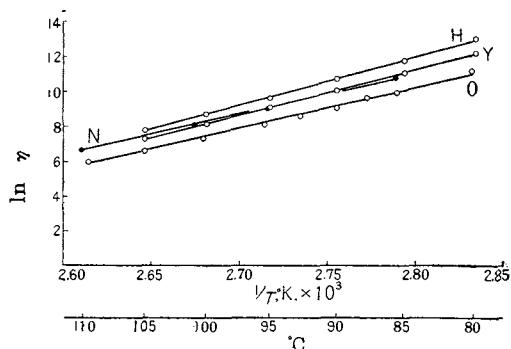


Fig. 5.—Temperature dependence of η :
 $\eta = Ae^{B/T}$.

about 1/3 by the increase of 5° of temperature, the sensitivity of η to temperature being remarkable compared with the ordinary low molecular weight liquids.

The author has used the Andrade formula

$$\eta = Ae^{B/T} \quad (5)$$

(6) See, for example, J. D. Ferry *et al.*, *J. App Phys.*, **20**, 144 (1949).

to express the temperature sensitivity of η , and determined A and B by the method of least squares. Results are given in Table 2, and the values for some other materials calculated from other authors' data are shown in Table 3⁽⁷⁾ for the sake of comparison. A high value of B indicates that the substance is highly associated, a large amount of energy being necessary to bring about the dissociation. To what is the large negative value of $\log A$ attributed?

Table 2

Material	$-\log A$	$B \times 10^{-3}$
Pitch N	23.4	23.2
O	23.7	23.2
H	27.9	27.2
Y	25.5	25.1

Table 3⁽⁷⁾

Material	Temperature range, °C.	$-\log A$	$B \times 10^{-3}$
Glass below T_g (1)	400~500	23.2	63.2
Glass below T_g (2)	400~500	26.0	65.7
Glass above T_g	700~1400	5.6	28.6
Undercooled glucose	22~40	62.4	51.8
Undercooled glucose	110~145	11.7	11.9
Rosin	25~60	44.1	38.1
Abietic acid	20~50	42.9	37
Pitch	20~40	35.6	30.9
Asphalt A	15~50	22.3	20
Asphalt A	80~130	10.8	11
Asphalt D	15~50	22.6	20
Asphalt D	80~130	11.0	11
Mercury	-20~300	2.23	0.29
Toluene	0~100	3.76	1.04
Water	0~20	5.44	2.32
Water	50~100	4.36	1.56

According to the theory of flow by the method of transition state,⁽⁸⁾ viscosity η is formulated as

$$\eta = \frac{h}{\lambda_1 \lambda_2 \lambda_3} e^{\Delta F^\ddagger / RT} \quad (6)$$

where h is Planck's constant, λ are dimensions of the unit of flow, and $\Delta F^\ddagger$ is the free energy

of activation which is necessary for the unit of flow to be activated up to the transition state from its initial state. Further, since $\Delta F^\ddagger$ may be replaced by

$$\Delta F^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger,$$

where $\Delta H^\ddagger$ and $\Delta S^\ddagger$ mean the heat of activation and the entropy of activation respectively, it is seen that

$$\eta = \left(\frac{h}{\lambda_1 \lambda_2 \lambda_3} e^{-\Delta S^\ddagger / R} \right) e^{\Delta H^\ddagger / RT}. \quad (7)$$

From the comparison of (7) with (5) it comes that

$$A = \frac{h}{\lambda_1 \lambda_2 \lambda_3} e^{-\Delta S^\ddagger / R}, \quad B = \Delta H^\ddagger / R. \quad (8)$$

It is therefore, from (8) and Table 2, that

$$\Delta H^\ddagger \doteq 50 \text{ kcal.}$$

From the rate-process view-point, the high value of $\Delta H^\ddagger$ is to be attributed to the fact that, in addition to the normal work required to make a hole, it is necessary for the secondary bonds, whereby a pitch particle is attached to the surrounding particles, to be broken before the activated state for flow can be attained. There is consequently what might be termed as a "structure activation energy", in addition to the normal activation energy, for the flow of such associated fluids as pitch.

The estimation of $\Delta S^\ddagger$, on the other hand, will meet with some complexity for the sake of the co-existing volume factor $\lambda_1 \lambda_2 \lambda_3$. The large negative value of $\log A$ in Table 2 nevertheless postulates that $\Delta S^\ddagger$ has a large positive value, which is about 85 E. U. if λ is assumed to be 100 Å, while the entropy of activation $\Delta S^\ddagger$ is usually negative in the case of flow of the ordinary non-associated substances. If, as suggested above, the unit of flow even in associated fluids is a single particle and the formation of the activated state involves the breaking of a number of secondary bonds, it is evident that the entropy of the activated state will be appreciably greater than that of the initial state. In other words, the entropy of activation for flow $\Delta S^\ddagger$ should be relatively large and positive in agreement with our experimental fact.⁽⁹⁾

At the higher temperature, there is no secondary bond that has to be broken before flow

(7) The data for constructing this table are borrowed from the following authors. Glass: F. B. Hodgdon and D. A. Stuart, *J. Appl. Phys.*, **21**, 1160 (1950). Glucose: G. S. Parks *et al.*, *Physics*, **5**, 193 (1934). Rosin, abietic acid, and pitch: E. C. Bingham and R. A. Stephens, *Physics*, **5**, 217 (1934). Asphalts: C. U. Pittman and R. N. Traxler, *Physics*, **5**, 221 (1934). Mercury, toluene, and water: "Smithsonian Physical Tables."

(8) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, 1941.

(9) Another example that the high value of $\Delta H^\ddagger$ is compensated by the large positive value of $\Delta S^\ddagger$ is illustrated in the kinetics of the protein denaturation (cf. note (8)).

can occur, and hence the activation energy $\Delta H^\ddagger$ will decrease and the entropy term $\log A$ will take a smaller negative value. See the case of glass in Table 3, where T_g is an abbreviation of the German "Temperatur des Glaszustandes" and T_f means "Temperatur des Fadenziehens."

The above-stated conception of the internal structure of tar pitch derived from the analysis of its viscosity in the softening range seems to be reconciled with the theory of the internal structure of coal, in which such nuclei as ash or graphite are considered to be strongly solvated with bitumen. It is probable that in the solid tar pitch, as in coal, the so-called "free carbon" or graphite-like particles are solvated with the bituminous substance, and that such associated structure is conserved even at the softening temperature.

Summary

(1) Visco-elastic properties of tar pitches in the softening range were measured by a dynamic method covering 3~20 minutes of period.

(2) No frequency dependence of viscosity was

observed in this range of period.

(3) Elastic effect was slight in this range of period. Its frequency dependence was appreciable.

(4) Tar pitch is a simple Maxwellian body rheologically above the softening point.

(5) Temperature dependence of viscosity was studied along the rate-process theory, and it was supposed that tar pitch has a highly associated or solvated structure, consistent with the present theory of the internal structure of coal.

The author wishes to express his gratitude to Professor J. Sameshima and Dr. H. Akamatu for their encouragement. He is also indebted to several organizations (Table 1), for samples. These experiments were largely supported by the Scientific Research Encouragement Grant defrayed from the Ministry of Education, to which the author's thanks are due.

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Thermal Diffusion Coefficient and its Relation to Ordinary Diffusion Coefficient of Solutions

By Kozo HIROTA and Isao MIYASHITA

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Though a number of theoretical formulas regarding thermal diffusion effect of solutions or the Ludwig-Soret effect have been proposed from the standpoint of kinetic theory or thermodynamics, it seems to us that they are not accepted generally. This is the reason why one of the present writers (K. H.)⁽¹⁾ derived a formula, adopting the cage model to the solution and applying the activated state method to the system. According to the formula, the Soret coefficient and thermal diffusion coefficient of the solute molecules whose molecular weight is 100 were calculated to be 1×10^{-3} and 6×10^{-8} respectively at 50° , if two kilocalories were assigned to the energy of activation for crossing the cage-barrier. They

fall in the range of usual experimental values of aqueous electrolyte solutions (HCl, KCl, NH_4Cl , H_2SO_4 , etc.). However, this successful result contained some ambiguity due not only to the absence of reliable data on the energy of activation and other quantities of such systems, but also to the inevitable occurrence of thermal diffusion potential. Because, in the case of electrolyte solutions each ion cannot behave as a perfectly independent particle hindered by their mutual electrical action as shown experimentally.^{(2), (3)}

Considering the matter, it is desirable to check the theory with some experimental data of non-electrolyte solutions, though they are

(1) K. Hirota, and O. Kimura, This Bulletin, 18, 111 (1943); cf., *Chem. Abst.*, 41, 436 (1947).

(2) K. Hirota, This Bulletin, 16, 475 (1941).

(3) G. Guthrie, J. N. Wilson and V. Schomaker, *J. Chem. Phys.*, 17, 310 (1949).

very few in number. However, as there appeared some reliable measurement which can meet the requirement, the present research was begun again with reference to ordinary diffusion, transforming the theoretical result into the formulas which can easily be checked experimentally.

Theoretical Formulas

a) Thermal Diffusion Coefficient.—According to the transition state method, the rate of jump of a solute molecule from a cage to a neighboring one can be given by the expression,⁽⁴⁾

$$\vec{R} = \frac{kT}{h} \exp\left(-\frac{\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R}\right), \quad (1)$$

where k , h , and R denote the Boltzmann, Planck, and gas constants, respectively, while $\Delta H^\ddagger$ and $\Delta S^\ddagger$ denote enthalpy of activation and entropy of activation, respectively. The transmission factor was regarded to be unity as is done usually.

Now the application of the above formula, which was deduced under the condition when the whole system is kept at constant temperature, is extended to the system in which thermal gradient exists stationarily. (The relation of the energy against distance x is shown schematically in Fig. 1.) Therefore, taking the

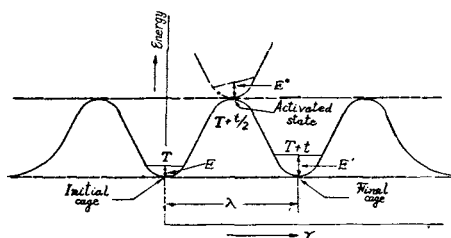


Fig. 1.—Schematic model of the cage-energy relation: Dotted lines at the activated state denotes that they are perpendicular to the plane of the paper.

temperatures of the equilibrium positions of initial and final cages (T and $T+t$) into consideration, the rate of translation from the initial cage to the final can approximately be given by

$$\vec{R} = \frac{k\left(T + \frac{1}{2}t\right)}{h} \exp\left(-\frac{\Delta H^\ddagger}{R\left(T + \frac{1}{4}t\right)} + \frac{\Delta S^\ddagger}{R}\right), \quad (2)$$

because T of the exponential term can be replaced by the mean of those of T and $T + \frac{1}{2}t$, the temperature of the activated state, while kT/h in Eq. (1) is to be replaced by $k\left(T + \frac{1}{2}t\right)/h$, as it was derived from the partition function over the coordinate of the reaction path at the activated state.

As the rate formula to the opposite direction $\overleftarrow{R}$ will be similarly given by

$$\overleftarrow{R} = \frac{k\left(T + \frac{1}{2}t\right)}{h} \exp\left(-\frac{\Delta H^\ddagger}{R\left(T + \frac{3}{4}t\right)} + \frac{\Delta S^\ddagger}{R}\right), \quad (2')$$

the mean distances moved per second by the solute molecule equal to or against the temperature gradient will be $\vec{R}$ or $\overleftarrow{R}$ multiplied by the distance of the neighboring cages, λ , respectively.

The flow velocity of the solute molecules, whose concentration c is so small that the flow of solvent is negligible, will be given by

$$v = c\lambda(\vec{R} - \overleftarrow{R}), \quad (3)$$

if $d\Delta H^\ddagger/dT$ and $d\Delta S^\ddagger/dT$ are assumed to be the quantities considered in the higher order of approximation.

Phenomenologically thermal diffusion coefficient D' in solution is defined by the proportional constant in the expression of diffusion flow v , which is produced by the temperature gradient dT/dx .

$$v = -D'c(dT/dx), \quad (4)$$

Thus from Eqs. (3) and (4),

$$D' = -(dx/dT) \cdot (\vec{R} - \overleftarrow{R}), \quad (5)$$

Considering that

$$\begin{aligned} & \exp\frac{-\Delta H^\ddagger}{R\left(T + \frac{1}{4}t\right)} - \exp\frac{-\Delta H^\ddagger}{R\left(T + \frac{3}{4}t\right)} \\ & \approx -\frac{t\Delta H^\ddagger}{2RT^2} \exp\frac{-\Delta H^\ddagger}{RT} \quad (6) \end{aligned}$$

and

$$\frac{dT}{dx} = \frac{t}{\lambda}, \quad (7)$$

we obtain from Eqs. (2), (2') and (5)

$$D' = \frac{\lambda^2 k}{2h} \frac{\Delta H^\ddagger}{RT^2} \exp\left(\frac{-\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R}\right), \quad (8)$$

(4) Glasstone, Laidler and Eyring, "Theory of Rate Processes," 1941, p. 522.

b) Relations between Thermal Diffusion and Ordinary Diffusion.—The ordinary diffusion coefficient D was derived theoretically by Eyring and others as follows:⁽⁵⁾

$$D = \frac{\lambda^2 k T}{h} \exp\left(\frac{-\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R}\right) \dots (9)$$

Differentiating Eq. (9) with respect to T , we obtain easily from Eqs. (8) and (9)

$$D' = \frac{1}{2} \left(\frac{dD}{dT} - \frac{D}{T} \right) \dots \dots \dots (10)$$

Soret coefficient defined by D'/D , therefore, can be expressed by

$$\text{Soret Coef.} = \frac{1}{2} (d \ln D / dT - 1/T) \dots (11)$$

For convenience sake of discussion in the last article, the corresponding formulas of Wirtz,⁽⁶⁾ who also used the cage model and applied the method of elementary kinetic theory, will be cited, *i. e.*,

$$D' = dD/dT, \dots \dots \dots (12)$$

$$\text{Soret Coef.} = d \ln D / dT \dots \dots \dots (13)$$

Experimental Method of Evaluating $\Delta H^\ddagger$, $\Delta S^\ddagger$, etc.

In order to determine the theoretical D' , it is necessary to evaluate λ , $\Delta H^\ddagger$ and $\Delta S^\ddagger$ in Eq. (8). The most direct way to meet the requirement is to make use of the data of ordinary diffusion, because the temperature dependence of thermal diffusion is not studied yet in details. But with the exception of mannitol, there is no system whose measurement on D as well as D' has been carried out over so wide a temperature range that $\Delta H^\ddagger$ can be determined by plotting in (D/T) against $1/T$ to make use of Eq. (9).

The second way of estimating is afforded by viscosity η . According to the transition state theory, it is given by the formula

$$\frac{1}{\eta} = \frac{\lambda_x \lambda_y \lambda_z^2}{\lambda_z h} \exp\left(\frac{-\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R}\right), (14)$$

where λ_x is the distance between the two adjacent layers of molecules (sliding each other), while λ_y and λ_z are perpendicular distances

between the neighboring positions in the plane perpendicular to the shearing motion. By a number of researches viscosity has been measured over such a wide and various temperature range that $\Delta H^\ddagger$ can be determined easily, but to our inconvenience it is difficult to know the required term $\exp(\Delta S^\ddagger/R)$. Because, even if the factor independent from temperature in Eq. (14) is determined experimentally, the factors λ_x , λ_y and λ_z and therefore their product $\lambda_x \lambda_y \lambda_z^{-1}$ are hard to be estimated from the other source of data.

The third method of estimation is based on the dielectric relaxation. According to Eyring, the so-called relaxation time τ_0 is given by

$$\frac{1}{\tau_0} = \left(\frac{kT}{h} \right) \exp\left(\frac{-\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R}\right) \dots (15)$$

Strictly speaking, these remains an important question if $\Delta H^\ddagger$ and $\Delta S^\ddagger$ evaluated by these three methods can be identified to those of thermal diffusion, because the mechanisms of these rate processes are not the same. Actually it was shown experimentally by the studies on the relation between τ_0 and η .⁽⁹⁾

However, as it seems that $\Delta H^\ddagger$ and $\Delta S^\ddagger$ can be estimated easily by the third method, the result obtained by the method will be used in the next paragraph for the check of Eq. (8). This attempt may, however, be admitted as the first approximation; because the solute molecule which rotates in the alternating electric field seems to produce as much disturbance on solvent molecules as that when the former jumps over the cage barrier, considering the situation that it is forced to rotate making the part of dipole which does not locate at the molecular center in the present cases.

Comparison of the Theoretical Diffusion Coefficient with the Observed

Recently, Higasi and Nukasawa⁽¹⁰⁾ determined $\Delta H^\ddagger$ and $\Delta S^\ddagger$ of the solutions of cane sugar and ethyl alcohol by measuring their complex dielectric constants at 0–30°, using the electric wave of 10.45 cm. in wave length and arranging the data by the Cole-Cole method. Their results are shown in the second and third columns of Table 1. For the sake of reference, the values of $\Delta H^\ddagger$ obtained from

(9) A. Bondi, *J. Chem. Phys.*, **14**, 541 (1946); Kauzmann, *Rev. Mod. Phys.*, **14**, 12 (1942); C. P. Smyth, *et al.*, *J. Am. Chem. Soc.*, **72**, 3447 (1950); **70**, 4102 (1948).

(10) K. Higasi and K. Nukasawa, unpublished result. Difference of the data between the preliminary report (*J. Chem. Phys.* **18**, 561 (1950)) and the present was brought about by the change of evaluation of their data.

(5) G. L. and E., *ibid.*, p. 524.

(6) K. Wirtz, *Naturwiss.*, **27**, 369 (1939); *Ann. Phys.*, **36**, 295 (1939).

(7) G. L. E., *ibid.*, p. 493.

(8) G. L. E., *ibid.*, p. 548.

viscosity data are shown in the fourth column of the table. They coincide with those obtained from relaxation time satisfactorily.

Table 1

Experimental Check of Eq. (8)

System	$\Delta H^\ddagger$ Calc. from τ_0 , kcal.	$\Delta S^\ddagger$ Calc. from τ_0 , e. u.	$\Delta H^\ddagger$ Calc. from η , kcal.	D' Calc., $\times 10^8$	D' Obs., $\times 10^8$
Ethyl alcohol (20wt%)-water	6.0	10	5.3	8	1.5 (40°C.)*
Cane sugar (10wt%)-water	5.4	9.7	4.3	7	0.34 (30°C.)**

* P. F. van Velden, H. G. P. van der Voort and C. J. Gorter, *Physica*, 12, 151 (1946).

** J. van Dranen and F. Bergsma, *Physica*, 13, 558 (1947).

On the other hand, thermal diffusion coefficients of ethyl alcohol and cane sugar in aqueous solution are calculated according to Eq. (8), by the use of 1.44 Å. (0°)–1.47 Å. (45°) as the distance between the two neighboring cages.⁽¹¹⁾ They are given in the fifth column of Table 1. It will be seen that the calculated value of ethyl alcohol (8×10^{-8}) is of the same order of magnitude as the experimental (1.5×10^{-8}) at 40°. However, the calculated value of cane sugar (7×10^{-8}) is larger at least by twenty times than the experimental one (3.4×10^{-9}).

A possible cause of such disagreement will be due, besides the neglect of transmission factor, not only to the use of the molecular diameter of water as λ , but also to the assumptions made in the theory, *i. e.*, substitution of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ determined from dielectric relaxation time for those of thermal diffusion. In fact, though the hindrance during diople rotation, which is brought about by electric force, may be large, the energy required seems to be less than that of making a sufficiently large hole in the neighboring cage crossing the potential barrier of the cage, while the entropy required will be also different in both phenomena. Considering the situation, the above agreement can be said to be satisfactory.

As the alternative cause of disagreement, the mechanism similar to that of ordinary diffusion must be mentioned: *i. e.*, according to Eyring the diffusion of large solute molecules is realized by the successive movement of small solvent molecules around the solute molecule. It will be shown by the discussion

in the next paragraph, which is the more plausible cause of the two.

Relation of Ordinary Diffusion Coefficients with Thermal Diffusion Coefficients

First, aqueous solutions of mannitol (0.01 mole/liter) and cane sugar (10 wt %) will be discussed as the example of the non-electrolyte solution, in order to check Eq. (10). Regarding the solution of mannitol, the Soret coefficient was measured carefully over the wide concentration range down to infinite dilution, while the diffusion coefficient was determined over the temperature ranges between 0° and 60°. (12) Thus the enthalpy of activation obtained by plotting $\ln(D/T)$ is 4.2 kcal. as described in Table 2 together with dD/dT at 35°. As the observed thermal diffusion coefficient is 0.6×10^{-8} at 35°, the one calculated according to Eq. (10) is given as 8×10^{-8} , the calculated is larger by twelve times than the observed. A similar result was obtained regarding to the cane sugar as is shown in the second system of Table 2.

Table 2

Experimental Check of Eq. (10)

System	Mean temp., °C.	D , $\times 10^7$	dD/dT , $\times 10^7$	$\Delta H^\ddagger$, kcal.
Mannitol	35	0.81	1.8	4.2
Cane sugar	15	0.36	1.06	4.8
Hydrogen chloride	50	5.8	8.1	—
AgNO ₃ -KNO ₃	400	4.3	0.96**	—

System	D' (calc.)	D' (obs.)
Mannitol	8×10^{-8}	0.6×10^{-8} (35°)
Cane sugar	4.7×10^{-8}	0.3×10^{-8} (30°)
Hydrogen chloride	3.1×10^{-7}	1.7×10^{-7} (50°)*
AgNO ₃ -KNO ₃	0.18×10^{-7}	1.5×10^{-7} (400°)

* Calculated from Soret coefficient and diffusion coefficient.

** Landolt-Börnstein, "Phys.-Chem. Tabellen," II Erg. Band, p. 199.

It is noteworthy that the above disagreement is the same in tendency as was found in the check of Eq. (8) regarding cane sugar, the molecule of which is large. Therefore, the second mechanism suggested in the last paragraph seems to be held to such systems, but it must be abandoned because the effect ascribable to the movement of small solvent

(11) These values were determined by the self-diffusion coefficient. Eyring, *J. Chem. Phys.*, 4, 283 (1936).

(12) Landolt-Börnstein, "Phys. Chem. Tabellen," II Erg. Band, p. 190.

molecules occurs in the case of an ordinary diffusion as well as in the case of a thermal diffusion, giving no net effect to the check of Eq. (10).

Second, hydrochloric acid will be utilized for our purpose, as the example of electrolyte solution. As shown in Table 2, the measured thermal diffusion coefficient of 1 *N* HCl is given to be 1.7×10^{-7} at 50° , while the calculated is 3.1×10^{-7} by the use of dD/dT (8.1×10^{-7}), and D extrapolated at 50° (5.8×10^{-5}).⁽¹⁾ Such an unexpectedly good theoretical result seems to be due to the cancellation of the effect of a thermal diffusion potential by that of an ordinary diffusion potential, because both effects are included in the observed values. However, the above good coincidence could not be obtained in the last system of Table 2, i. e., molten AgNO_3 (AgNO_3 , 3%); the observed value (1.5×10^{-7}) is about seven times larger than that of the calculated.⁽¹³⁾ The result obtained here may not be strange, considering that the system consists entirely of ions and electrical interaction is very large.

In concluding our discussion, it will be added that the calculated value by the use of Eq. (12) will become larger at least by two times than the above in every case, making the discrepancy increase by the same factor. Secondly it must be mentioned that Eq. (11) derivable from Eq. (10) was proposed already by Wereide⁽¹⁴⁾ from the standpoint of the elementary kinetic theory of solution, taking the motion of solvent molecules into account. However, according to this theory, the formula can be applied only when the size of a solute molecule is much larger than that of solvent

molecules, while Soret coefficient is to be negligibly small when the size of both molecules is of the same order of magnitude. The conclusion cannot be supported by the experimental result of Hirota and Kimura⁽¹⁵⁾; e. g., they confirmed by means of a Clusius-Dickel's thermal diffusion apparatus that though the separation of some sols (gelatine and hydrogen sulfide) was larger than that of usual electrolyte solutions, the separation of other sol (ferric hydroxide) was not observed definitely. Therefore, it is not wonderful that Wereide could not confirm his own formula experimentally regarding electrolyte solutions. According to the present theory, thermal diffusion coefficient will be given by Eq. (11) in the system whose molecule is not extremely large if compared with solvent molecules, while in the systems of large solute molecules it may become smaller than the value calculated by Eq. (11).

Summary

Theoretical formulas of thermal diffusion coefficient D' and its relation to ordinary diffusion coefficient D have been derived by applying the activated state method to the solution in which stationary thermal gradient exists. Regarding the solution of small solute molecules, whether it is electrolytic or non-electrolytic, the agreement with experimental result is good, while, regarding the solution of large solute molecule or molten salt, the discrepancy amounts to one order of magnitude.

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(13) K. Hirota and others, *J. Chem. Soc. Japan*, **64**, 811 (1943).

(14) T. Wereide, *Ann. de physique*, **2**, 55 (1914).

(15) O. Kimura and K. Hirota, *J. Chem. Soc. Japan*, **65**, 113 (1944).

Studies on Monomolecular Films. IV. Stabilization of Monoparticle Films of Nonpolar Substances by Stearic Acid

By Ryôhei MATUURA

(Received June 2, 1951)

Introduction

In order to spread on the surface of water and form a stable film a substance must have a polar-nonpolar structure, but we may be much interested in a surface film of a nonpolar substance which, if formed, would give a knowledge concerning the size and the shape of its particle on the surface of water. It is certainly true that a nonpolar substance is not capable of forming a stable film on water by itself, but it can be made to spread by mixing with a polar substance, such as fatty acids, as has been demonstrated by the work of Zisman.⁽¹⁾ The present author showed in the preceding paper⁽²⁾ the possibility of obtaining the stable surface films of a nonpolar substance according to this principle when it was mixed with a film-forming substance such as stearic acid, and there it was suggested that the structure of the surface film of various nonpolar substances or other nonspreadable matters might be studied by means of such mixed films. Stearic acid could be considered as a stabilizer for the surface film formation of nonspreadable substances. In the present work it was attempted to prepare the surface films of some nonpolar substances by mixing with stearic acid and to discuss the structure of the particles in the films thus formed on water as well as the mechanism of stabilizing action of stearic acid, taking into account of the results of measurements of pressure~area and area~composition characteristics.

Experimental

Apparatus.—The surface pressure of the film was measured by the simple method of Sasaki based on the principle of Wilhelmy's surface tension measurement. A glass slide 2.59 cm. wide and 0.151 cm. thick was used as a pendant plate, which enabled us to measure the surface pressure down to 0.1 dyne/cm.

Material.—Nonpolar substances used in this experiment were fully purified by the repeated

recrystallization or the vacuum distillation, except for the high-molecular substances such as raw rubber and polystyrene which were used without particular purification. As a fatty acid to be mixed with nonpolar substances, stearic acid, purified by recrystallization, was used. A nonpolar substance and stearic acid were mixed in varying proportions and the mixture was spread from benzene solution on the surface of *N*/100 hydrochloric acid by means of an automatic micro-volume pipette.⁽³⁾

Experimental Results.

As an example, a pressure~area diagram of mixed films of paraffin hydrocarbon (m. p. *ca.* 53°) and stearic acid on the surface of *N*/100 hydrochloric acid is shown in Fig. 1.

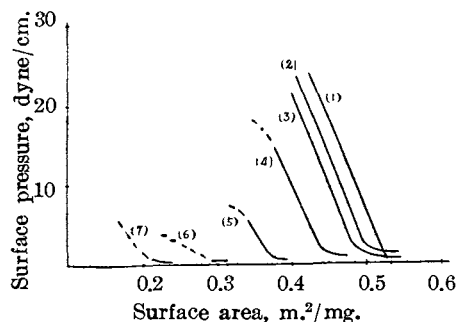


Fig. 1.—Pressure~area relations of mixed films of paraffin (m. p. 53°) and stearic acid on *N*/100 HCl at 22°. Stearic acid content in mixture: (1) 100%; (2) 95%; (3) 91%; (4) 77%; (5) 50%; (6) 33%; (7) 9%.

Paraffin was hardly capable of forming a surface film by itself on *N*/100 hydrochloric acid, but when mixed with stearic acid it could be made to spread and form a mixed film. The mixed film thus obtained was, however, very unstable and collapsed easily on compression when the acid content was low. It became more and more stable as the acid content increased. The dotted lines in Fig. 1 show the

(1) W. A. Zisman, *J. Chem. Phys.*, **9**, 534 (1941).

(2) R. Matuura, *Memoirs of the Faculty of Science, Kyushu University, Ser. C*, Vol. 1, 69 (1949).

(3) T. Sasaki, *J. Chem. Soc. Japan*, **62**, 796 (1941); R. Matuura and I. Hayasi, *Memoirs of the Faculty of Science, Kyushu University, Ser. C*, Vol. 1, 31 (1948).

pressure~area curves obtained temporarily by rapid compression. When the zero-compression areas in Fig. 1 are plotted against the composition of the mixture, a curve as shown in Fig. 2 is obtained. When the content of stearic acid in the mixture is small, the area of the mixed films cannot be determined exactly because of their instability, while when the content exceeds 50% the films are stable enough to allow the accurate determination of area. In this region the area~composition curve proves to be linear, suggesting that paraffin hydrocarbon and stearic acid form the mixed surface films without special interaction between two constituents, at least in an uncompressed state. Such a consideration is analogous to the case of three-dimensions where

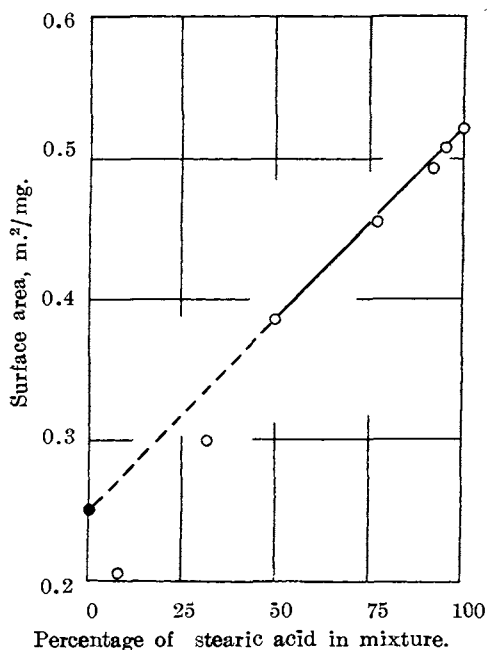


Fig. 2.—Area-composition relation of mixed films of paraffin and stearic acid on *N*/100 HCl at 22°.

the specific volume~composition curve is linear for ideal solutions. Thus the limiting area, obtained when the area-composition curve is extrapolated to the zero-acid content, is reasonably assumed to be the surface area occupied alone by paraffin film. The surface area of paraffin film thus obtained on *N*/100 HCl at 22° is 0.25 m.²/mg. Assuming the surface particle of paraffin to be spherical and one layer thick, and the density same as in bulk, its radius is calculated to be 40 Å. The size of the surface particle of another paraffin hydrocarbon (m.p. ca. 47°) is somewhat smaller,

its radius being about 30 Å. By a similar treatment we further calculate the dimension of particles of some other nonpolar substances in surface films stabilized by stearic acid on *N*/100 hydrochloric acid. The results are shown in Table 1. Some of them form thick films by themselves, but the films are often so unstable that they readily collapse under low lateral compression without the aid of stearic acid.

Table 1
The Size of Particles in Surface Film on *N*/100 HCl

Substance	Film area, m. ² /mg.	Radius of particle, Å.
Paraffin hydrocarbon (m. p. 53°)	0.25	40
Paraffin hydrocarbon (m. p. 47°)	0.32	30
Anthracene	0.11	55
Phenanthrene	0.10	71
Chlornaphthalene (m. p. 100–110°)	0.03	200
Triphenylmethane	0.01	—
Polystyrene	0.11	68
Raw rubber	0.02	370

Discussion

If a nonpolar substance is dropped alone as a benzene solution on the surface of water, it may spread temporarily due to the spreading force of benzene, but no surface film is left behind after the solvent evaporates up. We get merely macroscopic crystallines of the substance floating on water. On the other hand, high-molecular substances such as polystyrene or raw rubber form the thick films on water, but they are again too unstable to give the precise knowledge concerning their structure. However, when mixed with stearic acid, they form a fairly stable surface film on water in the case where the acid content is large, thus enabling us to discuss the structure of these films. Here stearic acid seems to act as a stabilizer for the surface films of nonpolar substances.

It is, however, seen in Table 1 that the surface films of nonpolar substances thus obtained in this experiment are not monomolecular but are much thicker. Even in the case of paraffin hydrocarbon where the surface film occupies rather larger area, the molecules of hydrocarbon cannot be considered as arranging themselves in monomolecular layer. Thus, with paraffin of melting point 47° which may well be considered as consisting largely of *n*-tricosane, the area per molecule of the paraffin in the film is calculated to be 15.5 Å.² with the

assumption that it can form a monomolecular layer on water by the aid of stearic acid. This value is still too small as the cross-sectional area of paraffin chain, therefore, it is evident that the above assumption cannot be adopted. Paraffin, and also all the other nonpolar substances studied in this experiment form polymolecular films, as pointed out by Harkins *et al.*⁽⁴⁾ and Aron and Frenkel.⁽⁵⁾ But the present author should like to call them "monoparticle films" or simply micellar films consisting of particles of aggregated nonpolar molecules instead of polymolecular films. The particles are held and interlocked with the molecules of stearic acid, forming together a stable surface film on water. The size of the particle in the surface film is given for each nonpolar substance studied as shown in Table 1. This particle may be taken as a comparatively stable unit appearing in the process of agglomeration of the nonpolar molecules into three-dimensional crystals. It is probable that the molecules of stearic acid cannot prevent the molecules of nonpolar substance from agglomerating into particles of this size but can arrest their further growth into macroscopic particles which would be the case if the molecules of the nonpolar substance exist without the intervening ones of stearic acid. These relations are illustrated schematically in Fig. 3.

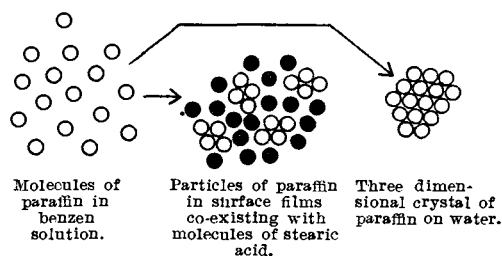


Fig. 3.—Schematic illustration of stabilization of surface film of paraffin by stearic acid: ○ represents a molecule of paraffin and ● a molecule of stearic acid.

The difference in the size of the particle in the film of the same kind of nonpolar substances will be explained by the difference in the strength of van der Waals force between molecules of the substance. Thus the particle size of paraffin of high melting point is larger than

that of low melting point. This is interpreted by the fact that the former is subjected to a stronger van der Waals force between molecules than the latter. But in the other cases the result is often so much complicated that a simple explanation is not applicable. Further it must be noted that the stabilizing action for surface film formation is exhibited not only by stearic acid but also by other acids, alcohols, etc., which form stable monomolecular films on water. The power of these film-stabilizing substances to prevent the molecules of nonpolar substance from agglomerating into three-dimensional crystals will, however, be different from substance to substance, and it will be possible to get some knowledge concerning the nature of various film-stabilizing substances from similar experiments as mentioned above. It must be emphasized that in these cases the special interaction between two substances in mixed films should also be examined if any.

When the film-stabilizing substance is different from stearic acid, the size of the particle stabilized might be expected to be different from that in Table 1. Namely it would depend upon the balance existing between an agglomerating tendency of the nonpolar molecules and an action of the film-stabilizing molecules to prevent them from agglomerating. This property is to be interpreted in relation to the other properties of each substance, which will be discussed later when the further investigation on mixed films is performed.

Summary

It was shown that stable surface films of nonpolar substances could often be formed on water by mixing them with stearic acid, and that in the resulting mixed films the nonpolar substance existed in the state of rather stable unit of particles, forming monoparticle films. The dimension of the surface particles could be calculated for some nonpolar substances. The mechanism of the film-stabilizing action of stearic acid was discussed and it was suggested that the different film-stabilizing substances would stabilize the film of nonpolar substance in a different manner.

In conclusion the author wishes to express his hearty thanks to Prof. Tunetaka Sasaki for his kind guidance in the course of this study.

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(4) W. D. Harkins, and J. W. Morgan, *Proc. Natl. Acad. Sci.*, **11**, 63 (1925); R. J. Myers and W. D. Harkins, *J. Phys. Chem.*, **40**, 959 (1936).

(5) Ya. B. Aron and Ya. I. Frenkel, *Zhur. Fiz. Khim. (J. Phys. Chem.)*, **22**, 1245 (1948); *C. A.* **43**, 1240 (1949).

Studies on Monomolecular Films. V. Monomolecular Films of Hardly Spreadable Substances Stabilized by Stearic Acid and Cetyl Alcohol

By Tunetaka SASAKI, Ryôhei MATUURA and Nobumasa FUJIMOTO

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In the preceding paper⁽¹⁾ the monoparticle films of nonpolar substances stabilized by stearic acid were discussed. Now it is our problem whether or not a stable monomolecular film on water will be obtained for a substance which is hardly capable of forming a stable monomolecular film by itself, by stabilizing with molecules of fatty acids or alcohols in just the same way as mentioned in the preceding paper. There are many insoluble substances, the molecule of which has polar-nonpolar structure but forms no stable monomolecular films on water due to the lack of balance between polarity and nonpolarity. It is the purpose of the present experiment to prepare stable monomolecular films of some of these substances using stearic acid and cetyl alcohol as stabilizers and to discuss the properties of films thus obtained on the surface of water.

Experimental

Film pressures were measured with the same apparatus as described already.⁽²⁾

All the substances studied in this experiment were purified by recrystallization except for polymer substance such as novolac resin. The substance was mixed with stearic acid or cetyl alcohol in varying proportions and the mixture was dropped as a benzene or benzene-alcohol solution on the surface of water. The pressure-area characteristics were investigated for the resulting surface films.

Results and Discussions

Various insoluble and nonvolatile substances were examined first of all if any monomolecular film is formed by mixing with stearic acid or cetyl alcohol and it was found that there are not so many which form stable monomolecular films on water by this procedure.

The typical example of film stabilization by fatty acid or alcohol are novolac and some

azo dye compounds.

(1) **Mixed Film of Novolac and Stearic Acid.**—The pressure-area diagram of mixed film composed of novolac and stearic acid on *N*/100 hydrochloric acid is shown in Fig. 1.

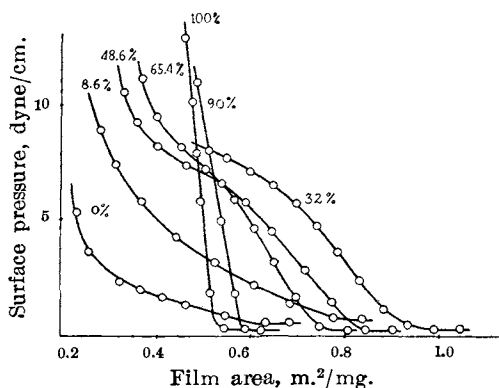


Fig. 1.—Pressure-area diagram of the mixed film composed of novolac and stearic acid on *N*/100 HCl. Percentage refers to stearic acid content.

Novolac does not dissolve in benzene, so alcohol-benzene mixture was used as a solvent for spreading surface film. The surface film of novolac is not stable by itself and its limiting area fluctuates from 0.55 to 0.65 m²/mg. for each experiment, depending chiefly on the nature of the solvent. But when mixed with stearic acid the film becomes very stable and shows a definite limiting area. The pressure-area curve of the mixed film is similar to that of stearic acid only when the acid content is high and to that of novolac only when it is low. In the intermediate region of acid content there exists a mixed film exhibiting the characteristic pressure-area curve of S-shape.

In Fig. 2 the area composition curve of the mixed film consisting of novolac and stearic acid is shown. The limiting area per mg. of the mixture proves to be in linear relation with the composition of the mixture in the region of the acid content from 100% to 30%.

(1) R. Matuura, *This Bulletin*, **24**, 200 (1951).

(2) T. Sasaki, *J. Chem. Soc. Japan*, **62**, 796 (1941); R. Matuura and I. Hayasi, *Memoirs of the Faculty of Science, Kyushu University, Ser. C*, Vol. 1, 31 (1948).

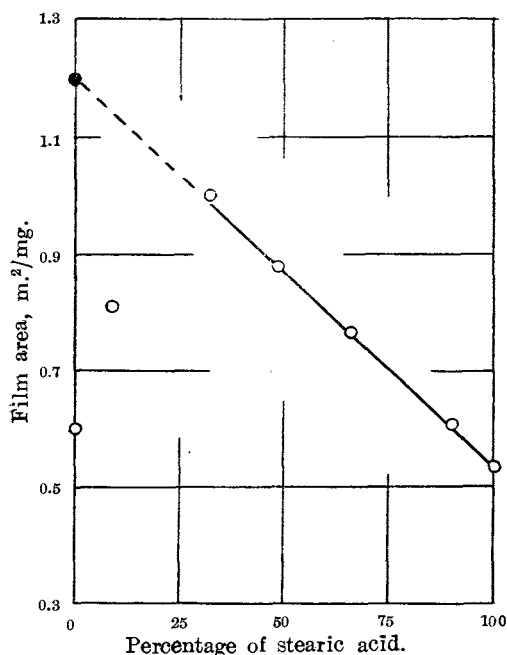


Fig. 2.—Area~composition curve of mixed film composed of novolac and stearic acid on $N/100$ HCl.

This shows presumably, according to the assumption proposed and discussed in the preceding paper,⁽¹⁾ that novolac and stearic acid behave in the mixed film just as if they exist separately. When this linear portion is extrapolated to the zero acid content, the surface area of novolac film without the stabilizing substance is obtained as $1.2 \text{ m}^2/\text{mg}$. This value is to be taken as the film area of novolac considered to be spread only on the surface of water. On the other hand, as mentioned already, the limiting area of the novolac film which is not stabilized by any film-stabilizing substance fluctuates from 0.55 to $0.65 \text{ m}^2/\text{mg}$, about a half of the value expected from the mixed film. This small value might be attributed to the fact that the surface film of novolac is unstable and imperfect unless it is stabilized by a film-stabilizing substance.

The molecule of novolac has more or less a stretched structure and it is reasonable to assume that the chain will lie rather flat on the surface of water. This is explained also by the present experiment on the mixed film which shows that the surface area of novolac is fairly large and the compressibility of the film is much greater than that of stearic acid, as it is usual in the case with surface films of long chain high-molecular substances.⁽³⁾

(2) **Mixed Film of Some Azo Dyes and Cetyl Alcohol.**—Film experiments were carried out with some azo dyes using cetyl alcohol as a stabilizer. The molecular structures of the dyes studied are shown in Table 1. These dyes are all incapable of forming stable monomolecular films on the surface of water by themselves. It has been known that some dyes used in this experiment form complex compounds with metallic ions in the bulk reaction. Cetyl alcohol was selected as a stabilizer because it is inert towards metallic ions in the substrate and therefore does not cover the remarkable effect of metallic ions generally encountered for dyes studied.

Pressure~area diagram of the mixed film composed of *p*-toluene-azo- β -naphthol, the compound (I) in Table 1, and cetyl alcohol is shown, as an example, in Fig. 3, where the

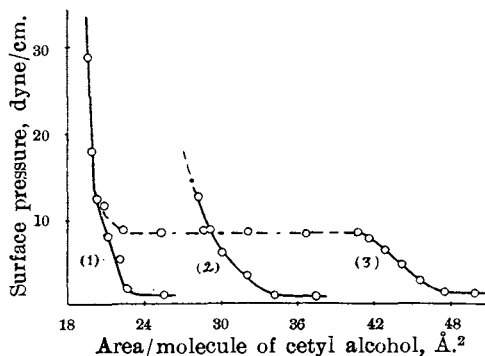
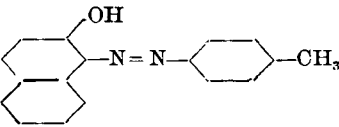
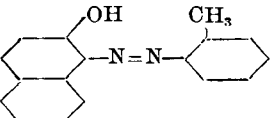
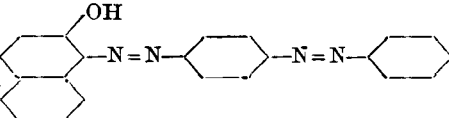
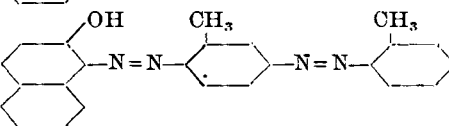


Fig. 3.—Pressure~area curve of mixed film composed of *p*-toluen-azo- β -naphthol and cetyl alcohol on water at $\text{pH}=7$: (1) monolayer of cetyl alcohol; (2) mixed film of dye and cetyl alcohol (1:2); (3) mixed film of dye and cetyl alcohol (1:2), water containing $10^{-4} M$ Cu^{++}/l .

surface area of the mixed film is represented by the area ($\text{\AA}^2$) per molecule of cetyl alcohol. The content of the dye is one third in weight of the mixture and the pH of the underlying water is about 7. From this figure the limiting area occupied by a molecule of the dye in the mixed film can be calculated as $45.5 \text{ \AA}^2$. In the same figure the effect of cupric ion is shown. When 10^{-4} mole/liter of cupric ion is present in the underlying water, the area occupied by a molecule of the dye is reduced to $23.5 \text{ \AA}^2$. This effect is not perceptible when the underlying water is acidic. In the same way we can estimate the area occupied by a molecule in the surface film for the rest of the dyes studied with or without the influence of cupric ion.

(3) W. D. Harkins, E. F. Carman and H. E. Ries, *J. Chem. Phys.*, **3**, 692 (1935); D. J. Crisp, *J. Colloid Sci.*, **1**,

Table 1
The Molecular Area of Some Azo Dyes

Dye	Structural Formula	Molecular area, Å. ²	
		on water (pH 7)	on water containing Cu ⁺⁺ (pH 7)
I <i>p</i> -Toluene-azo- β -naphthol		45.5	23.5
II <i>o</i> -Toluene-azo- β -naphthol		44.7	43.9
III Benzene-azo- benzene-azo- β - naphthol (Sudan III)		58.5	24.3
IV <i>o</i> -Toluene-azo- <i>o</i> -toluene-azo- β - naphthol (Sudan IV)		67.6	67.7

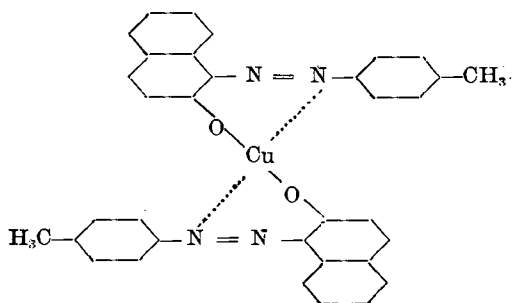
The results are shown in Table 1.

Four compounds studied in this experiment have the same molecular structure, in that each has a β -naphthol radical at one end while the rest part is rather hydrophobic, although it contains one or two azo groups. It is very much likely that the molecule will be oriented on the surface of water with hydroxyl group of the β -naphthol directing to water and the other part to air. The molecule will be bent at the part of azo radical, as is well known in the organic chemistry. From Table 1 it is seen that, although the compounds (I) and (II) have nearly the same molecular area, the molecule of the compound (IV) has larger area than that of the compound (III). This might be due to the existence of methyl groups at the ortho position for azo radical provided that the hydrophobic chain is fairly long.

It is interesting to pay more attention to the effect of metallic ions on them. In Table 1 it is shown that the surface film of the compounds (I) and (III) undergoes a remarkable condensation by the presence of cupric ion, while that of the compounds (II) and (IV) does not. The chief difference of molecular structure worth noticing here between these two groups of the dye compounds consists in that the latter two compounds have a methyl group attached to the ortho carbon atom for azo radical, while the former two have not. If it is assumed that the remarkable condensation of the surface film of the compounds (I) and (III) by cupric ion is attributed

to the formation of the complex compounds between the dye molecule in the surface film and cupric ion in the underlying water, it can be presumed that in the case of the compounds (II) and (IV) which are unaffected by cupric ion, the methyl group at the ortho position for azo radical shows hindrance against the formation of such complexes. In fact in a bulk reaction too, it is easy to confirm the formation of a copper complex with the compounds (I) and (III), but very difficult with the compounds (II) and (IV).

The copper complex of the compound (I) is considered to have a chelated structure as follows.



The dye molecule seems to be packed much more compactly with such a complex formation than without. This explains the remarkable condensation of the surface films of the dye compounds (I) and (III) by cupric ion. We can also interpret the further detail of the

pressure~area curves studied, but the precise discussion should be made when more empirical data are available.

Summary

Monomolecular film of novolac and some azo dyes, which are not capable of forming stable monomolecular films by themselves on the surface of water, were prepared using stearic acid or cetyl alcohol as a stabilizer and their pro-

perties were measured and discussed. It was shown that the molecule of novolac lies rather flat on the surface of water. The remarkable effect of cupric ion in the underlying water on the dye monolayers was discussed in connection with the molecular structure of the dye compounds.

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On the Mechanism of Evaporation in Vacuum. I. Evaporation of Silica Gel⁽¹⁾

By Masayuki NAKAGAKI

(Received June 25, 1951)

The replica methods are usually used to observe the solid surfaces by the electron microscope. Among these, the polystyrene-silica replica method^{(2), (3), (4)} is generally accepted as the method of the best reliability. The cause of the high reliability of silica replica is, as Heidenreich and Peck⁽²⁾ suggested, due to the high mobility of silica on the polystyrene surface. It is supposed from these facts that silica may evaporate in the form of very low molecular weight, such as a single molecule SiO_2 , and deposit and migrate freely on the polystyrene surface, and then polymerize to form a glass-like film. The polystyrene-silica method, however, has some defects. Above all, the evaporation of silica needs a fairly difficult technique. Wyckoff⁽⁵⁾ and some others entertained some doubts on the propagation of such a difficult method. Baker and Nicoll⁽⁶⁾ tried to obtain the silica film by blowing SiCl_4 against the surface of specimen and hydrolysing it on the surface. No satisfactory result was, however, obtained.

The present author used silica gel instead of quartz, and was able to evaporate it very easily. Silica gel was prepared as follows: Dilute commercial water glass to 10 times, add the excess of hydrochloric acid of 1 *N* drop by drop to form jelly, filter by suction, wash with water, adjust it in a rod-like shape, and heat in a crucible. Silica gel was, thus, obtained in a rod shape, the diameter of which was 4 mm. The apparatus used for evaporation was an ordinary one, as shown in Fig. 1. B is a bell jar and G. P. is a rubber packing.

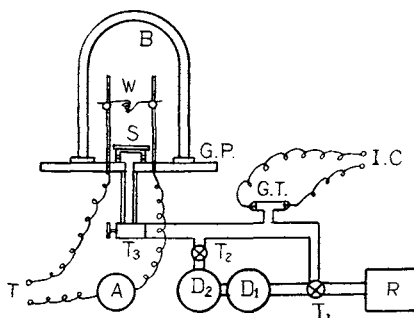


Fig. 1.—Apparatus for evaporation.

Specimen, that is, the polystyrene film, the slide glass, and so forth, are placed at S, and a piece of silica gel is put in the tungsten basket W. A bell jar is evacuated by a rotary pump R and two oil diffusion pumps D_1 and D_2 . A tungsten filament W is made of wire

(1) These results were presented before the Meeting of Colloid Chemistry held by the Chemical Society of Japan at Osaka, November 1950.

(2) R. D. Heidenreich and V. G. Peck, *J. Appl. Phys.*, **14**, 23 (1943).

(3) C. H. Gerould, *J. Appl. Phys.*, **18**, 333 (1947).

(4) R. B. Barnes, C. J. Burton and R. G. Scott, *J. Appl. Phys.*, **16**, 730 (1945).

(5) R. W. G. Wyckoff, "Electron Microscopy," New York, 1949, pp. 71 and 93.

(6) R. F. Baker and F. H. Nicoll, *J. Appl. Phys.*, **15**, 803 (1944).

of 0.5 mm. in diameter, which is coiled about 6 times in corn of 8 mm. in height and 30° in the vertical angle. Various voltages are applied on the filament by a transformer T and current is read by the ammeter A. G.T. is a Geisler's tube and I. C. is an induction coil, by which vacuum in the bell jar is known.

Heating silica gel in a crucible does not seem to be sufficient to dehydrate it. By a rapid evaporation of water contained in the gel, it bursts and splashes, if much current is hastily applied. In order to avoid such trouble, and to keep vacuum in the bell jar better, preheating of the filament for 15 or 30 sec., with 150 watts or so, is desirable. Some examples of data are shown in Table 1. In this table, w_0

Table 1
Evaporation of Silica Gel

Exper. No.	w_0 , mg.	V , volt	A , amp.	t , sec.	W , watt	Wt/w_0
1	4	{ 10 15	{ 14 18	{ 15 20	{ 140 270	{ (preheating) = 1350
2	6	{ 10 13	{ 15 18	{ 60 30	{ 150 234	{ (preheating) = 1170
3	8	{ 10 15	{ 20 24	{ 15 30	{ 200 360	{ (preheating) = 1350
4	8	{ 8 15 17	{ 12.5 17 18	{ 180 30 10	{ 100 255 306	{ (preheating) = 1339
5	18	{ 5 10 13 15	{ 10 14.5 17 18	{ 15 15 60 30	{ 50 145 221 270	{ (preheating) = 1186
6	20	{ 5 10 15	{ 10 13 18	{ 15 30 110	{ 50 130 270	{ (preheating) = 1485

is the weight of silica gel evaporated, V and A are voltage and current applied to the tungsten basket, respectively, t is the time in which current is closed, W is the product of V and A , that is the power supplied, and Wt/w_0 corresponds to the energy provided for the evaporation of 1 mg. of silica gel. The most part of this energy is emitted away as radiation, and only a very small part of it is used to evaporate the gel. Wt/w_0 may have, therefore, no theoretical meaning. If the experiments are done, however, under a definite condition, Wt/w_0 may be used as a practical measure of the easiness of evaporation. From Table 1, it is seen that

$$Wt/w_0 = 1,000 \sim 1,500 \text{ joule/mg.}$$

In the case of quartz, data of Heidenreich and Peck⁽²⁾ and Gerould⁽³⁾ shows that

$$Wt/w_0 = 3,800 \sim 14,000 \text{ joule/mg.}$$

which is 3~9 times greater than the value for silica gel. It is recognized from these values that silica gel evaporates much more easily than quartz. It is experienced that silica gel evaporates as easily as chromium.

Polystyrene silica replica is made as follows. Polystyrene replica is made by the low pressure method or the lacquer method. In the low pressure method, 1 cm.² of the polystyrene film, 0.02 mm. in thickness, is placed on a slide glass, and heated on a metal plate to $150 \sim 200^\circ\text{C}$. The specimen, another slide glass, and a weight of 1 kg. are put on the film and cooled below 80° . Specimen is splitted from the film, and silica gel is evaporated on the film according to the method described above. In the lacquer method, one drop of polystyrene lacquer, that contains 1 g. of polystyrene in 15 cc. of benzene, is placed on the specimen and dried. The replica film is stripped after 2 days, and placed on a slide-glass and silica is evaporated to it. The thickness of silica film deposited is calculated by the equation:

$$d = \frac{h w_0}{4\pi (h^2 + r^2)^{3/2} \rho} \quad (1)$$

where h is the height of tungsten basket above the polystyrene replica, 6~7 cm., r is the horizontal distance of the basket from the film, 4~5 cm., and w_0 is the weight of silica gel used, 4~5 mg. ρ is the density of silica film. A reliable value of ρ is not known. The value of bulk quartz $\rho = 2.22$ is used. The thickness calculated was usually 200~300 Å. Williams and Backus⁽⁷⁾ asserted that the value of d of equation (1) should be multiplied by an "efficiency factor" 3/4. The foundation of their opinion is somewhat uncertain, and a preliminary experiment by the present author to determine the thickness of the silica film directly from the interference color for somewhat thicker one seemed to show that such a factor is rather unnecessary. No efficiency factor is, therefore, used. The polystyrene-silica replica film thus obtained is cut off in pieces of 3~5 mm. square. One of the pieces is pasted on a holder for the electron microscopy, facing the silica surface downward and the polystyrene surface upward. The difficulty of "Fishing" is thus avoided. Paste used must be insoluble in benzene. Usual starch paste is available. These holders are laid in benzene for 1~2 days and put out carefully, holding the replica film vertically, from benzene and laid on a filter paper and dried. Some electron micrographs obtained are shown in Fig. 2. (a) is the surface

(7) R. C. Williams and R. C. Backus, *J. Appl. Phys.*, **20**, 98 (1949).

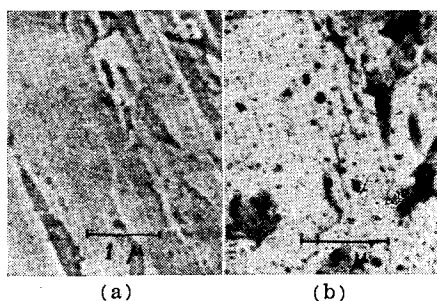


Fig. 2.—Electron micrograph.

of a brass polished by sandpaper. The lacquer method is used and silica film is 250 Å. thick. (b) is the surface of a carbon brush. The low pressure method and silica film of 200 Å. are used. Reliability of these replica method is not yet tested, but, at least, the granular structure of silica film is not found. In Fig. 2 the applicability of this replica method for electron micrography are shown.

In order to comprehend the easiness of the evaporation of silica gel, it is necessary to know the vapor pressure of it. The estimation of vapor pressure is tried. Clapeyron-Clausius' equation, usually used to describe the vapor pressure curve, is written under some approximation as:

$$\frac{d \ln P}{dT} = \frac{L}{RT^2}, \quad (2)$$

where P is vapor pressure, T is absolute temperature, R is gas constant, and L is heat of sublimation or evaporation. Using Nernst's assumption:

$$L = L_0 + 1.5 T - \varepsilon T^2 + RT \quad (3)$$

Eq (1) is integrated to

$$\log P(\text{atm.}) = -L_0/2.303 RT + 1.75 \log T - \varepsilon T/2.303 R + \kappa, \quad (4)$$

where $P(\text{atm.})$ is the pressure expressed in atmosphere, and κ is the conventional chemical constant and ε is a parameter determined from experimental data, *e. g.*, boiling point.

It is known⁽⁸⁾ that the boiling point, T_v , of rock crystal or quartz is 2590°. It is assumed that silica evaporates as SiO_2 , which is thought to be a linear molecule. The conventional chemical constant⁽⁹⁾ κ is, then,

$$\kappa = -3.273 + 1.5 \log M + \log (N_A A \times 10^{16}) \quad (5)$$

where M is molecular weight, 60.06, N_A is Avogadro's number, and A is the moment of inertia of the molecule. Assuming the $\text{Si}=\text{O}$ distance to be 1.62 Å., the value of κ of Eq. (5) is obtained as 1.319. If the value of L_0 is obtained, vapor pressure P is calculated from Eq. (4), with the estimated value of ε by the use of T_v .

The heat of sublimation of quartz $L_0^{(4)}$ is approximately equal to twice the bond energy of $\text{Si}-\text{O}$,

$$L_0^{(4)} \simeq 2D(\text{Si}-\text{O}) \quad (6)$$

This is easily seen from Fig. 3 (a), because four bonds should be broken to produce a molecule of SiO_2 , and each bond is held in

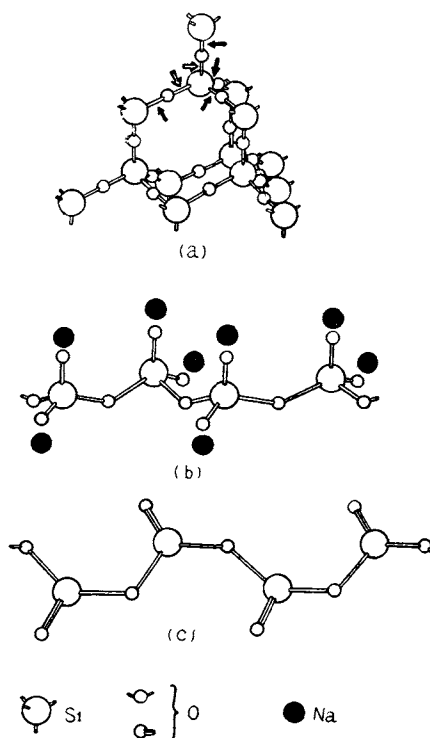


Fig. 3.—Molecular structure of silica.

common with two SiO_2 molecules. The bond energy $D(\text{Si}-\text{O})$ is calculated by Pauling⁽¹⁰⁾ from the data of the heat of generation of quartz as:

$$D(\text{Si}-\text{O}) = 89.3 \text{ kcal./mol.} \quad (7)$$

Seitz⁽¹¹⁾ cited the cohesive energy of quartz E as

(8) Edited by Tokyo Astronomical Observatory, "Rika-Nenpyo", Tokyo, 1950.

(9) R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics", Cambridge, 1939, p. 171.

(10) L. Pauling, "The Nature of the Chemical Bond," New York, 1940, p. 53.

(11) F. Seitz, "The Modern Theory of Solid", New York, 1940, p. 61.

$$E' = 405.7 \text{ kcal./mol.} \quad (8)$$

E is the energy necessary to produce one gram atom of Si and two gram atom of O from quartz, and equals to the sum of $L_0^{(A)}$ and $2D(\text{Si-O})$, as shown in Fig. 3 (a). Therefore,

$$E \simeq L_0^{(A)} + 2D(\text{Si-O}) \simeq 4D(\text{Si-O}) \quad (9)$$

From Eqs. (8) and (9),

$$D(\text{Si-O}) \simeq 101.4 \text{ kcal./mol.} \quad (10)$$

This is the same order of magnitude with Pauling's value, Eq. (7), but is not exactly equal. The mean value

$$D(\text{Si-O}) = 95.4 \text{ kcal./mol.} \quad (11)$$

is used in the following estimations. From Eq. (6),

$$L_0^{(A)} = 190.8 \text{ kcal./mol.} \quad (12)$$

Silica gel is prepared from water glass, $(\text{Na}_2\text{SiO}_3)_n$, which is considered as a chain polymer as shown in Fig. 3 (b). The idealized structure of silica gel, therefore, will be also a chain polymer. The heat of sublimation of idealized silica gel, $L_0^{(B)}$, will be, as explained easily from Fig. 3 (c),

$$L_0^{(B)} \simeq D(\text{Si-O}) = 95.4 \text{ kcal./mol.} \quad (13)$$

As for actual silica gel, the probability of dehydration from two hydroxyl groups of adjacent molecules forming an oxygen bridge should be taken into account, beside with the probability of dehydration from two hydroxyl groups belonging to the same silica atom in meta-silicic acid molecule. Under the somewhat arbitrary assumption that the latter probability is twice as large as the former probability, the heat of sublimation of real silica gel $L_0^{(C)}$ becomes:

$$\begin{aligned} L_0^{(C)} &= \frac{2L_0^{(B)} + L_0^{(A)}}{3} = \frac{4}{3} D(\text{Si-O}) \\ &= 127.2 \text{ kcal./mol.} \end{aligned} \quad (14)$$

Using these values of the heat of sublimation L_0 , vapor pressure is calculated for various temperatures, using $\kappa = 1.319$ and $\varepsilon = -0.01145$,

the latter is obtained from boiling point for quartz. For some metals, vapor pressure curves are estimated in an analogous way, and temperature corresponding to some vapor pressure are cited in Table 2. In this table, $\text{SiO}_2(\text{A})$ means

Table 2
Calculated Vapor Pressure—Temperature Relations

Substances	Temperature corresponding to the vapor pressure, °K.			
	10 mm.Hg	10^{-1} mm.Hg	10^{-3} mm.Hg	10^{-5} mm.Hg
Pt	3300	2600	2200	1900
$\text{SiO}_2(\text{A})$	2650	2450	2250	2050
Au	2200	1850	1550	1350
$\text{SiO}_2(\text{C})$	2000	1800	1650	1500
Cr	2050	1750	1500	1300
$\text{SiO}_2(\text{B})$	1650	1450	1300	1150
Al	1700	1400	1200	1050

quartz, $\text{SiO}_2(\text{B})$ means idealized silica gel and $\text{SiO}_2(\text{C})$ means actual silica gel. It is seen that the evaporation of quartz is almost as difficult as platinum, while silica gel, $\text{SiO}_2(\text{C})$, evaporates as easily as gold or chromium. These agree well with the results described above.

Summary

The evaporation of silica is facilitated by the use of silica gel, instead of quartz. The silica film thus obtained is available as replica for the electron microscopy. The difference of the easiness of evaporation between quartz and silica gel is attributed to molecular constitutions. Under the assumption that quartz consists of three dimensional net work of covalent linkage, while silica gel is constructed by linear chain having some oxygen bridges between chains, vapor pressure is calculated, and the ease of evaporation is accounted for by the comparison to some usual metals.

Thanks are due to Mr. S. Okada for his kind help to the operation of the electron microscope.

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LETTER

Electrophoresis of Desoxypentose Nucleic Acids Treated with Acid and Alkali

By Nobuo UI and Itaru WATANABE

(Received September 15, 1951)

Recently, some physico-chemical studies of the effect of acids and bases on the macromolecular properties of desoxypentose nucleic acid (DNA) have been carried out by several investigators.⁽¹⁾

During the electrophoretic studies on nucleic acids⁽²⁾ now in progress, the present authors have found an appreciable variation of the mobility of DNA after the treatment with alkali as well as acid. The acid-treatment also causes a change in the electrophoretic pattern.

DNA was prepared from herring sperm or calf thymus by the modified Hammarsten's method and dissolved in water. A neutral solution was brought to pH 12.0 by adding sodium hydroxide and immediately neutralised again directly with hydrochloric acid or by dialyzing against the phosphate buffer of pH 7.7. In both cases, only one homogeneous component was found, as in the case of native DNA, when examined by electrophoresis in phosphate buffer (pH 7.7, ionic strength 0.2) using a Tiselius-type apparatus. The mobility of the alkali-treated samples, however, was considerably lower than that of the untreated DNA, while Creeth *et al.*⁽³⁾ reported the absence of any difference between the mobilities of both treated and untreated samples in the wide pH

Table 1

Electrophoretic Mobilities of Alkali-treated DNA at 0°C. (In phosphate buffer of pH 7.7 and ionic strength 0.2)

Samples	Mobilities (calcd. from descending pattern), $\times 10^3 \text{ cm}^2/\text{sec. volt}$
(a) Untreated DNA	-16.0
(b) Alkali-treated DNA	-15.0
(c) (a) + (b)	-15.2, -16.4
(d) Alkali-boiled DNA	-15.5
(e) (d) + YNA	-15.3, -13.9*

* The mobility of YNA.

range. Representative results are shown in Table 1, together with the mobility of the sample which had been boiled in an alkaline solution for one hour and precipitated with HCl-containing ethanol. It is rather curious that the mobility of this alkali-boiled DNA is still larger than that of yeast nucleic acid (YNA), the latter being *ca.* $-14 \times 10^{-5} \text{ cm}^2/\text{sec. volt}$, though those two nucleic acids have similar molecular size and shape.⁽⁴⁾ This result also differs from Cohen's data⁽⁵⁾ that Leven's DNA migrates with the same mobility as YNA.

On the other hand, somewhat different phenomena have been observed after the acid treatment. For example, the sample, once brought to pH 3.0 and immediately neutralised again, showed a slightly inhomogeneous pattern indicating the presence of a small amount of faster component. When kept at pH 3.0 for 48 hours before the neutralisation, this faster component became more distinct. In both cases, the mobility of the main (slower) component was exactly the same as that of the alkali-treated DNA.

Details of this work will be published elsewhere with the discussion on the possible explanations for these experimental results.

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(1) C. F. Vilbrandt and H. G. Tennent, *J. Am. Chem. Soc.*, **65**, 1896 (1943); J. M. Gulland, D. O. Jordan and H. F. W. Taylor, *J. Chem. Soc.*, **1947**, 1131; J. M. Creeth, J. M. Gulland and D. O. Jordan, *ibid.*, **1947**, 1141; R. Cecil and A. G. Ogston, *ibid.*, **1948**, 1382; I. Jungner, *Acta physiol. Scand.*, **20**, Suppl. 69 (1950); S. Zamenhof and E. Chargaff, *J. Biol. Chem.*, **186**, 207 (1950).

(2) I. Watanabe and N. Ui, *Repts. Radiation Chem. Research, Inst., Tokyo Univ.*, **5**, 17 (1950).

(3) J. M. Creeth, D. O. Jordan and J. M. Gulland, *J. Chem. Soc.*, **1949**, 1406.

(4) I. Watanabe and T. Kitamura, unpublished data.

(5) S. S. Cohen, *J. Biol. Chem.*, **146**, 471 (1942).

Studies on the Magnetic Dichroism of Dye-Gelatin Films. III. Magnetic Dichroism of Dye-Gelatin Films Excited by Light

By Daijiro YAMAMOTO

(Received May 4, 1951)

In the previous papers⁽¹⁾⁽²⁾ the magnetic dichroism of dye-gelatin films and its theoretical consideration have been reported. The magnetic dichroism in this case was due to diamagnetic orientation of dye-molecules, and its relaxation phenomena seemed to be due to the visco-elastic properties of solid gelatin.

If dye molecules were paramagnetic, the orientation would be changed, and the magnetic dichroism-time curves would alter their forms. During the last decade G. N. Lewis, M. Calvin, M. Kasha and their collaborators⁽³⁾ have shown that organic molecules, having conjugated double bonds, turn into a phosphorescent state in rigid media by the illumination of visible and near ultraviolet rays, and its effect is due to a triplet state of π -electrons. Molecules in triplet state are paramagnetic, and these investigators confirmed the fact by determining the paramagnetic susceptibility of acid fluorescein dissolved in rigid boric acid glass by means of an excellent method using Theorell's micro balance.⁽⁴⁾ This phenomenon is the so-called "Photomagnetism," named by them. Dye molecules have remarkable conjugated double bonds. Dye-gelatin films are also good phosphors⁽⁵⁾; in them, gelatin is to a certain extent a suitable rigid glassy solvent. Dye-gelatin phosphors may be due to a triplet state of π -electrons of double bonds.

From this view-point the author has examined the magnetic dichroism of dye-gelatin films excited by light, and obtained the following results.

Experimental

Materials.—The materials used were the same as mentioned in the previous paper. Dyes were dissolved in a gelatin-water solution at 50°, and smeared on glass plates and then dried. They were

good phosphors. Nonphosphoric dyes like azo-dyes were also examined.

Apparatus.—All equipment is shown in Fig. 1. The magnet and measuring polarimeter were the same as mentioned in the previous paper, but the distance of the poles was taken as 7 mm. and all experiments were carried out under 9800 gauss (measured by fluxmetre). The sample was a strip of 6 mm. $\times$ 20 mm. and it was set in a magnetic field, whose direction was parallel to the surface of the film. The exciting light source was a 6–8 amp. carbon arc or a mercury lamp. Between the light source and the sample along the optical path were set filters of water, CuSO₄-water solution, CuCl₂-alcohol solution or colored glass filters for each purposes. The excitation of materials by light was carried out by a uniform image of diaphragm projected on the film. The opening of the diaphragm was 10 mm. $\times$ 10 mm., and the size of the image was 6 mm. $\times$ 6 mm.

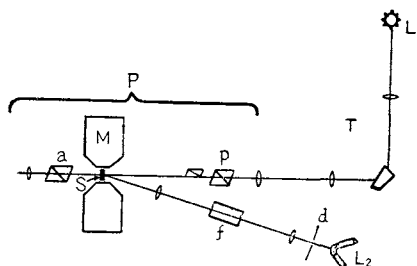


Fig. 1.—Schematic diagram of the equipment for studying the magnetic dichroism: S, sample; P, polarimeter; M, magnet; T, monochrometer; L₁, measuring light source; L₂, exciting light source; p, polariser; a, analyser; f, filter; d, diaphragm.

Dichroism was measured by means of the polarimeter which F. Weigert⁽⁶⁾ used for his studies on the photodichroism. In this method dichroism D is given according to the following relation,

$$D = 2 \log \tan (45^\circ \pm \alpha) = 0.015 \times 2 \alpha$$

where α is the angle of rotation of the analyser.

Difficulties in the Experiments.—There are many difficulties in this experiment. They are as follows:

(1) D. Yamamoto, *J. Chem. Soc. Japan*, **72**, 693 (1951).

(2) D. Yamamoto, *ibid.*, **72**, 782 (1951).

(3) Their works have been summarized by M. Kasha, *Chem. Rev.*, **41**, 401 (1947).

(4) G. N. Lewis, M. Calvin and M. Kasha, *J. Chem. Phys.*, **17**, 804 (1949).

(5) e. g., P. Fröhlich and Z. Gyulai, *Z. Phys.*, **104**, 549 (1937). Now in the author's laboratory dye-gelatin phosphors are being studied by the author with Mr. R. Iwaki.

(6) F. Weigert, *Z. Physik. Chem.*, (B) **3**, 377, (1929).

(1) Dyes are decomposed by light (bleaching or discoloring), especially by near ultraviolet rays.

(2) Phosphorescence and fluorescence of films lead to errors in measured values of dichroism.

(3) Absorption bands of dyes are not necessarily in a suitable position for excitation.

The Difficulty of (1) is removed by using proper filters, and the author's studies on the photodichroism of such materials make clear the effect of bleaching or discoloring in dyes, so we are able to know the most suitable condition for experiments.⁽⁷⁾ (2) is very troublesome because of the interruption of the measuring light, so that monochromatic rays for observation diminish. But if we use such materials as phosphorescent bands in long wave length region *e. g.* orange or red, and if their intensities are weak, we can read the correct value of dichroism. (3) is not so troublesome, for we can choose proper materials which have absorption band in the vicinity of 430 or 546 $m\mu$ for mercury lamp. But in practice the intensity of a mercury lamp is not very satisfactory, so that an arc light and proper filters are used for examination after testing by the monochromatic rays of a mercury lamp.

Results Obtained

Results obtained on the malachite green, rhodamine-B, fuchsin, fluorescein, pinachrome, pinacyanol, azo-dyes *e. g.* chrysoidine, congo red-gelatin films were as follows:

(1) 1.25% Malachite Green-Gelatin Film.

—Malachite green-gelatin film has an absorption band near 620 $m\mu$ ⁽⁸⁾ which is due to shift of π -electron. By intense illumination of red rays (600~650 $m\mu$, filter: red glass+water) dark deep red phosphorescence⁽⁹⁾ (probably about 700~800 $m\mu$) is found. There was no discoloring by excitation for 10 minutes, and it is confirmed by means of a study on photo-

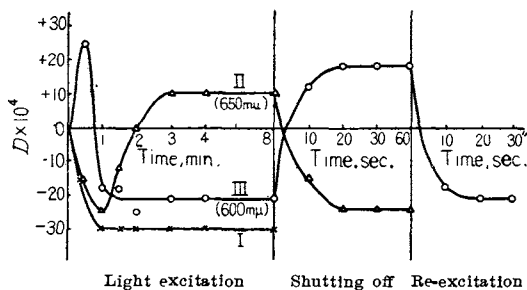


Fig. 2.

(7) D. Yamamoto and R. Iwaki, *J. Chem. Soc., Japan*, **72**, 852, 854 (1951).

(8) Absorption bands of following dye-gelatin films were given by unpublished works of Mr. R. Iwaki.

(9) Phosphorescence of dye-gelatin films was examined by 1800 r. p. m. phosphorscope.

dichroism. Magnetic dichroism—time curves are shown in Fig. 2. A curve in no excitation was the same as mentioned in the previous papers. But by excitation of red rays, curves had altered their shapes as seen in the figure. As soon as the exciting light was shut off the value of dichroism came back rapidly to that of mere magnetic dichroism.

In Fig. 2, curve I is due to mere magnetic dichroism, and its dichroism is measured by 650 $m\mu$, curve II is due to the excitation by red rays and measured by 650 $m\mu$, and curve III is due to the same exciting light, but measured by 600 $m\mu$. The opposite sign is due to dispersion. The dispersion of magnetic dichroism in both non-exciting and exciting states was examined. Results obtained are shown in Fig. 3. Both curves are in relation to mirror images.

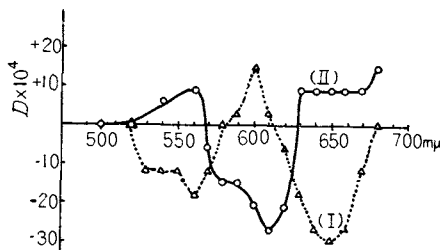


Fig. 3.—Dispersion of dichroism: (I), non-excitation; (II), excitation.

(2) 1.25% Rhodamine B-Gelatin Film.—

Rhodamine B-gelatin film has a green absorption band, and its phosphorescence is orange-red. As exciting light, the following filters were used. (1) CuSO_4 -water for 546 $m\mu$ Hg, (2) blue glass+water, (3) CuCl_2 -alcoholic solution and (4) blue glass+ $\text{K}_2\text{Cr}_2\text{O}_7$ -water for arc light. In each case phosphorescence was visual, and so measuring was hard. (Bleaching was not found.) The effect is evident in the case of filter (2), (3) and (4). Results obtained are shown in Fig. 4. Dispersion of both states is shown in Fig. 5.

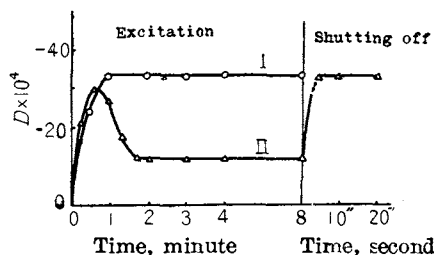


Fig. 4.—(I), non-excitation; (II), excited by blue light (filter No. 2), measured by 560 $m\mu$.

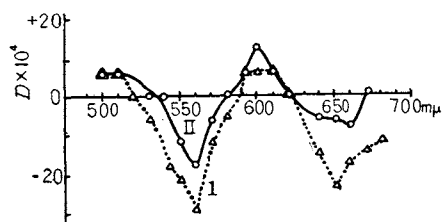


Fig. 5.—Dispersion of dichroism; (I), non-excitation; (II), excited by green light (filter No. 4).

(3) **1% Fuchsine-Gelatin Film.**—Fuchsine-gelatin film has an absorption band near 546 $m\mu$ Hg. Phosphorescence is yellowish orange. The effect of excitation by green light was evident. One of the results is shown in Fig. 6.

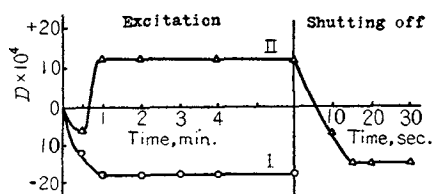


Fig. 6.—(I), non-excitation; (II), excited by green light.

(4) **0.75% Fluorescein-Gelatin Film.**—Fluorescein- and uranin (Na-fluorescein)-gelatin films are not so good as phosphors. They show, however, the effect by the excitation of blue light. They have absorption bands in 480~490 $m\mu$. Excitation by 490 $m\mu$ Hg is suitable, but it is so weak that it can not be used for excitation. Then, excitation by blue light (blue glass+water, arc light) showed the effect. Results obtained are shown in Fig. 7.

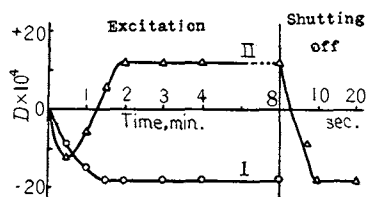


Fig. 7.—(I), non-excitation; (II), excited by blue light, measured by 570 $m\mu$.

(5) **Cyanine Dyes-Gelatin Films.**—1.25% Pinachrome- and 1.25% pinacyanol-gelatin films were examined. They showed weak phosphorescence. Pinachrome-gelatin films showed effect by excitation of blue light, and pinacyanol-gelatin films by red light. But in

them slight bleaching was observed. Results are shown in Figs. 8 and 9.

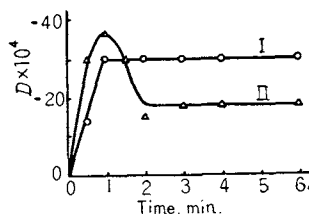


Fig. 8.—1.25% Pinachrome-gelatin film: (I), non-excitation; (II), excited by blue light, measured by 610 $m\mu$.

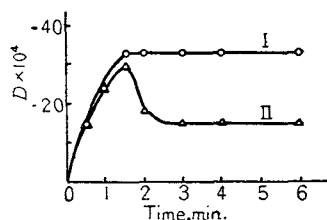


Fig. 9.—1.25% Pinacyanol-gelatin film: (I), non-excitation; (II), excited by red rays, measured by 580 $m\mu$.

(6) **Azo-dyes-Gelatin Films.**—For azo-dyes chrysoidine and congo red were used. Azo-dyes-gelatin films are non-phosphors and they show strong bleaching by illumination of light. Chrysoidine is a very simple monoazo-dye, on the other hand, congo red is a very complicated disazo-dye. On 1% chrysoidine-gelatin film

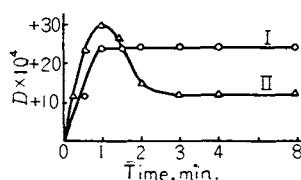


Fig. 10.—1% Chrysoidine-gelatin film: (I), non-excitation; (II), excited by blue light (without water filter), measured by 550 $m\mu$.

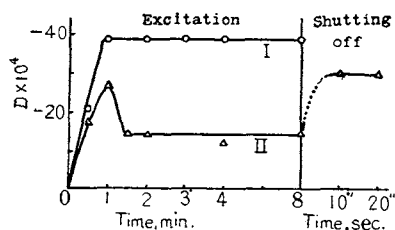


Fig. 11.—1.5% Congo red-gelatin film: (I), non-excitation; (II), excited by blue light, measured by 580 $m\mu$.

the effect was not distinct. 1.5% congo red-gelatin film showed the effect by excitation of blue light, but after shutting off the light the value of dichroism did not come back to that of mere magnetic dichroism. These results are shown in Figs. 10 and 11.

Summary

There were found considerable changes in magnetic dichroism of some dyes-gelatin films by excitation of light. In malachite green and rhodamine B-gelatin films this effect was very evident, and cyanine dyes and azo-dyes-gelatin films also showed the same effect. This effect may have something to do with the phosphorescent state of dye molecules, having conjugated double bonds, but nothing to do with bleaching by light. Azo-dyes-gelatin films are non-phosphors, but G. N. Lewis and M. Kasha⁽¹⁰⁾ thought that these materials would

have a phosphorescent band in near infra red regions. It is difficult to decide between phosphor and non-phosphor by limited observation in the visible region. This will be discussed in another paper if those experimental results are due to photomagnetism or to other causes.

The author wishes to express his sincere thanks to Prof. Jitaro Shidei for his kind guidance and to Mr. Ryojiro Iwaki for his valuable discussions of these problems, and also to the Ministry of Education for grants in aid out of the Scientific Research Expenditure.

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(10) G. N. Lewis and M. Kasha, *J. Amer. Chem. Soc.*, **66**, 2100 (1944).

Studies on the Magnetic Dichroism of Dye-Gelatin Films. IV. Confirmation of Photomagnetism by means of Magnetic Dichroism in Dye-Gelatin Films Excited by Light

By Daijiro YAMAMOTO

(Received May 4, 1951)

In the last paper⁽¹⁾ the author reported the changes of magnetic dichroism of dye-gelatin films by excitation of light. As to the cause of this effect, the author briefly pointed out elsewhere that this effect would be due to photomagnetism of dye molecules in solid gelatin.⁽²⁾ But its treatment did not include the saturation effect of excited molecules, and the ground conception of the mechanism of magnetic dichroism was not so correct. The author⁽³⁾ made phenomenologically a theoretical consideration on the magnetic dichroism of dye-gelatin films as visco-elastic properties of gelatin, taking phosphorescence and photo-dichroism into consideration. In the visco-elastic model entropy-elasticity of chains in net-work structure of gelatin was assumed. This conception would not be so correct. But the results obtained by such a conception could

explain the relaxation phenomena well, and the dichroism--time relations accorded with experimental results very well. In an ordinary way, magnetic dichroism is due to diamagnetic orientation, but in the case of paramagnetic molecules, the orientation may differ from diamagnetic ones, and dichroism-time relations are also different. The author obtained a distribution function for paramagnetic orientation and combined it with a diamagnetic one, and then obtained dichroism-time relations in co-existent state of dia- and paramagnetism. These relations can well explain qualitatively the experimental results, reported in the preceding paper. So the author supposes that the differences which appeared in magnetic dichroism-time relations by the excitation of light would be due to the photomagnetism effect, discovered by G. N. Lewis, M. Calvin and M. Kasha⁽⁴⁾.

(1) D. Yamamoto, This Bulletin, **24**, 211 (1951).

(2) D. Yamamoto, *Kagaku (in Japanese)*, **20**, 574 (1960).

(3) D. Yamamoto, *J. Chem. Soc. Japan*, **72**, 782 (1951).

(4) G. N. Lewis, M. Calvin and M. Kasha, *J. Chem. Phys.*, **17**, 804 (1949).

Theoretical

Distribution Function in Paramagnetic Orientation.—As in the previous case, the author took the following four assumptions in dye-gelatin systems:

(1) Gelatin has a net-work structure and elements of a chain are allowed of micro-brownian motion to some extent. In this, entropy-elasticity is assumed.

(2) One of dye molecules attaches to one element, and its combination is fairly strong, but weaker than valence combination.

(3) Paramagnetic action of dye molecules in magnetic field is stronger than diamagnetic action of chain, so we neglect the diamagnetic orientation of chains.

(4) By the orientation of dyes, combined elements are set in rotation, and then the elongation or compression in neighboring chains of those elements appears. But in that case knots of network do not slide.

According to those assumptions, the following phenomenological equations were taken for the rotation of dye molecules;

$$\left. \begin{aligned} \frac{d\vartheta}{dt} &= \frac{2}{\alpha \cdot G} \cdot \frac{dF_1}{dt} \\ \frac{d\vartheta}{dt} &= \frac{2}{\alpha \cdot \eta} \cdot F_2 \\ F_1 + F_2 &= M/\alpha \times \gamma \end{aligned} \right\} \quad (1)$$

where α is the diameter of a sphere, regarding a molecule with a combined element as a sphere, ϑ is the angle of rotation of a sphere, G is the mean elastic constant, η is the viscosity for inner flow, M is the moment of rotation, γ is a correction term which has the value of $0 < \gamma < 1$, presumably it is proper to take about $1/3$, and F_1 and F_2 are components for elastic and viscous action. This relation is Voigt's parallel model for visco-elastic system.

Distribution function f is represented by the following differential equation with time, as mentioned in the previous treatment.

$$\frac{\partial f}{\partial t} = - \left\{ \frac{2\gamma \cdot M}{\alpha^2 \eta} \cdot \exp(-G/\eta \cdot t) \right\} \times \frac{1}{\sin \theta} \cdot \frac{\partial}{\partial \theta} (\sin \theta \cdot M \cdot f) \quad (2)$$

where θ is the angle between direction of paramagnetic dipole moment and magnetic field. We can obtain a distribution function by solving this equation under given moment of rotation M . Moment M is given by the following relation for paramagnetic dipole

$$M = d \cdot H \cdot \sin \theta$$

where d is a constant proportional to the magnitude of paramagnetic dipolemoment of dye molecule and H is the strength of magnetic field in gauss.

Distribution function is usually represented by the following expanded series:

$$f = \frac{1}{4\pi} \{1 + A_1 P_1(\cos \theta) + A_2 P_2(\cos \theta) + \dots\} \quad (3)$$

where $P_1, P_2, \dots$ are Legendre's spherical functions and $A_1, A_2, \dots$ are constants without θ . By the second order approximation, we can write a distribution function f_{para} for paramagnetic orientation as follows

$$f_{para} = \frac{1}{4\pi} \{1 + R(t) P_1(\cos \theta) + S(t) P_2(\cos \theta)\} \quad (4)$$

where $R(t)$ and $S(t)$ are functions with time. They are obtained approximately by the following method. At first $R(t)$ is obtained by the first order approximation;

$$f_{para} = \frac{1}{4\pi} \{1 + R(t) P_1(\cos \theta)\} \quad (5)$$

Combining Eqs. (2), (5) and relation $P_1(\cos \theta) = \cos \theta$, we obtained $R(t)$ as follows.

$$R(t) = - \frac{2\gamma \cdot d \cdot H}{\alpha^2 G} \{1 - \exp(-G/\eta \cdot t)\} \quad (6)$$

Next, we take the second order approximation as

$$f_{para} = \frac{1}{4\pi} \{1 + R(t) P_1(\cos \theta) + S(t) P_2(\cos \theta)\} \quad (7)$$

and by (2), (6), (7) and use $P_2(\cos \theta) = 1/2 \times (3 \cos^2 \theta - 1)$, we obtain the following equation;

$$\frac{dS(t)}{dt} = - \frac{2\gamma \cdot d \cdot H}{\alpha^2 \eta} \cdot \exp(-G/\eta \cdot t) \cdot R(t). \quad (8)$$

By introducing (6) in (8), we obtain the following equation for $S(t)$

$$S(t) = \frac{4\gamma^2 d^2 H^2}{\alpha^4 G \cdot \eta} \{1 - \exp(-G/\eta \cdot t)\}^2. \quad (9)$$

So we obtain the distribution function for paramagnetic orientation as follows:

$$f_{para} = \frac{1}{4\pi} \left\{ 1 - \frac{2\gamma dH}{a^2 G} [1 - \exp(-G/\eta \cdot t)] \right. \\ \left. \times P_1(\cos \theta) + \frac{4\gamma^2 d^2 H^2}{a^4 G \eta} [1 - \exp(-G/\eta \cdot t)]^2 P_2(\cos \theta) \right\}. \quad (10)$$

On the other hand, the distribution function for diamagnetic orientation f_{dia} is as follows, as mentioned in a previous paper;

$$f_{dia} = \frac{1}{4\pi} \left\{ 1 + \frac{2\gamma b H^2}{a^2 G} [1 - \exp(-G/\eta \cdot t)] \cdot P_2(\cos \theta) \right\}, \quad (11)$$

where b is a diamagnetic constant depending on the diamagnetic susceptibility of a dye molecule.

Magnetic Dichroism—Time Relations for Paramagnetic Molecules.—Prior to the consideration for magnetic dichroism in co-existent state of dia- and paramagnetic molecules, magnetic dichroism owing merely to paramagnetic molecules are treated. If paramagnetic molecules have molecular dichroism $(\alpha_1' - \alpha_2')$ in voluntary measuring wave length, in which α_1' is the molecular extinction coefficient parallel to the dipole moment and α_2' is one perpendicular to the α_1' direction. This conception is the same as used by W. Kuhn *et al.*,⁽⁵⁾ for exposition of electric dichroism of dye molecules.

Let α_p' be parallel component along to the direction of magnetic field H_z , directions perpendicular to H_z are H_y and H_x , and component α_s' be along the direction H_y , direction of observation is parallel to H_z , and φ be the angle between α_2' and H_y as shown in Fig. 1, the following equations are obtained.

$$\alpha_p' = (\alpha_1' - \alpha_2') \cos^2 \theta + \alpha_2' \\ \alpha_s' = (\alpha_1' - \alpha_2') \sin^2 \theta \cos^2 \varphi + \alpha_2'.$$

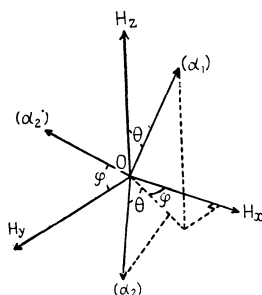


Fig. 1.

So, the factor of dichroism for a molecule $\alpha_p' - \alpha_s'$ is as follows:

$$\alpha_p' - \alpha_s' = (\alpha_1' - \alpha_2') (\cos^2 \theta - \sin^2 \theta \cdot \cos^2 \varphi). \quad (12)$$

Dichroism of a film is represented by the following relations for N -molecules (in the material used $N = c \cdot l$, where c is mol concentration per cm^2 , and l is thickness of film in cm .)

$$D = N \int (\alpha_p' - \alpha_s') f d\Omega \\ = \frac{N}{4\pi} \int_{\varphi=0}^{2\pi} \int_{\theta=0}^{\pi} (\alpha_1' - \alpha_2') (\cos^2 \theta - \sin^2 \theta \cdot \cos^2 \varphi) \\ \times \{1 + R(t) P_1(\cos \theta) + S(t) P_2(\cos \theta)\} \sin \theta \cdot d\theta \cdot d\varphi, \quad (13)$$

where Ω is solid angle involving θ . While

$$\int \int (\cos^2 \theta - \sin^2 \theta \cdot \cos^2 \varphi) \sin \theta \cdot d\theta \cdot d\varphi = 0 \\ \int \int P_1(\cos \theta) (\cos^2 \theta - \sin^2 \theta \cdot \cos^2 \varphi) \sin \theta \cdot d\theta \cdot d\varphi = 0 \\ \int \int P_2(\cos \theta) (\cos^2 \theta - \sin^2 \theta \cdot \cos^2 \varphi) \sin \theta \cdot d\theta \cdot d\varphi = \frac{4}{5} \pi,$$

so we obtain for dichroism D the following formulas

$$D = \frac{1}{5} N (\alpha_1' - \alpha_2') S(t) \\ = \frac{4}{5} N (\alpha_1' - \alpha_2') \cdot \frac{\gamma^2 d^2 H^2}{a^4 G \eta} \\ \times \{1 - \exp(-G/\eta \cdot t)\}^2 \quad (14)$$

$$= D_{\infty \cdot para} \{1 - \exp(-t/\tau)\}^2, \quad (15)$$

where $D_{\infty \cdot para}$ is the value of dichroism for $t = \infty$.

Magnetic Dichroism—Time Relations in the Case of Co-existence of Dia- and Paramagnetic Molecules.—In the case of diamagnetic orientation D is given by the following equation after distribution function f_{dia} , as mentioned in the previous paper,

$$D_{dia} = D_{\infty} \{1 - \exp(-t/\tau)\} \quad (16)$$

where $1/\tau = G/\eta$.

On the other hand, in the case of co-existence of both states, two factors should be considered. One of them is the degree of

(5) W. Kuhn, H. Dürkop and H. Martin, *Z. physik. Chem.*, (B) **45**, 121 (1939).

saturation, *i. e.*, paramagnetic molecules/total molecules, and the other is molecular dichroism of paramagnetic state. If the saturation factor is put ξ , the number of paramagnetic molecules is $N\xi$, and the number of diamagnetic molecules is $N(1-\xi)$, and they are in equilibrium. As the life time of excited state τ' is shorter than relaxation time of magnetic dichroism, *i. e.*, $\tau' \ll \tau$, orientation is governed by $(1-\xi)N'$ s diamagnetic molecules and $N\xi$ paramagnetic molecules statistically, so dichroism observed is as follows;

$$D_{dia} = (1-\xi)^2 D_{\infty dia} \{1 - \exp(-t/\tau)\} + (1-\xi)\xi \cdot D'_{\infty dia} \{1 - \exp(-t/\tau)\} \quad (17)$$

for molecules in diamagnetic part, and

$$D_{para} = (1-\xi) \cdot \xi \cdot D_{\infty para} \{1 - \exp(-t/\tau)\}^2 + \xi^2 D'_{\infty para} \{1 - \exp(-t/\tau)\}^2 \quad (18)$$

for paramagnetic part, after Eqs. (15) and (16), where

$$D_{\infty dia} = \frac{4}{5} N(\alpha_1 - \alpha_2) \cdot \frac{\gamma b H^2}{a_2 G}, \quad (19)$$

$$D_{\infty para} = \frac{4}{5} N(\alpha_1 - \alpha_2) \cdot \frac{\gamma^2 d^2 H^2}{a^4 G \cdot \eta}, \quad (20)$$

$$D'_{\infty dia} = \frac{4}{5} N(\alpha_1' - \alpha_2') \cdot \frac{\gamma b H^2}{a^2 G}, \quad (21)$$

$$D'_{\infty para} = \frac{4}{5} N(\alpha_1' - \alpha_2') \cdot \frac{\gamma^2 d^2 H^2}{a^4 G}, \quad (22)$$

and $(\alpha_1 - \alpha_2)$ is molecular dichroism for a diamagnetic molecule, and $(\alpha_1' - \alpha_2')$ is for paramagnetic molecules. In dye-gelatin phosphors, ξ is not so large that we are able to neglect ξ^2 for ξ . So we can neglect the second term of Eq. (18). By combining the two cases, we obtain the following relation in the case of co-existence of both states.

$$D = (1-\xi)[(1-\xi)D_{\infty dia}\{1 - \exp(-t/\tau)\} + \xi \cdot D_{\infty para}\{1 - \exp(-t/\tau)\}^2 + \xi \cdot D'_{\infty dia}\{1 - \exp(-t/\tau)\}]. \quad (23)$$

Comparison with Experimental Results

On Eq. (23), we consider two processes to compare theoretical works with experimental results.

(1) **In the Case of $(\alpha_1' - \alpha_2') = 0$.**—At first we consider the case of $D'_{\infty dia} = 0$, *i. e.*, $(\alpha_1' - \alpha_2') = 0$. In this case, Eq. (23) is taken as follows :

$$D = (1-\xi) \cdot D_{\infty dia} [(1-\xi)\{1 - \exp(-t/\tau)\} + \xi \cdot D_{\infty para} / D_{\infty dia} \times \{1 - \exp(-t/\tau)\}^2] \quad (24)$$

In the dye-gelatin phosphors, ξ is very small in comparison with dye-boric acid glass phosphor, so we are able to put it down as follows, for $(1-\xi) \approx 1$:

$$D = D_{\infty dia} [1 - \exp(-t/\tau)] + \xi \cdot D_{\infty para} / D_{\infty dia} \times \{1 - \exp(-t/\tau)\}^2. \quad (25)$$

For various values of $\xi \cdot D_{\infty para} / D_{\infty dia}$, curves of (25) are shown in Fig. 2. As $b < 0$, and $(d^2) > 0$, so the sign of $D_{\infty para} / D_{\infty dia}$ is negative.

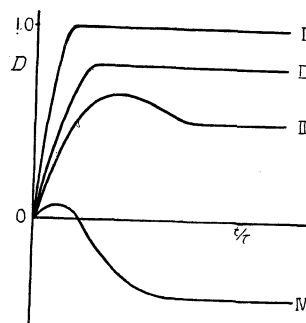


Fig. 2.— $\xi D_{\infty para} / D_{\infty dia} =$: I, 0; II, $-1/5$; III, $-1/2$; IV, $-7/5$.

(2) **In the case of $(\alpha_1' - \alpha_2') \neq 0$.**—If $\xi D'_{\infty dia}$ is fairly large, the term $\xi D'_{\infty dia} / D_{\infty dia} \cdot \{1 - \exp(-t/\tau)\}$ is added into Eq. (25):

$$D = D_{\infty dia} [\{1 - \exp(-t/\tau)\} + \xi \cdot D'_{\infty dia} / D_{\infty dia} \cdot \{1 - \exp(-t/\tau)\} + \xi \cdot D'_{\infty para} / D_{\infty dia} \{1 - \exp(-t/\tau)\}^2] \quad (26)$$

and its curves are changed into what is shown in Fig. 3, for some cases.

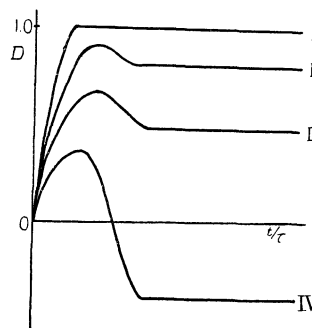


Fig. 3.—The case of $D'_{\infty dia} / D_{\infty dia} = 1/10 \sim 1/2$; I, II, III and IV correspond to I, II, III and IV in Fig. 2 respectively.

Experimental results as mentioned in the preceding paper on the malachite green-, fuchsine and fluorecein-gelatin films are in good accordance with curve IV in Fig. 3, and results on the other dyes-gelatin films with curve III in Fig. 2 or curve III in Fig. 3, in the range of measuring errors. In the former there may be molecular dichroism in paramagnetic molecules, in the measuring wave length.

Behavior in the Case of Shutting off the Excitation of Light

By shutting off the excitation of light, the value of dichroism returns rapidly to that of mere magnetic dichroism. Its behavior is represented by the following equation, after Eq (25) or (26).

$$D = D_{\infty \cdot ata} [1 + \xi \cdot D_{\infty \cdot para} / D_{\infty \cdot ata} \cdot \exp(-t/\tau')] \quad (27)$$

or

$$D = D_{\infty \cdot ata} [1 + \xi \cdot D_{\infty \cdot para} / D_{\infty \cdot ata} \cdot \exp(-t/\tau') + \xi \cdot D'_{\infty \cdot ata} / D_{\infty \cdot ata} \cdot \exp(-t/\tau')] \quad (28)$$

where τ' is the mean life time of paramagnetic molecules. So, in this effect, relaxation time is equal to the life time of paramagnetic molecules. Experimental results mentioned before are in good accordance with this consideration, in the range of measuring errors.

Quantitative Considerations

It is very difficult to compare theoretical calculations with experimental results, and to get an accurate value of d , the important value for paramagnetic dipole moment. Because in the case of mere magnetic dichroism, G and η were not such suitable values for the materials used.

Summary

The Differences which appeared in the magnetic dichroism-time relations of dye-gelatin films by excitation of light were discussed under assumption of photomagnetism effect. Results obtained are to some extent in good accordance with experimental results qualitatively. The author, however, can not decide that this effect is entirely due to the photomagnetism. It will be valid, to some extent, to regard the effect to be due to photomagnetism.

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Research on Activation Energy. I. A New Empirical Rule for the Calculation of Activation Energy⁽¹⁾

By Kiyoteru OTOZAI

(Received May 8, 1951)

Introduction

Because of the difficulty of calculating in a solely theoretical way the activation energy for any sort of reaction, various kinds of empirical or semi-empirical rules have been proposed for the estimation of that energy. The general feature of the purely empirical rules so far

proposed is the simplicity of their forms. But at the same time they can be applied only to a specified type of reaction. Moreover, none of these empirical rules provide any information on the geometrical configuration of the activated complex. Compared with these purely empirical methods, the so-called semi-empirical method of Eyring has a marked advance. It can be applied not only to any kind of reaction but it also enables us to presume the geometrical configuration and the

(1) Details will be published in Scientific Papers from the Osaka University.

dimensions of the activated complex. But unfortunately the estimation of the constant ρ , which represents a fraction of the Coulombic part in the total energy of the bond, and the knowledge of which is always necessary for the calculation of the activation energy according to this method, is at least at present not quite free from ambiguity. For this reason the author has sought a new empirical method of calculation, which makes use only of the experimentally measurable constants but gives us almost as accurate information as the semi-empirical method on the magnitude of the activation energy and the geometrical dimensions of the activated complex. The method reported here is one such which satisfies the above-mentioned requirements, although the theoretical basis for the calculation is not yet quite clear.

Fundamental Assumption

The distance r^* , which corresponds to the inflexion point on the potential-energy curve or the point, where the attractive force between two atoms becomes maximum, (cf. Fig. 1), is

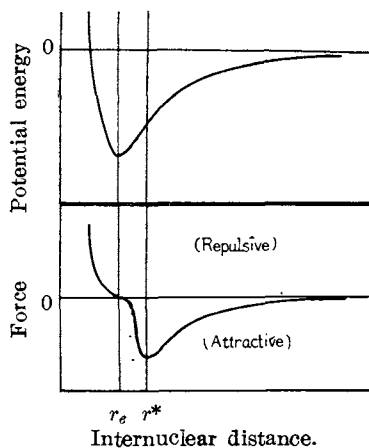
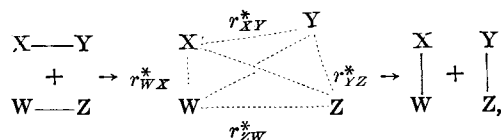


Fig. 1.—The activated internuclear distance.

assumed to represent the length of the bond in an activated complex. This distance r^* will, therefore, be called the activated internuclear distance. Furthermore we will denote the bond, which appears only in an activated complex (see below) an activated bond. Then the present empirical rule can be summarized as follows: among all the possible structures, which can be constructed by the use of the fixed values of the activated internuclear distances of the bonds to be broken as well as to be formed, such a structure, in which the sum of the energies of the activated bonds

becomes minimum, represents the structure of the activated complex and this minimum sum of the energies of the activated bonds gives the activation energy of the reaction, when it proceeds in the exothermic direction. The activation energy of the reaction in the endothermic direction can readily be calculated by the use of the so computed value of the activation energy in the exothermic direction and the heat of the reaction.

Thus, for the tetratomic reaction of the type:



the bonds to be broken are X-Y and W-Z, those to be formed are X-W and Y-Z and the activated bonds, which appear only in an activated complex, are X...Z and Y...W. Hence, according to the present rule, among all the possible structures, which can be constructed by the use of the fixed values of the activated internuclear distances r_{XY}^* , r_{WZ}^* , r_{XZ}^* , and r_{YW}^* , such a structure, in which the sum of the energies of the activated bonds X...Z and Y...W becomes minimum, represents the structure of the activated complex, and this minimum sum of the energies gives the activation energy of the reaction, when it proceeds in the exothermic direction.

Carrying out the Calculation

One of the most important parts of the calculation according to the present rule is the determination of the potential-energy $U(r)$ between two atoms as a function of their internuclear distance. But as the ordinarily used Morse's equation was found not accurate enough for this purpose (see below), we have made use of Rydberg's equation:⁽²⁾

$$U(r) = -D_e \{ \alpha(r - r_e) + 1 \} e^{-\alpha(r - r_e)},$$

in which D_e is the equilibrium dissociation energy, α is the characteristic constant for the given pair of atoms and r_e is the equilibrium internuclear distance. All of these constants can be calculated from the spectroscopic data according to the equations:

$$D_e = D + E_0,$$

(2) R. Rydberg, *Z. Phys.*, **73**, 381 (1932).

$$E_0 = \frac{1}{2} N_{\infty} k \nu = 1.45 \times 10^{-2} \omega_e,$$

$$\alpha = 9.28 \times 10^{-8} \omega_e \sqrt{\mu / D_e},$$

where E_0 represents the zero point energy and μ the reduced mass of the pair of atoms. Furthermore, it can readily be shown from Rydberg's equation that the activated distance r^* , which corresponds to the inflexion point on the potential energy curve, is expressed by the equation:

$$r^* = r_e + 1/\alpha.$$

The activation energies of some triatomic and tetratomic reactions calculated according to the present method are summarized in Tables 1 and 2 respectively, and compared with the experimental values given in the textbook of Glasstone, Laidler and Eyring⁽³⁾ as well as the values calculated by means of the semiempirical method of Eyring, where the energies are all expressed in kcal. units.

Table 1
Activation Energies of Some Triatomic Reactions

No.	Reaction	Observed	Activation energy	
			Calculated	
			i	ii
1	$\text{H} + \text{p-H}_2 \rightarrow \text{o-H}_2 + \text{H} + 0$	7	10.1	7.63 (20%)
2	$\text{H} + \text{I}_2 \rightarrow \text{HI} + \text{I} + 35$	0	0.2	2.5 (10%) 1.8 (14%)
3	$\text{I} + \text{H}_2 \rightarrow \text{IH} + \text{H} - 32$	34.2	41.2	43.3 (10%) 40.4 (14%)
4	$\text{H} + \text{Br}_2 \rightarrow \text{HBr} + \text{Br} + 41$	1.2	0.3	3 (10%) 2.1 (14%)
5	$\text{Br} + \text{H}_2 \rightarrow \text{BrH} + \text{H} - 16$	18	23.2	25.5 (20%)
6	$\text{H} + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl} + 45$	2	0.7	2.7 (14%)
7	$\text{Cl} + \text{H}_2 \rightarrow \text{ClH} + \text{H} - 1$	6	9.0	11.6 (20%)
8	$\text{F} + \text{H}_2 \rightarrow \text{FH} + \text{H} + 45$	8	10.4	10.6 (10%) 6.3 (14%)

i, according to the present method.

ii, according to the semi-empirical method of Eyring, where the number in bracket indicates the value of the constant ρ used for the respective calculation.

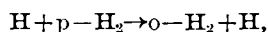
(3) G. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes", McGraw-Hill Company, New York and London, 1941.

Table 2
Activation Energies of Some Tetratomic Reactions

No.	Reaction	Observed	Activation energy	
			Calculated	
			i	ii
1	$\text{H}_2 + \text{H}_2 \rightarrow \text{H}_2 + \text{H}_2 + 0$	> 59	76.4	ca. 90 (10%)
2	$\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI} + 3$	40	38.2	48.3 (14%)
3	$\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr} + 25$	> 43	41.8	45 (10%) 39 (14%) 26.5 (20%)
4	$\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl} + 44$	> 36	51.0	54 (10%) 44.5 (14%) 29.5 (20%)
5	$\text{H}_2 + \text{F}_2 \rightarrow 2\text{HF} + 129$	> 25	92.2	50 (10%)
6	$\text{Br}_2 + \text{Cl}_2 \rightarrow 2\text{BrCl} + 1$	14	11.3	—
7	$\text{D}_2 + \text{HCl} \rightarrow \text{HD} + \text{DCl} + 0$	57	ca. 58	53 (17%) 43.6 (20%)

Discussion of Errors

When the results shown in Table 1 are compared with those in Table 2, it may be seen that the activation energies calculated according to the present method are generally somewhat too high (in the average about 3 kcal.) in comparison with the experimental values for the triatomic reactions (except for the endothermic reactions), while just the reverse is the case for the tetratomic reactions. However, the same tendency can also be seen for the values calculated by means of the semi-empirical method, although in this case the adequate choice of the constant ρ makes this difference somewhat obscure. Just this tendency seems to betray the difficulty in calculating the activation energy for both sorts of reactions by use of a single relation, as it is the case for the other empirical rules. Although the reason for this discrepancy is not yet clear, the following fact may tell us that at least a part of the inaccuracy attached to the present method is due to the lack of accuracy of the Rydberg's equation for large internuclear distances. Thus, for the activation energy of reaction No. 1 in Table 1:



Morse's equation gives 14.6 kcal. and Rydberg's equation gives 10.1 kcal. While from the potential-energy curve directly constructed by the use of the spectroscopic data we obtain 7.5 kcal., which agrees very well with the experimental value 7 kcal.

Geometrical Dimensions of Activated Complex

According to the present method of calculation the total length of the activated complex of the type $X...Y...Z$ is given by the sum of the activated distances r_{XY}^* and r_{YZ}^* , since the form of this sort of complex must be linear. When we compare the values so calculated of $X...Y$, $Y...Z$ and $X...Y...Z$ with those calculated by means of the semi-empirical method of Eyring, we find an interesting result, namely, that the total length of the activated complex calculated according to both methods agree very well whereas the respective distances $X...Y$ and $Y...Z$ in the complex sometimes show remarkable differences between two methods, as is shown in Table 3.

Table 3
Dimensions of Activated Complex of Some Triatomic Reactions

Activated complex $X...Y...Z$	Length of $X...Y$, Å.		Length of $Y...Z$, Å.		Length of complex $X...Y...Z$, Å.	
	i	ii	i	ii	i	ii
H...H...H	1.12	0.75	1.12	1.35	2.24	2.10
H...Br...H	1.80	1.40	1.80	2.10	3.60	3.50
Br...H...H	1.80	1.42	1.12	1.50	2.92	2.92
H...Cl...H	1.65	1.33	1.65	2.10	3.30	3.43
Cl...H...H	1.65	1.30	1.12	1.40	2.77	2.70
H...H...Na	1.12	1.69*	2.55	1.94*	3.67	3.63*
H...H...K	1.12	1.84*	2.99	2.29*	4.11	4.13*

i, the present method. ii, the semi-empirical method.

* S. Shida and K. Nakata, the 2nd meeting of the Chemical Society of Japan, April 2, 1949.

Furthermore, as the constant a in Rydberg's equation does not vary so much from bond to bond and its mean value becomes 2.69 Å.^{-1} , we can roughly put

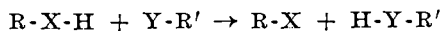
$$r^* = r_e + 1/a \\ = r_e + 0.37 \text{ Å.}$$

So it may be said that the average length of a bond in an activated complex is about 0.37 Å. longer than the equilibrium bond-distance.

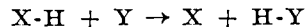
Length of Hydrogen Bond

The present method of calculation gives us some interesting information on the length of the hydrogen bond. If we assume, namely, the hydrogen bond of the type $R-X...H...Y-R'$ as a sort of an activated complex of the

reaction



the length of the activated complex $X...H...Y$ of the reaction



may give at least the lower limit of the distance between X and Y in the above-mentioned hydrogen bond, because the bond energies of the diatomic molecules $X-H$ and $H-Y$ will appreciably be greater than those of $RX-H$ and $H-YR$, so that the activated distances of the former will be shorter than those of the latter. This expectation was found actually the case as shown in Fig. 2, except for $F...H...F$, in which, however, our calculated value 2.38 Å. agrees fairly well with the value 2.32 Å. calculated* by Pauling.⁽⁴⁾

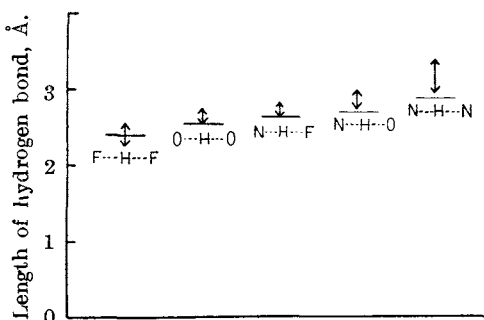
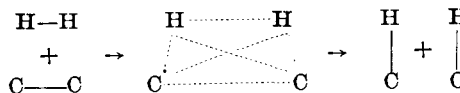


Fig. 2.—Length of the hydrogen bond.

Dissociated Adsorption of Hydrogen on Charcoal

As an example for the application of the present method to the heterogeneous reaction, we may cite the calculation of the activation energy for the dissociated adsorption of hydrogen on the surface of charcoal:



The activation energy calculated by means of the present method as a function of the $\text{C}-\text{C}$ distance is plotted in Fig. 3 and compared with that of Sherman and Eyring,⁽⁵⁾ who

(4) L. Pauling, "The Nature of Chemical Bonds", Cornell University Press, New York, 1940, p. 297.

(5) A. Sherman and H. Eyring, *J. Am. Chem. Soc.*, **54**, 2661 (1932).

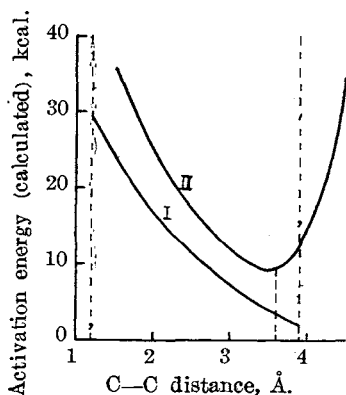


Fig. 3.—Activation energy of the dissociated adsorption of hydrogen on charcoal: I, by the present author; II, by Sherman and Eyring.

calculated the same energy by the use of the semiempirical method of Eyring putting $\rho=10\%$. The most favorable C—C distance for the adsorption, that is the distance, where the activation energy becomes minimum according to the present method, is 3.92 Å. corresponding to the structure of the linear form of the activated complex $C \dots H \dots H \dots C$, while this energy becomes minimum at the distance 3.6 Å. according to the semi-empirical method. But it may be worth while to mention that both curves in Fig. 3 coincide completely if the value of ρ in the calculations according to the semi-empirical method is taken somewhat larger than 10%.

Summary

1. It has been assumed that the bond-distance in an activated complex is equal to the bond-distance corresponding to the inflexion point on the potential-energy curve of the pair of atoms.

2. According to this fundamental assumption, a new simple method of calculation of activation energy of reactions has been devised.

3. The method has been applied to some kinds of triatomic reactions and the double decompositions between two diatomic molecules with satisfactory results.

4. For the triatomic reactions, the geometrical length of the activated complexes computed by means of the present method agrees well with those calculated by means of the semi-empirical method of Eyring.

5. It has been shown that the present method of calculation gives some information on the lower limit of the length of the hydrogen bond.

6. The activation energy for the dissociated adsorption of hydrogen on the surface of charcoal has been calculated as a function of the distance between two carbon atoms. The result obtained agrees well with that obtained by Sherman and Eyring according to the semi-empirical method.

The author wishes to express his sincere thanks to Prof. T. Titani for his interest in this research. The author is also indebted to Dr. T. Horie for his kind information on the spectroscopic data.

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The Electrical Conductivity of the Condensed Polynuclear Aromatic Compounds

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Introduction

In the previous paper,⁽¹⁾ the electrical conductivity of violanthrone, isoviolanthrone and pyranthrone has been reported. These substances belong to the condensed polynuclear

aromatic compound. The electrical conductivity of these substances has been attributed to π -electrons of the conjugated double bonds of network-plane of carbon atoms. The highest limit of this network-plane is graphite, which has the electrical resistivity of $10^{-3} \Omega\text{cm}$. (powdered state). On the other hand, the electrical resistivity of benzene, the lowest limit of these substances, is higher than $10^{18} \Omega\text{cm}$.

(1) H. Akamatsu and H. Inokuchi, *J. Chem. Phys.*, **18**, 810 (1950).

in the solid state. Therefore the electrical conductivity of these compounds in the solid state are closely correlated to the numbers of rings which are contained in the network-planes, and also to the π -electrons of these molecules. From this standpoint, the study has been extended over a series of compounds belonging to this group.

Experimental Procedure

Because the single crystals could not be obtained, eleven samples of this group, described below, were examined in the state of compressed powdered form. For the higher conductive substances, the method has been already described, apparatus-I, which was like that used by Brunner and Hammerschmid for measuring the conductivity of powdered graphite.^{(1),(2),(3)} In this method, the specimen was compressed between the metal end and piston in the polished ebonite cylinder of good quality or ambroide cylinder, and the electrical resistivity was measured by the potential drop method with the aid of direct current amplifier.

For the lower conductive substances, another apparatus was used (Fig. 1: apparatus-II). The specimen was compressed on a cylindrical dish, which was made of brass coated by chromium, by a piston to 80 kg./cm.² with a lever system. This piston was insulated by ambroide (1) (5) and pyrex glass (4). The electrical resistivity observed depends, in the first approximation, on the area of the end of the piston, which is 0.503 cm.². This apparatus has an advantage over the former in regard to the problem of the effects

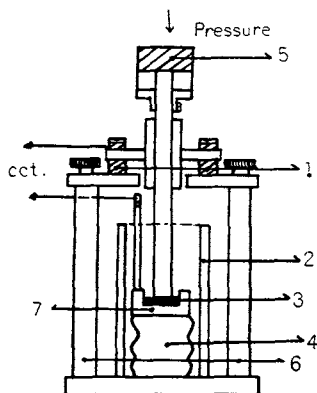


Fig. 1.—Apparatus-II: (1) and (5) ambroide insulated a piston; (2) electrical oven, shielded by copper plate; (3) specimen; (4) pyrex glass; (6) brass; (7) cylindrical dish, coated by chromium.

(2) H. Akamatsu and H. Inokuchi, *J. Chem. Soc. Japan*, **70**, 185 (1949).

(3) J. Brunner and H. Hammerschmid, *Z. Electrochem.*, **40**, 60 (1934).

of the temperature and surface leakage. The surface leakage could be avoided and the temperature could be increased to 300°, because the ebonite cylinder was not used.

In the previous paper,⁽¹⁾ it was found that in each case the constancy of the electrical conductivity of these powdered specimens is obtained when the compressed pressure upon them is over 80 kg./cm.². This fact was supported again in the following manner.

The electrical conductivity of anthanthrene (C₂₂H₁₂; m. p. 257.5°-258°) was measured by the apparatus-II under 80 kg./cm.² pressure. The temperature was increased to 264°, above the melting point of this crystal, and then decreased to the room-temperature. The hysteresis of electrical conductivity upon the increasing and decreasing of temperature was almost negligible (Fig. 2). This fact shows that the contact resistance between the powdered crystals was not affected practically under 80 kg./cm.² or more in pressure. Therefore, the value of electrical conductivity measured by these methods was assumed to be intrinsic.

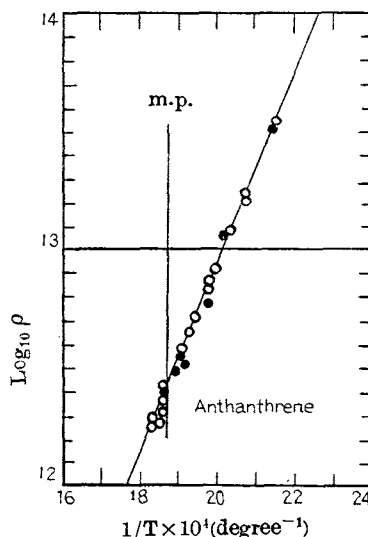
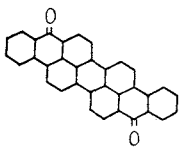
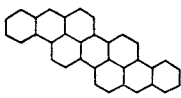
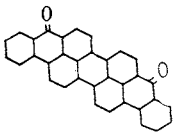
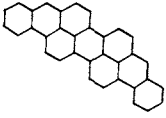
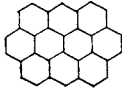
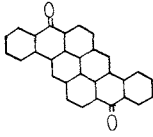
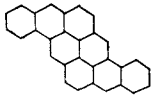
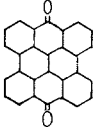
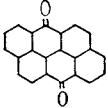
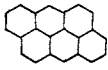


Fig. 2.—The relation between resistivity and temperature for anthanthrene by the apparatus-II: ○ 80 kg./cm.², before melted; ● 80 kg./cm.², after melted.

The samples were purified chemically⁽⁴⁾ and then sublimed in vacuum (10⁻²-10⁻⁵ mm. Hg.) more than two times until the conductivity was constant. The vacuum sublimation is an extremely advantageous method; the impurities—starting substances, by-products and carbonous matters etc.—were completely separated in the manner just like chromatography, and also there was no trace of solvent between crystals at all.

(4) H. Akamatsu and K. Nagamatsu, *J. Colloid Sci.*, **2**, 593 (1947).

Table 1
The Value of ρ_{15} , $\Delta\zeta$ and ρ_0 of the Condensed Polynuclear Aromatic Compounds.

No.	Substance	Structure	ρ_{15} , $\Omega\text{cm.}$	$\Delta\zeta$, e. V.	ρ_0 , $\Omega\text{cm.}$
1	Isoviolanthrone		5.7×10^9	0.75	1.5×10^3
2	Isoviolanthrene		8.4×10^{13}	0.82	6.3×10^6
3	Violanthrone		2.3×10^{10}	0.78	2.9×10^3
4	Violanthrene		2.1×10^{14}	0.85	6.85×10^6
5	Ovalene		2.3×10^{13}	1.13	3.1×10^5
6	Pyranthrone		3.9×10^{13}	1.06	3.7×10^6
7	Pyranthrene		4.5×10^{16}	1.07	2.0×10^7
8	Meso-naphthodianthrone		1.5×10^{16}	1.30	6.0×10^6
9	Meso-naphthodianthrene		4.0×10^{18}	1.2	1.8×10^8
10	Anthanthrone		7.7×10^{16}	1.70	9.7×10^3
11	Anthanthrene		1.5×10^{19}	1.67	3.4×10^4

Results and Discussion

The names and colours of solid specimens used are;

(1) isoviolanthrone (dark green), (2) isoviolanthrene (red), (3) violanthrone (violet), (4) violanthrene (dark red), (5) ovalene (reddish-orange), (6) pyranthrene (orange-red), (7) pyranthrene(brown), (8) meso-naphthodianthrene (greenish-yellow), (9) meso-naphthodianthrene (dark green), (10) anthanthrone (scarlet) and (11) anthanthrene (brownish-yellow). Their molecular structures were illustrated in Table 1.

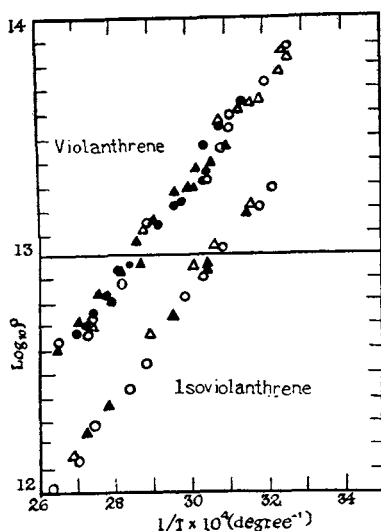


Fig. 3a.—The relation between resistivity and temperature for violanthrene and isoviolanthrene by the apparatus-I: Δ 82.1 kg./cm.², rising temperature; $\blacktriangle$ 82.1 kg./cm.², falling temperature; $\circ$ 119.5 kg./cm.², rising temperature; $\bullet$ 119.5 kg./cm.², falling temperature.

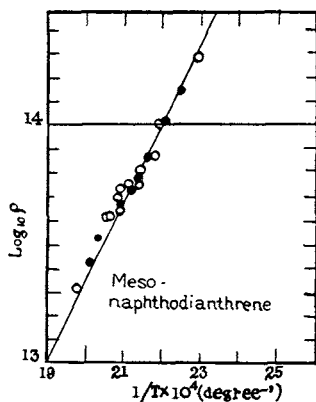


Fig. 3b.—The relation between resistivity and temperature for meso-naphthodianthrene (apparatus-II): $\circ$ 80 kg./cm.², rising temperature; $\bullet$ 80 kg./cm.², falling temperature.

The logarithm of electrical resistivity $\log \rho$ and the reciprocal of temperature $1/T$ have the linear relation as in the case of violanthrone etc.,

$$\rho = \rho_0 \exp (\Delta \epsilon / 2kT). \quad (1)$$

Some examples of this relation are illustrated on Figs. 2 and 3. The value of ρ_0, ρ at 15° (extrapolated value), and $\Delta \epsilon$ are shown in Table 1.

The good reproducibility of electrical resistivity against temperature, non-effect from the moisture and independency of the current upon the time proved the electronic conduction.

We think these substances to be the electronic semi-conductor from the characteristics of Eq. (1), and this assumption is also supported by the fact that violanthrone and violanthrene, for example, have the sensitive photoconductivity which is now under investigation. As these organic compounds are perfect molecular crystals, we cannot consider the possibility of impurity-level such as in the cases of CuS or PbS.

For these reasons they must be intrinsic semi-conductors. In Table 1 it is found that the electrical conductivity is increased together with the numbers of π -electron or the conjugated double bonds in molecule, and $\Delta \epsilon$, corresponding to the energy difference between the empty level and the occupied level of the crystal on the model of semi-conductors, is decreased with the increasing of the numbers of π -electron in the molecule.

To confirm the contribution of π -electron to the electrical conductance, the conductivity of Hydro-violanthrene (yellow), which was made by the strong reduction from violanthrone by the red phosphorus and hydrogen iodide, was measured by the apparatus-II. The numbers of the π -electron of this substance are decreased by the strong reduction illustrated as Fig. 4, and also the mobility of electrons will be restricted in the molecule. The measurement was carried out under 80 kg./cm.² in pressure and heated above 250°, over the melting point of this compound.

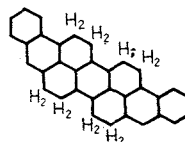


Fig. 4.—The structure of hydro-violanthrene.

Compared with the other compounds, the result of temperature-resistivity relation was

the same, Fig. 5, but the difference of energy band, $\Delta\epsilon$, and extrapolated resistivity to 15° , ρ_{15} , have exceedingly higher value. These results were tabulated on Table 2 with violanthrene and violanthrene. It is shown by this result that the existence of π -electrons in these substances leads to electrical conductance.

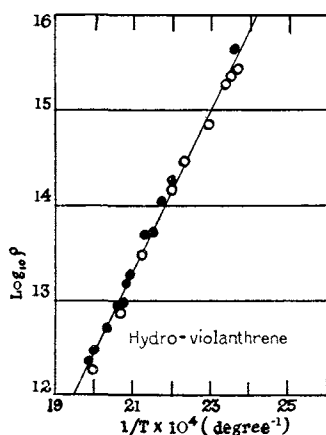


Fig. 5.—The relation between resistivity and temperature for hydro-violanthrene: the same symbols as in Fig. 3b.

Table 2

The Value of ρ_{15} , ρ_0 and $\Delta\epsilon$ of Hydro-violanthrene, Violanthrene and Violanthrene.

	Hydro-violanthrene	Violanthrene	Violanthrene
Colour	yellow	dark red	violet
$\rho_{15}, \Omega\text{cm.}$	1.1×10^{23}	2.1×10^{14}	2.3×10^{10}
$\rho_0, \Omega\text{cm.}$	3.0×10^{-5}	6.85×10^6	2.9×10^3
$\Delta\epsilon, \text{e. V.}$	3.4	0.85	0.78

The quinonoid structures of this group lead to a great increase of electrical conductivity as compared with its hydrocarbons, but the intervals of energy band, $\Delta\epsilon$, have the same value. And in comparison with the magnetic susceptibility of this group, it is interesting

to note that the electrical conductivity was not affected greatly by the shape of the molecule, but by the numbers of π -electron alone.

Summary

The electrical conductivity of the condensed polynuclear aromatic compounds; (1) isoviolanthrene, (2) isoviolanthrene, (3) violanthrene, (4) violanthrene, (5) ovalene, (6) pyranthrene, (7) pyranthrene, (8) meso-naphthodianthrene, (9) meso-naphthodianthrene, (10) anthanthrene and (11) anthanthrene,—has the character of a semi-conductor. The resistivity of these compounds can be expressed as $\rho = \rho_0 \exp(\Delta\epsilon/2kT)$. The value of $\Delta\epsilon$ and ρ at 15° were found as, (1) 0.75 e. V., $5.7 \times 10^9 \Omega\text{cm.}$, (2) 0.82 e. V., $8.4 \times 10^{13} \Omega\text{cm.}$, (3) 0.78 e. V., $2.3 \times 10^{10} \Omega\text{cm.}$, (4) 0.85 e. V., $2.1 \times 10^{14} \Omega\text{cm.}$, (5) 1.13 e. V., $2.3 \times 10^{15} \Omega\text{cm.}$, (6) 1.06 e. V., $3.9 \times 10^{15} \Omega\text{cm.}$, (7) 1.07 e. V., $4.5 \times 10^{16} \Omega\text{cm.}$, (8) 1.30 e. V., $1.5 \times 10^{18} \Omega\text{cm.}$, (9) 1.2 e. V., $4.0 \times 10^{18} \Omega\text{cm.}$, (10) 1.70 e. V., $7.7 \times 10^{18} \Omega\text{cm.}$, (11) 1.67 e. V., $1.5 \times 10^{19} \Omega\text{cm.}$. The good reproducibility and non-hysteresis of the electrical conductivity for temperature suggests electronic conduction. As these organic compounds have a perfect molecular lattice, the possibility of impurity-level cannot be considered. For this reason the mechanism of the conduction is assumed to be that of the intrinsic semi-conductor.

The author expresses hearty thanks to Prof. H. Akamatu for his kind direction in this work and also to Mr. T. Handa who prepared most of the samples of this work, especially the synthesis of ovalene was due to his effort. The cost of this research has been defrayed from the Scientific Research Encouragement Grant from the Ministry of Education to Prof. H. Akamatu, to which the author's thanks are due.

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So-called Silica Content of Natural Waters

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After the work of Dienert and Wandenbulcke⁽¹⁾, many workers have given various analytical methods for the determination of silica in natural waters and have discussed the state of silica. It is probable that various kinds of silicon compounds, such as soluble silica and silicate, colloidal silica, silicates, organic substances (biological materials) containing silicon or silica, etc., exist in natural waters, especially in river waters. Practically, it is very difficult to distinguish these silicon compounds respectively. So we use, for convenience sake, the word silica instead of silicon compounds in this paper.

Silica in natural waters is mainly determined by colorimetric methods, but it is doubtful that the value obtained by the colorimetric method shows the total silica content. It seems that silica obtained by colorimetry is in ionic form and not in colloidal state⁽¹⁾. After the treatment with alkali bicarbonate or carbonate solution, so-called colloidal silica is also considered to produce a yellow color similar to that developed by the compounds in ionic form treated by the same method. On contrary, very small particles of colloidal silicates and quartz, etc., in the waters can not be determined by the colorimetric method, unless these compounds are converted into soluble silicate by fusion with alkali carbonate or hydroxide. (Compare with the suggestive investigations of W. Noll⁽²⁾, F. W. Correns,⁽³⁾ etc.).

On the other hand, A. R. Tourkey⁽⁴⁾ thought that silica obtained by colorimetric method is mainly colloidal. C. J. Roy⁽⁵⁾ stated that in natural waters silica is actually present in the form of acid ions and not in the colloidal state.

We had a doubt concerning these conclusions described above, and have carried out the following experiments to ascertain the real facts.

Experiments

Colloidal Silica in the Mineral Water of Shiroike Hot Spring at Beppu, Oita Prefecture.—The spouting water of Shiroike Hot Spring is colorless and transparent, its temperature is 99°, and the pool water of Shiroike Hot Spring is milky white. Both spouting water and pool water are nearly neutral and the silica contents of these mineral waters show the same value by gravimetric method. The chemical composition of the mineral water of Shiroike Hot Spring is shown in Table 1.

Table 1

	Spouting water		Pool water	
	Sept., 1949	March, 1950	Sept., 1949	March, 1950
Evaporated residue	5.052g./l. 5.045g./l. 5.227g./l. 5.348g./l.			
SiO ₂	0.559	0.572	0.537	0.529
CaO	0.146	0.244	0.154	0.196
MgO	trace	trace	trace	trace
Cl	—	2.383	—	2.539
SO ₄	—	0.235	—	0.263
Alkali halide	3.941	3.642	3.575	3.963
pH	7.6	7.4	7.8	7.4

The value of silica content of pool water obtained by colorimetric method is very small compared with that by gravimetric method. From the results of electrodialysis and gravimetric analysis, we found that the pool water contains a considerable quantity of colloidal silica. In the spouting water immediately after sampling, the silica content obtained by colorimetric method is the same as that obtained by gravimetric method, but after sampling, as time goes on, the value of the silica content obtained by colorimetric method decreases until the constant value is reached (Table 2). We found the same phenomena in sodium silicate solution, and Aoki⁽⁶⁾ found the same fact independently. More detailed reports will be published elsewhere.

(1) F. Dienert and F. Wandenbulcke, *Compt. rend.*, **176**, 1478 (1923).

(2) W. Noll, *Chem. der Erde*, **6**, 1 (1931).

(3) C. W. Correns, *Chem. der Erde*, **13**, 92 (1940); etc.

(4) A. R. Tourkey and D. H. Bangam, *Nature*, **138**, 564 (1936).

(5) C. J. Roy, *Am. Jour. Sci.*, **243**, 393 (1945).

(6) F. Aoki, *J. Chem. Soc. Japan*, **72**, 15 (1951).

Table 2

March, 1950 A		March, 1950 A		Sept., 1949 B		Sept., 1949 C ³⁾		July, 1947 D	
Time ¹⁾	SiO ₂ mg./l. ²⁾	Time	SiO ₂ mg./l. ²⁾	Time	SiO ₂ mg./l. ²⁾	Time	SiO ₂ mg./l. ²⁾	Time	SiO ₂ mg./l. ²⁾
15 min.	640	15 min.	640	5 days	250	0	366	436 days	128
30	455	1 days	145	7	225	15 min.	343	586	114
45	310	2	140	8	193	30	338		
1 hr.	310	3	138	15	130	40	329		
2	242	4	139	19	126	4 hr.	236		
5.5	153	5	133	160	125	26	149		
22	145	6	100						
48	140	10	101						

1) The time measured from sampling.

2) Value obtained colorimetric method.

3) The sample is the aged sample of 5 days from sampling. (Sample B, SiO₂ = 250 mg./l.). Measurements are started after boiling for 3 minutes.

We transferred a 100 cc. spouting water into a platinum dish (the silica content of this spouting water reached the constant value by colorimetry), and added 0.4 g. of sodium bicarbonate in it, and heated it on a boiling water-bath for an hour. We found that the silica content of the aged spouting water treated with sodium bicarbonate found by colorimetry is the same value as that by gravimetric method. Next we tried the electro-dialysis of aged spouting water which showed the constant silica content by colorimetry to ascertain the existence of colloidal silica and could obtain colloidal silica. We used in this case cellophane membrane having the pore size of 2-3 m μ measured with dyes.

Colloidal silica in residual water produced no color with ammonium molybdate by the usual colorimetric method, but after treatment with sodium bicarbonate, the silica content obtained by colorimetry is the same as that by gravimetric method (Table 3).

Table 3

	I	II	III	IV
Spouting water	0.559g./l.	0.130g./l.	0.223g./l.	0.222g./l.
Pool water	0.537	0.116	0.338	0.336

I. Total SiO₂ (With gravimetry).

II. SiO₂ reached constant value (Colorimetry).

III. Residual SiO₂ after dialysis (Gravimetry).

IV. SiO₂ treated with sodium bicarbonate of residual sample after dialysis (Colorimetry).

From these results of experiments, we could show that colloidal silica is actually present in the mineral water of Shiroike Hot Spring and colloidal silica having a larger particle size than about 2-3 m μ can not produce the yellow color by ammonium molybdate in acidic solution. The loss of silica content obtained by colorimetry as time goes on after sampling

is considered to be due to the fact that ionic silica is coagulated and produces colloidal silica.

Various Kinds of Silicon Compounds in River Water and Japanese Standard Sea Water.—In order to ascertain the presence of various kinds of silicon compounds in natural waters, we have carried out experiments according to the following four different methods for the colorimetric determination of silica.

Method 1. (Usual colorimetric method). To 20 cc. of sample solution are added 2 drops of sulfuric acid (1:1) and 0.5 cc. of 10 % ammonium molybdate solution, and the yellow color developed is compared after about ten minutes with that of the standard solution (picric acid and potassium chromate solution). By this method soluble silica and silicate are determined.

Method 2. (Colorimetric method after treatment with sodium bicarbonate). To 50 cc. of sample solution is added 0.2 g. of sodium bicarbonate in a platinum dish, the mixture is heated on a boiling water bath for an hour. Then it is cooled and neutralized with sulfuric acid (1:1) and diluted with water to 50 cc. Colorimetric determination of silica in the solution thus obtained is carried out as the method 1.

Method 3. (Colorimetric determination of silica after treatment with sodium carbonate). In this method, 0.5 g. of sodium carbonate is used instead of sodium bicarbonate. All other procedures are the same as the methods 1 and 2 described above.

By the methods 2 and 3, soluble silica, soluble silicate, so-called colloidal silica, etc. are determined.

Method 4. (Colorimetric determination of silica after carbonate fusion). 20 cc. of sample solution is gently evaporated up to dryness in a platinum crucible, and the residue is covered with about 1 g. of anhydrous sodium carbonate, and then the crucible is heated over a small flame, and the mixture is fused for a further 10 minutes. The crucible is allowed to cool down. After the

crucible has cooled down completely it is filled with water to 2/3 of its height and its bottom is gently heated. The melted substance is treated with water, and then the pH-value of the solution thus obtained is adjusted to about 1.4 by means of diluted sulfuric acid (1:1) and 1 cc. of 10 % solution of ammonium molybdate is added. The colorimetric method after this treatment is the same as the usual method. By this method, all silicon compounds are determined.

By these analytical methods we can distinguish various silicon compounds in natural waters from each other. For example, the silica content of the water of Tamagawa river, flowing into the Bay of Tokyo, is shown in Tables 4 and 5. Silica content in Table 4 was determined by gravimetric method and in Table 5 by colorimetric method described above.

Table 4

	mg./l.
Evaporated residue (110°C.)	155
Si	41.4
Al	5.8
Fe	0.18
Ca	15.6
Mg	1.8
Na	6.6
K	0.8
Mn	0.032
Cl	12
pH	6.4

Table 5

Silicon Content of the River Water of Tamagawa

Date	Method 1	Method 2	Method 3	Method 4
	mg./l.	mg./l.	mg./l.	mg./l.
9, August	20.0	—	—	—
10, "	20.0	21.4	—	44.5
11, "	19.5	20.5	20.3	—
13, "	18.5	20.7	20.9	35.4
14, "	15.8	—	20.2	24.3

As seen in Tables 4 and 5, as time goes on after sampling, the silica content of river water in the sample bottles decreases owing to deposition of dispersed particles in the waters.

As seen in Table 5, the silica content obtained by method 1 is the smallest and that by method 4 is the greatest among them. The silica content obtained by method 2 is almost the same as that by method 3.

From these results we concluded that there are various kinds of silicon compounds in the water of Tamagawa river in addition to the soluble silica and silicates.

In Table 6, similar results obtained on Japanese standard sea water are shown.

Table 6

Silicon Content of the Japanese Standard Sea Water

	Method 1	Method 2	Method 3	Method 4
	mg./l.	mg./l.		mg./l.
Sample No. 1	4.1	4.5	—	—
Sample No. 2	4.0	—	—	6.8

As seen in Table 6, these values are too high compared with that of J. Robinson's and Wattenberg's values. In the other experiments of sea water, however, the silica content of sea water at, for example, Fukuoka, or Enoshima is lower than that described above.

We also observed that the yellow color of the sea water at Hakozaki, Fukuoka City, produced by ammonium molybdate after treatment with sodium bicarbonate is remarkably deeper than that developed by method 1.

The silica content of the sea water containing cultivated diatom is measured by the methods described above, and the results obtained are shown in Table 7.

The silica content of the sea water containing cultivated diatom is 20.7 mg. SiO₂/l. by gravimetric method, and the same value was obtained by method 4. As seen in Table 7, most of the silica in this sample does not produce yellow color by method 1. The silica content of sample 1, obtained by method 2 is greater than that given by method 1, but less than that by method 4. However, in the cases of samples 2 and 3 which are diluted to double volume with distilled water before treatment, there is no difference between the value obtained by method 2 and that by method 4.

Table 7

	Method 1	Method 2	Method 3	Method 4
	mg./l.	mg./l.		mg./l.
Sample No. 1	<1.0	8.6	—	20.7
Sample No. 2	<1.0	10.6	—	10.6
Sample No. 3	<1.0	10.6	—	11.0

Conclusions

From the results obtained above, we reached the following conclusions.

1. Colloidal silica is actually present in natural waters such as Shiroke Hot Springs, the Tamagawa river, etc.

2. Colloidal silica, which has a diameter larger than 2-3 m μ , does not produce yellow

colour with ammonium molybdate in the acidic solution.

3. As ionic silica is coagulated and produces colloidal silica in natural waters, colorimetry for the determination of silica must be performed immediately after sampling. The silica content of an aged sample by method 1 is frequently remarkably less than that obtained from a fresh sample.

4. As colloidal silica can not be determined by method 1, even if it is present, methods 2, 3, and 4 must be used for the determination of silica content.

5. Various kinds of silicon compounds are actually present in natural waters, such as the Tamagawa river, etc.

6. In many cases, the total silica contents of natural waters are obtained by methods 2,

and 3, but for the determination of the total silicon in natural waters method 4 must be used.

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Physicochemical Properties of the Surface of Aqueous Solutions. II. Foam Stability and Mechanical Properties of Surface

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Introduction

It has been generally accepted that the viscoelastic properties of the surface of a solution has an intimate relation to the various phenomena occurring in them such as the foam or the emulsion formation.⁽¹⁾ In these relations, we have already studied the foam of saponin solution, especially in connection with the surface tension, the membrane effect and the semiquantitative measurement of the surface viscosity of the aqueous solution.^{(2), (3)} In the present paper the results of further experiments on these lines are described.

Apparatus and Method

Up to the present, various methods have been employed for the measurement of the surface vis-

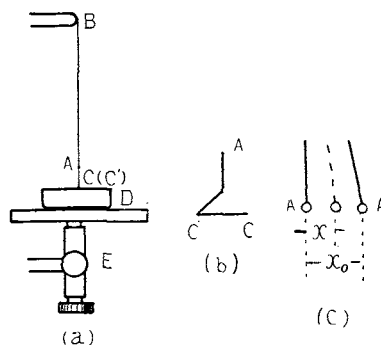


Fig. 1.—Surface viscometer.

cosity.^{(1), (4)} In the present study, however, a new and simple apparatus was employed as shown in Fig. 1a. In this figure AB shows a fine thread of glass with the diameter of 0.02 cm. and the length of 30 cm., of which one end (B) is fused to a firm glass rod support, while a platinum wire with horizontal part CC' of 1 cm. in length as shown in Fig. 1b is fixed to the other end (A). Again in Fig. 1a, D is a shallow glass vessel with the diameter of 6 cm. and the depth of 1.5 cm., in which a solution for measurement is introduced. E is a table, carrying the vessel on it and is able to move vertically by means of a screw.

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(2) T. Sasaki, *This Bulletin*, 15, 449 (1940); T. Sasaki and S. Mitui, *ibid.*, 18, 259 (1943).

(3) H. Kimizuka and T. Sasaki, *Mem. Fac. Sci., Kyūsyū University, Ser. C*, 1, 197 (1950); T. Sasaki, unpublished.

(4) L. Fourt and W. D. Harkins, *J. Phys. Chem.*, 42, 897 (1938); E. R. Washburn and H. R. R. Wakeham, *J. Am. Chem. Soc.*, 60, 1294 (1938); L. Fourt, *J. Phys. Chem.*, 43, 887 (1939).

The measurement of the surface viscosity is carried out as follows. Platinum wire CC' is first forced to shift from the rest position A (in the air), fixed by a suitable device to a certain position A' as shown in Fig. 1c, and the distance between A and A' is measured. Then the surface of solution is carefully forced up until it just touches the platinum wire at A'. After a desired time of aging of the surface, the platinum wire is set free and allowed to return from A' to A under the action of force chiefly exerted by the elasticity of glass thread. Now the successive measurements of the position of platinum wire and accordingly the distance X from A is measured with the time t . When we plot $\ln X$ against t is plotted, and a linear relation can be obtained, as follows;

$$\ln X = \ln X_0 - kt. \quad (1)$$

Differentiating Eq. (1) with respect to time, an equation of the form can be gained:

$$l \frac{dx}{dt} + mx = 0,$$

where

$$k = m/l. \quad (2)$$

Eq. (2) means that the motion of platinum wire is governed by two forces: namely a restoring force mx , proportional to the deflection of glass thread, and a viscous resistance $l \, dx/dt$, proportional to the velocity of platinum wire, mainly exerted by the surface of a solution. Consequently, m is a constant relating to the elasticity of glass thread, and l is a measure of surface viscosity. Since m is known ($m = 2.16 \times 10^{-3}$ dynes/cm.), the relative surface viscosity coefficient l can be calculated according to Eq. (2). It can be noted here, that a lack of a constant term in Eq. (2) is an indication of the absence of surface elasticity. For carrying out the experiment, the initial displacement given to the platinum wire, x_0 , is kept constant to 0.2 cm., and x is measured by means of a comparator to the accuracy of 10^{-3} mm. Whole apparatus is set in a large glass vessel to keep it free from the occasional contamination such as dust.

The surface tension was measured by means of du Noüy's tensiometer and a capillarmeter. The membrane effect was also measured which was expressed by the difference between the apparent surface tension calculated from the capillary rise under the condition of receding and advancing menisci.⁽³⁾

For the measurement of the foam formation, 10 cc. of solution is introduced in a well stoppered test tube of 1.5 cm. in diameter and 17 cm. in length, and is shaken fifty times for ten seconds with an amplitude of 12 cm. After shaking, the height of the foam zone (h) produced just after the stop of shaking and the time (τ) required for the foam to breakdown into half of its initial volume were measured.

Samples used were the commercial one and

were not purified further. Water used for the preparation of the solution is freshly distilled. The experiments were carried out at room temperature.

Results of Experiments

In order to visualize the surface viscosity of a certain solution, a series of experiments was carried out which is shown in Table 1. Accuracy of the value l is ± 0.01 g./sec.

Table 1

Sample	Experimental condition	Time of aging, hr.	Surface viscosity l , g./sec.
Water	Pt wire touching a surface	0	0.00
	"	5	0.00
	Pt wire dipping in water	5	0.00
Saponin solution (0.030 g./l.)	Pt wire touching a surface	5	0.60
	Pt wire dipping in solution	5	0.00

The results of measurements of the surface tension σ , surface viscosity l , foam height h and life of foam τ are shown in Fig. 2 where l and σ are the values referred to a solution surface aged for one hour. In Fig. 2 the ordinate represents the substances under investigation where the numbers in brackets indicate the concentration (in percentage) of solutions employed, and the abscissa, τ , h , σ and l .

The measurements of the surface viscosity, surface tension, height of foam, life of foam and membrane effect were also carried out with the saponin~ethyl alcohol~water system containing a fixed amount of saponin (0.030 g./l.) and varying amount of ethyl alcohol. These values were plotted against the logarithm of concentration in mol./l. of ethyl alcohol as shown in Fig. 3, where the values of the surface viscosity and surface tension are those

Table 2

Effect of Electrolyte on the Life and Height of Foam of Saponin Solution (0.030 g./l.)

Electrolyte	Concentration, N	pH	Surface viscosity l , g./sec.	Life of foam τ , hr.	Height of foam h , cm.
—	0	5.9	0.10	0.5	1.2
HCl	1×10^{-2}	2.0	0.10	0.5	1.2
KCl	5×10^{-1}	5.9	15.0	4.0	1.2
BaCl ₂	5×10^{-4}	5.9	145.	25	1.2
AlCl ₃	3×10^{-5}	3.0	280.	26	1.2
Th(NO ₃) ₄	5×10^{-6}	2.0	350.	28	1.2

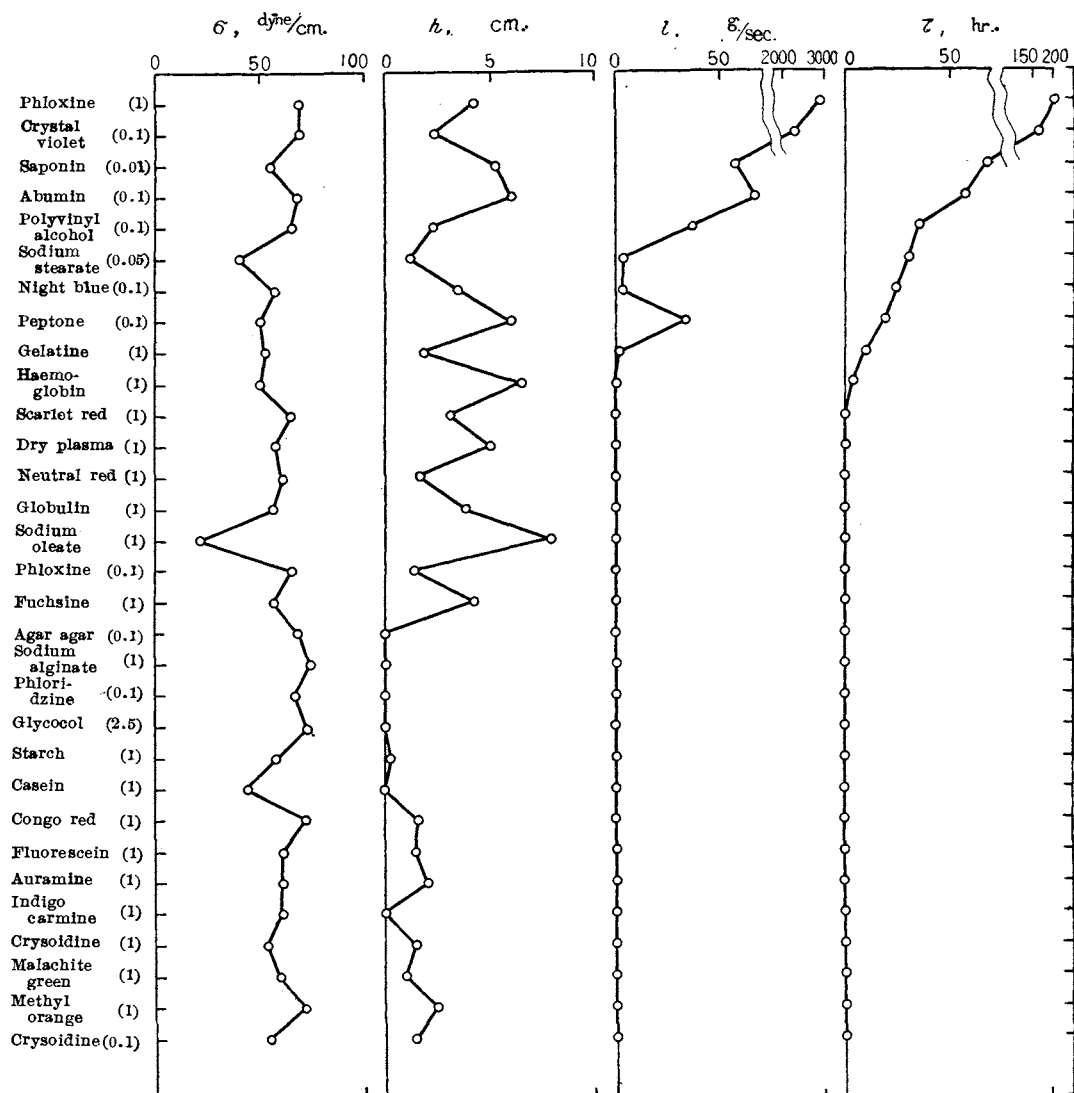


Fig. 2.—Surface tension σ , height of foam h , surface viscosity l and life of foam τ of solutions.

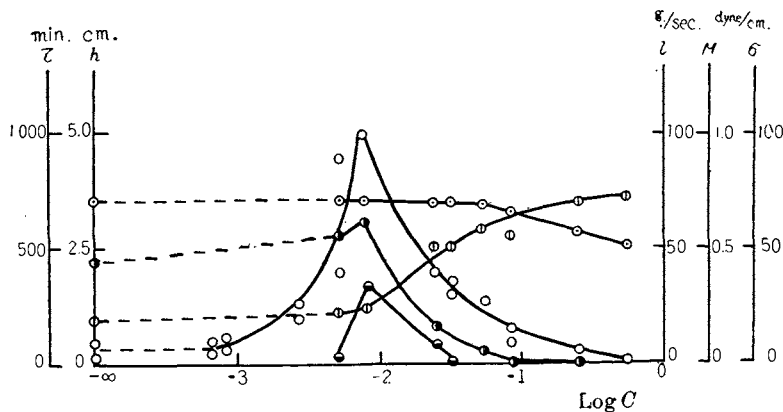


Fig. 3.—Saponin-ethyl alcohol-water system: C ; concentration of ethyl alcohol in mol./l.; $\circ$ life of foam, τ ; $\odot$ height of foam, h ; $\bullet$ surface viscosity, l ; $\odot$ surface tension, σ ; $\bullet$ membrane effect, M .

of the solution surface aged for one hour. The similar measurements were also carried out for the saponin~electrolyte~water systems containing the fixed amount of saponin (0.030 g./l.) and varying amount of electrolyte. The results are tabulated in Table 2. Here pH was controlled by hydrochloric acid.

Discussion

As shown in Table 1, no appreciable amount of viscosity was susceptible by the present device in the surface and interior of distilled water, and also in the interior of many solutions. Consequently, it must be emphasized that the apparent viscosity frequently observed in the surface of aqueous solution is considered to be due to the surface only.

Many investigators have studied the formation of the coherent adsorbed layer in the surface of the aqueous solution. Wilson and Ries⁽⁷⁾ showed qualitatively that the surface plasticity is parallel with the foam stability. Rehbinders⁽⁸⁾ also reported a similar result. It can be seen in Fig. 2 that a close correlation can be found only between the surface viscosity and the life of foam, while no correlation between any other pairs of properties can be found. Wo. Ostwald⁽⁹⁾ pointed out that the solutions of saponin, sodium stearate, night blue, gelatine, albumin and peptone which showed a remarkable membrane effect were capable of producing the extremely stable foam. These circumstances are just the same as in present experiment.

The result of measurements with the saponin~ethyl alcohol~water system is shown in Fig. 3, in which a distinct correlation between the membrane effect, the surface viscosity and the life of the foam can be found, i. e., all these quantities exhibit sharp maxima at the same concentration of alcohol. The surface tension and the foam height, however, do not show a simple correlation to these quantities. Wo. Ostwald⁽⁹⁾ made the measurements of the membrane effect and the foam height, and concluded that no direct correlation could be found between them. As discussed in the preceding paper,⁽³⁾ however, the membrane effect can be interpreted as the measure of mechanical strength of surface layer, so it might well be considered to relate rather to the foam stability than to the foaminess or

foam height as in the present experiment. The formation of such a stable coherent adsorbed layer by the addition of ethyl alcohol is considered to be due to its action of dehydration towards saponin with a subsequent promotion of the saponin adsorption to the surface. At a high concentration of alcohol, however, the life of foam again becomes almost zero resulting perhaps from the preferential adsorption of alcohol in the surface layer with the exclusion of saponin. This may also offer an explanation for the fact that the surface tension and the life of foam decrease rapidly at the same region of the concentration of alcohol.

In Table 2, the effect of electrolytes upon some properties of the aqueous saponin solution is shown. There we can see a marked valency effect of added cation even in high dilution upon the surface viscosity and the life of foam of the saponin solution. Cataphoretic behavior indicates that saponin is a negative colloid,⁽⁷⁾ so that these effects may be explained as the coagulation of the adsorbed layer of saponin by electrolytes, which will be compared with the case of the stabilization of the gelatine foam by the added electrolytes studied by one of the present authors⁽⁸⁾ and also with some other cases of the protein foam.^{(9), (10)} In Table 2, it is also confirmed that the surface viscosity and the foam life are closely related to each other, while the height of foam shows no simple relation to both of them.

Further, the assumption in the preceding paper⁽³⁾ that the membrane effect is not a phenomenon of the hysteresis of wetting, but is the indication of the formation of the coherent adsorbed layer and is therefore a measure of strength of surface film, is in good agreement with the experimental facts shown in Fig. 3. Recently Nakagaki⁽¹¹⁾ accounted for the foam formation of aqueous solutions of alcohols and several electrolytes assuming that the foam stability is closely related to the energy required to remove the unit area of adsorbed layer from the surface of the solution, thereby using the Gibbs' adsorption equation. But the systems studied in our experiment are those in which the surface tension changes irregularly with time, and frequently even an irreversible surface gelation takes place. Therefore Gibbs' adsorption equilibrium cannot be considered to hold in such a case. We should seek for some other factors to arrive at a more

(5) P. A. Rehbinders and A. A. Trapeznikov, *Comptes rends (Doklady) de l'Academie des Sciences de l'U. S. S. R.*, 18, No. 7, 423 (1938); *ibid.*, 427 (1938).

(6) Wo. Ostwald and A. Steiner, *Kolloid-Z.*, 36, 342 (1925); Wo. Ostwald and M. Meisner, *Kolloidchem.-Beih.*, 26, 1 (1926).

(7) R. Ruyssen and R. Loos, *J. Colloid Sci.*, 2, 429 (1947). Present authors also confirmed this.

(8) T. Sasaki, unpublished.

(9) J. M. Perri and F. Hazel, *J. Phys. Colloid Chem.*, 51, 661 (1947).

(10) W. C. Tolman, A. G. Brown and J. W. McBain, *J. Am. Chem. Soc.*, 71, 3129 (1948).

plausible explanation. Burcik⁽¹²⁾ and Matalon⁽¹³⁾ explained the foam formation upon somewhat different viewpoint. Burcik emphasized the importance of the change with the time of the surface tension, and regarded the surface viscosity to be required only in the case of a remarkable foam formation. Our systems are considered to belong rather to the latter case, but a more precise explanation of the mechanism should be made in future.

Summary

1. The surface viscometer, the main part of which consisted of a fine vertical thread of

glass, carrying a horizontal platinum wire at its lower end, was devised for the measurement of the surface viscosity of solutions.

2. The measurements of the surface viscosity as well as some other surface properties of solutions of a number of dyes and saponin were carried out. The effect of coexisting alcohol and inorganic electrolyte for the saponin solution were also examined. The results showed a close correlation between the surface viscosity, the life of foam and so called membrane effect.

The cost of this research was defrayed from the Scientific Research Expenditure of the Department of Education.

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Studies on Monomolecular Films. VI. On the Surface Films of Diphenylsiloxane Polymers

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Introduction

Recently the studies on organosiloxane polymers have become very active and extensive because of their practical importance and structural chemical interests. A great many compounds have been synthesized and their physical and chemical properties have been discussed. As to the surface chemical properties of organosiloxane polymers, the elaborate works have been performed by Hunter *et al.*,⁽¹⁾ Zisman *et al.*,⁽²⁾ and Newing⁽³⁾. They studied the surface tension, spreading and monolayer formation on the surface of water and the built-up film and the lubricating property of silicones, but the substances used in these experiments were chiefly the linear polymers. It is hoped to elucidate the surface chemical properties of the cyclic polymers as well. So it is attempted in the present work to investigate the surface films of the cyclic diphenylsiloxane trimer on water and compare

their properties with those of the linear one.

Experimental

Apparatus.—The film balance used in this experiment is the same as described already.⁽⁴⁾

Material.—Diphenylsiloxane polymers were prepared with the method of Kipping.⁽⁵⁾ That is, diphenyldichlorosilane (B. P. 200–210° at 45mm. Hg), prepared by the Grignard method from pure silicon tetrachloride and monobromobenzene, was hydrolysed with ice water and the resulting white solid was washed repeatedly with chloroform and petroleum ether. Then it was dissolved in the 5% potassium hydroxide solution and neutralized with acetic acid. Diphenylsilandiol thus obtained was recrystallized from acetone solution several times. For the purpose of preparing polymers of diphenylsilandiol the crystal was heated to the temperature above its melting point (132°). The polymers of various molecular structure were obtained by controlling the temperature and the period of heating, but by the suitable choice of the condition the polymers of

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(2) H. W. Fox, P. W. Taylor and W. A. Zisman, *ibid.*, **39**, 1491 (1947).

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(5) F. S. Kipping, *J. Chem. Soc.*, **101**, 2108, 2125 (1912); F. S. Kipping and R. Robinson, *ibid.*, **105**, 484 (1914).

rather simple and definite construction could be obtained. The film experiments were carried out with these simple polymers by spreading from benzene solution on the surface of water. The variety of samples studied are tabulated in Table 1.

Results

In Fig. 1 pressure~area curves of nine samples obtained by the procedure mentioned above are shown. The substrate is fresh distilled water (pH 5.4) and the temperature of experiment is $14-15^\circ$. The numeral in parentheses for the curve in Fig. 1 corresponds to

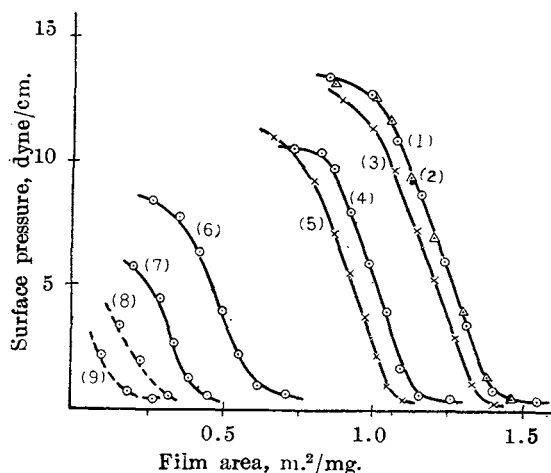


Fig. 1.—Pressure~area relations of surface films of diphenylsiloxane trimers.

that in Table 1. When the polymers of diphenylsilandiol are prepared by heating the monomer above its melting point, the dehydration takes place during the process and, therefore, the weight decreases by the amount

Table 1
Experimental Data of Linear and Cyclic Trimers of Diphenylsilandiol and their Mixtures

No. of sample	Loss of weight, %	Molecular weight	Film area	
			in $m^2/mg.$	in $\text{\AA}^2/molec.$
(1)	5.61	601	1.40	139
(2)	5.73	610	1.40	140
(3)	6.01	618	1.35	138
(4)	6.93	620	1.15	118
(5)	7.02	605	1.09	109
(6)	7.91	681	0.61	69
(7)	8.16	630	0.38	40
(8)	8.47	622	0.30	31
(9)	8.28	590	0.20	20

of water lost. This decrease is shown in Table 1 as a loss of weight (in percentage). The molecular weight of each sample was determined cryoscopically in benzene solution.

The samples (1) and (2) spread well and form the stable monolayers on water but the samples (3) to (7) spread with less easiness and form more and more unstable surface films as the loss of weight increases until at last in the case of samples (8) and (9) a surface film can hardly be obtained and the agglomeration readily occurs resulting in the formation of the three-dimensional crystals. The dotted lines shown in Fig. 1 represent the temporary pressure~area curves obtained by the rapid compression.

Discussion

Kipping reported several linear and two cyclic polymers obtained by the condensation of diphenylsilandiol. When diphenylsilandiol is heated above its melting point, it seems to condense first to the linear polymers and then to the cyclic ones if the chain grows long enough. The final product is, according to Kipping, mainly hexaphenylcyclotrisiloxane. In the present experiment the samples (1) and (2) consist mainly of a linear trimer and (8) and (9) of a cyclic trimer, as are confirmed by comparing the data of weight loss by the dehydration and the molecular weight observed as shown in Table 1 with those expected from the structural formulas shown in Table 2. It seems probable that a linear trimer is readily produced by heating diphenylsilandiol above its melting point for a short period and by further heating it turns to a cyclic trimer by the dehydration between hydroxyl groups at both ends of the chain. Each of the samples (3) to (7) in this experiment is considered to be a mixture of these two compounds. This is also confirmed by the result of the molecular weight determination. Since the molecular weight of the linear trimer and the cyclic one is approximately the same, about 600, the mixture of these two is expected also to have nearly the same molecular weight as above, irrespective of the composition. This is really the case as shown in Table 1. The content of the cyclic trimer in the mixture will become larger as the loss of weight in Table 1 increases.

The monolayer of the linear trimer is very stable and occupies $140 m^2/mg.$ which corresponds to $140 \text{\AA}^2$ per molecule, while the cyclic trimer forms no stable surface films on water, readily forming large aggregates of molecules. This difference should be accounted for from the stereochemical point of view with

Table 2

Comparison of the Observed Data with the Theoretical Ones

	Structural formula	Loss of weight, %		Molecular weight	
		Theor.	Obs.	Theor.	Obs.
Linear trimer	$ \begin{array}{c} \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \\ \quad \quad \\ \text{HO}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{OH} \\ \quad \quad \\ \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \end{array} $	5.56	5.61 (1)	613	601 (1)
			5.73 (2)		610 (2)
Cyclic trimer	$ \begin{array}{c} \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \\ \quad \\ \text{Si} \\ / \quad \backslash \\ \text{O} \quad \text{O} \\ \quad \\ \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \\ \quad \\ \text{Si} \quad \text{Si} \\ \backslash \quad / \\ \text{O} \quad \text{O} \\ \quad \\ \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \end{array} $	8.33	8.47 (8)	594	622 (8)
			8.28 (9)		590 (9)

these two polymers. In the linear trimer, six phenyl groups can be arranged on one side of siloxane chain so that this surface is wholly nonpolar while the opposite surface, consisting of siloxane chain, is polar. That is, the molecule is clearly separated into polar part of siloxane chain and nonpolar part of phenyl groups. This polar-nonpolar character of the linear trimer is essential for it to form a stable monolayer on the surface of water. Here, of course, two hydroxyl groups attached to both ends of the chain will play a role in the film formation by anchoring to the surface of water. On the other hand, in the cyclic trimer the polar siloxane chain is almost completely concealed among six phenyl groups with no anchoring groups appearing on the surface of molecule. This leads to the lack of formation of the stable surface films on water.

The difference in the molecular structure mentioned above can also be confirmed by the experiment on the stabilization of emulsion. Namely, the benzene~water emulsion of a suitable composition was remarkably stabilized by the linear trimer but little by the cyclic trimer. This is interpreted in such a manner that the molecule of the linear trimer which has a decided polar-nonpolar structure plays an important role in stabilizing benzene~water emulsion, while that of the cyclic trimer which lacks such a structure does not. It is natural that the samples (3) to (7), being presumably the mixture of these two compounds, should be intermediate in the surface chemical properties. In fact, as mentioned already, the mixture becomes less and less spreadable as the content of the cyclic trimer increases.

Adam⁽⁶⁾ reported that the area per phenyl group attached to the end of the hydrocarbon

chain is $24 \text{ \AA}^2$. Assuming this value also in the present experiment, six phenyl groups of the diphenylsiloxane trimer should occupy the area of $144 \text{ \AA}^2$, if the area of each phenyl group takes part in the area of the molecule as a whole. This is very close to the molecular area ($140 \text{ \AA}^2$) of the linear trimer obtained in this experiment. Therefore it is allowed to assume that six phenyl groups are packed compactly in the film, rendering the upper film surface completely hydrophobic. This also explains the remarkably water repellent nature of the silicon film as pointed out by many workers⁽⁷⁾. On the other hand in the cyclic trimer, the molecular area should not be less than $72 \text{ \AA}^2$, the area of three phenyl groups, no matter how the molecule may orient itself. The reason is that, since the siloxane ring in the cyclic trimer has been confirmed to be planar⁽⁸⁾, two phenyl groups attached to every silicon atom may overlap when projected on a horizontal plane if the molecule is oriented in such a way that the plane of the siloxane ring is horizontal, and it is impossible for the molecule to be oriented in any other way to occupy the area smaller than this. The molecular area of the cyclic trimer observed in this experiment is far smaller than this, *i. e.*, $20 \text{ \AA}^2$, showing again that the molecule is not arranged in a monomolecular way, but forms large aggregates owing to its lack of polar-nonpolar balance.

Summary

The surface films of diphenylsiloxane polymers obtained by heating the monomer above its melting point were formed on the surface

(6) N. K. Adam, *Proc. Roy. Soc., A* 103, 676 (1923); N. K. Adam, W. A. Berry and H. A. Turner, *ibid.*, 117, 532 (1928).

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of water and their properties were discussed in connection with their molecular structure. The linear trimer formed a very stable monolayer on water and its molecular area was approximately equal to the area of six phenyl groups, while the cyclic trimer formed no surface film, readily aggregating into three-dimensional crystals. This difference was explained by the difference in molecular structure; the former has a decided polar-nonpolar structure, while the latter lacks such a structure. This was

also confirmed by the experiment on emulsion stabilization.

In conclusion, the author wishes to express his sincere thanks to Prof. Tunetaka Sasaki for his guidance and encouragement given to the author during this experiment.

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The Etched and Corroded Surfaces of Iron Single Crystal as Revealed by Means of Electron Microscopy and Diffraction

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The electron microscopic observation of the etched surface of iron single crystal made it possible to assign the crystallographic axes of iron single crystal. The corrosion of iron was here investigated with an iron single crystal thus oriented. The most inactive surface plane of ferritic crystals was the $\{110\}$ plane consisting of the closest packed atoms. The Fe_3O_4 crystals formed on the etched surface of iron single crystal were oriented by microscopy and diffraction. It was explained atomistically through the results obtained that the Fe_3O_4 formed on Fe substrate might protect the substrate from corrosion.

Experimental

The single crystal used in the present study was a piece of wire (diameter: 2 mm., length: 10 mm.). This specimen was etched with an etching solution (ethanol-bromine 10:1 by vol.) for 10-30 seconds. Many etching grooves running parallel to each other were recognized by the naked eye on the side face of specimen. The oxide replica of this side face was prepared by the procedures described in the previous paper⁽¹⁾, and it was stripped from the substrate by Mahla-Nielsen's method⁽²⁾. The electron micrograph obtained is shown in Fig. 1, in which there are octahedral crystals (size: 50-300 $\text{m}\mu$) oriented parallel to each other. All octahedrons found in Fig. 1 are inclined by 22° regarding the $\{001\}$ planes to the replica

film, as is illustrated in Fig. 2. The $\{111\}$ planes of these octahedrons are inclined by 32° to the replica film (*vid.* Fig. 2). The other octahedral planes $\{\bar{1}11\}$, $\{1\bar{1}1\}$ and $\{\bar{1}\bar{1}1\}$ planes are inclined by 56° , 56° and 70° to the replica film respectively. These inclination angles are larger than 32° . (The inclination angles given here are not strict, but within the limits of error $\pm 5^\circ$.)

The electron beam running parallel to the etching grooves of specimen gave a diffraction pattern of Fig. 3. Fig. 3 verifies the existence of α -iron single crystal, whose $\{001\}$ planes are inclined by 29° to the macroscopic surface of specimen given by shadow edge in diffraction pattern. This fact is in accordance with the results obtained in microscopy ($29^\circ \approx 22^\circ$). It is concluded in this way that the etched face of iron single crystal was composed of the $\{111\}$ and its equivalent planes, as is shown in Fig. 2.

The electron beam running vertical to the replica film of Fig. 1 gave a diffraction pattern of Fig. 4, which verified the existence of oriented Fe_3O_4 crystals. It was comprehended through Fig. 4 that the incident beam was parallel to one of the principal axes of Fe_3O_4 crystal. When c-axis of Fe_3O_4 crystal was selected as this principal axis, the $\{102\}$ plane of Fe_3O_4 was approximately parallel to the $\{111\}$ plane of Fe substrate; because the angle between the $\{102\}$ and the $\{001\}$ planes of Fe_3O_4 was 27° , and that between the $\{111\}$ planes of Fe and the replica film (*vid.* Fig. 2) was 32° , i. e., $27^\circ \approx 32^\circ$ (*vid.* Fig. 5a). The equivalent planes of $\{111\}$ shown in Fig. 2 were so steep inclined by 56° and 70° to the replica plane or macroscopic plane of specimen, that these planes were opaque for electrons (*vid.* Fig. 1). Therefore, the diffraction pattern of Fig. 4 had to be given only by the replica part of the $\{111\}$ faces of Fe

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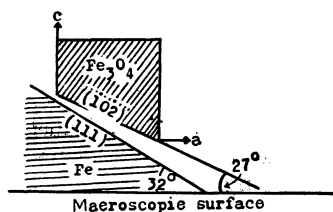


Fig. 5a.

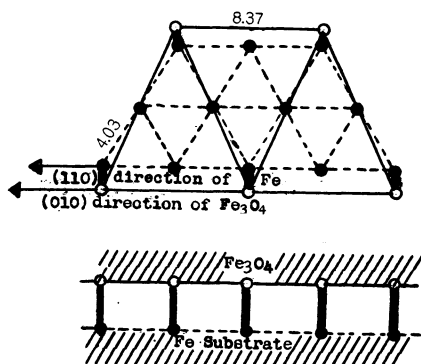


Fig. 5b.

substrate inclined by 32° to the macroscopic face of specimen. The relation between the (102) plane of Fe_3O_4 and the (111) plane of Fe substrate is shown atomistically in Fig. 5b by taking into consideration the etching grooves directed in Figs. 1, 2, 3 and 4. (The (010) direction of Fe_3O_4 was parallel to the (110) direction of Fe substrate, because the etching grooves were parallel to the (010) direction to Fe_3O_4 and to the (110) one of Fe.)

Discussion

Activity of Metal Faces.—According to the previous report of the present author⁽³⁾, the corrosion rate of metal crystals depended on the activities of boundary lattice planes of crystals. So far as the cubic face-centred metal crystals were concerned, the (111) planes, which consist of the closest packed atoms, was most inert among the lattice planes. The (110) plane with coarse atom density was most active among the principal planes. In the cubic body-centred metal crystals there was a relation between the activities and the indices of lattice planes, which was quite similar to the case of cubic face-centred metal.

The (110) faces of cubic body-centred metal, whose atomic density is largest among the lattice planes, was most inert among the surface lattices of this metal. The etched surface of Fe-Cr alloy (Cr: 13%) was composed of the

dodecahedral (110) and its equivalent planes (*vid.* Fig. 6)⁽⁴⁾, so that it was considerably corrosion-resisting. (The specimen of Fig. 6 was a rolled plate. Etchant: methanol-bromine, 100:1 by vol.) On the contrary, iron single crystal composed of the (111) and its equivalent planes, which were shown in Fig. 1, became much more rapidly in the air at room temperature than Fe-Cr alloy of Fig. 6.

According to the theory of ionization series, Cr is by no means more inactive than Fe. Nevertheless, Fe-Cr alloy is more corrosion-resisting than pure Fe. This is due to the fact that there are the dodecahedral planes of cubic body-centred crystal on the substrate surface. The Cr in Fe-Cr alloy gives rise to the (110) planes on the etched surface of ferritic crystal.

Nature of Protective Film.—It was reported by Nelson that the $(\sqrt{2}/10)$ direction of Fe_3O_4 formed on iron was parallel to the (111) direction of substrate⁽⁵⁾. The results obtained in the present study did not agree with those of Nelson.

The (102) plane of Fe_3O_4 is composed of Fe^{++} only. It is possible that these Fe^{++} ions and the Fe atoms of α -iron combine chemically with each other by exchanging their valency electrons. In consequence of this, the Fe_3O_4 crystals can adhere solid to the metal substrate. Metal substrate is protected from further corrosion by being masked with the corrosion products, especially when the corrosion products are not only stable, but also adhere to the substrate under the given conditions. One of the Fe^{++} - Fe^{++} distances in the (102) plane of Fe_3O_4 is 8.37 Å. and the Fe-Fe distance in the (111) plane of iron is 4.03 Å. $8.37 \approx 4.03 \times 2$. It is, therefore, plausible to give a boundary structure between oxide and metal, as is shown in Fig. 5b. The experimental results on the corrosion products of metals and alloys might be referred to the previous papers of the present author⁽⁶⁾.

Steps of Corrosion.—The corrosion of metals should be divided into the following two steps: In the first step of corrosion the rate depends on the indices of surface lattices, *i. e.*, here this is determined by the activities of the surface lattice planes. (The rate will be expressed in a form of $e^{-E/kT}$ in this case.) In the second step of corrosion the rate depends on the properties of the corrosion products

(4) The angles measured in a (110) plane in Fig. 6 coincided approximately with those of a geometrically exact dodecahedron.

(5) H. R. Nelson, *J. Chem. Phys.*, **5**, 252 (1937).

(6) S. Yamaguchi, *This Bulletin*, **18**, 53 (1943); S. Yamaguchi, T. Nakayama and T. Katsural, *J. Electrochem. Soc.*, **95**, 21 (1949).

(3) S. Yamaguchi, *This Bulletin*, **24**, 122 (1951).

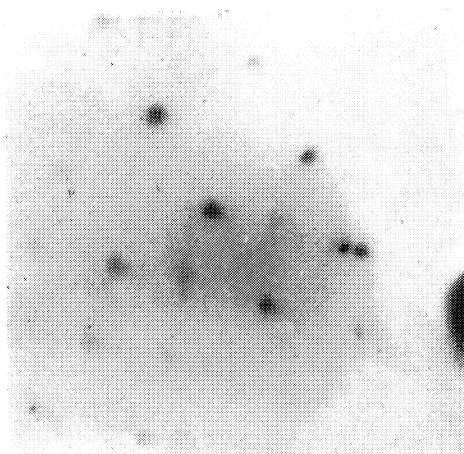


Fig. 3.

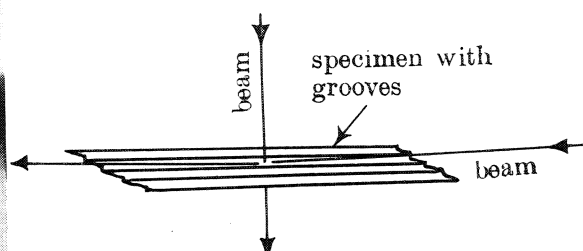


Fig. 1.

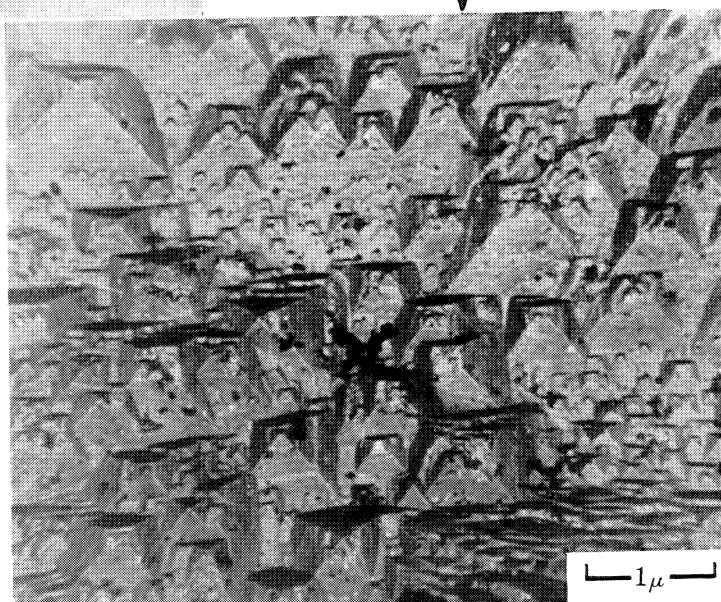
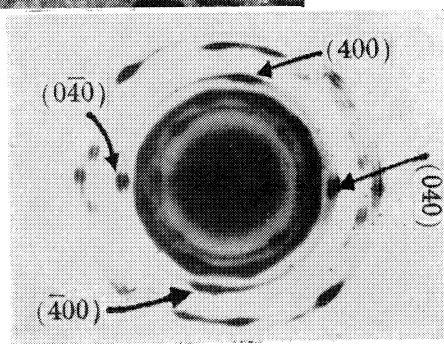


Fig. 4.



- Fig. 1.—A magnified image of oxide replica formed on the etched surface of iron single crystal.
- Fig. 3.—A reflection pattern obtained with the beam running parallel to the etching grooves of specimen.
- Fig. 4.—A diffraction pattern obtained with the beam running perpendicular to the replica film of Fig. 1.

[To face page 238.

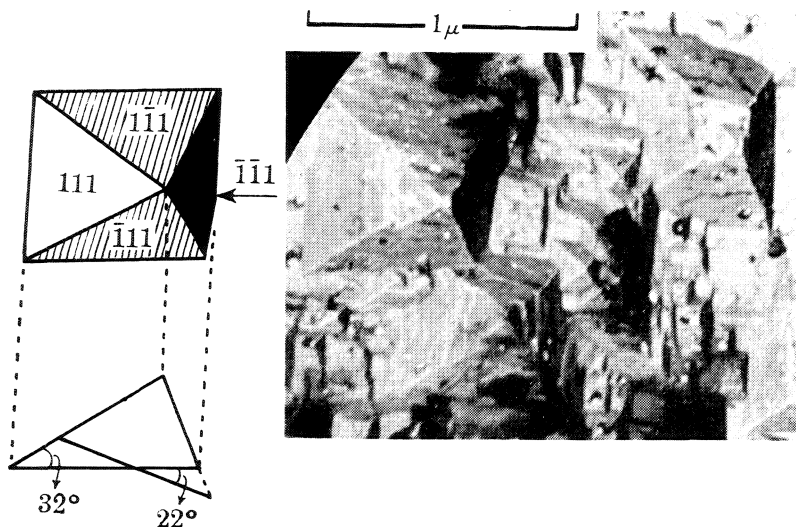


Fig. 2.—The etched surface of iron single crystal: the inclination angle between the (001) plane of octahedron and the replica film is shown schematically.

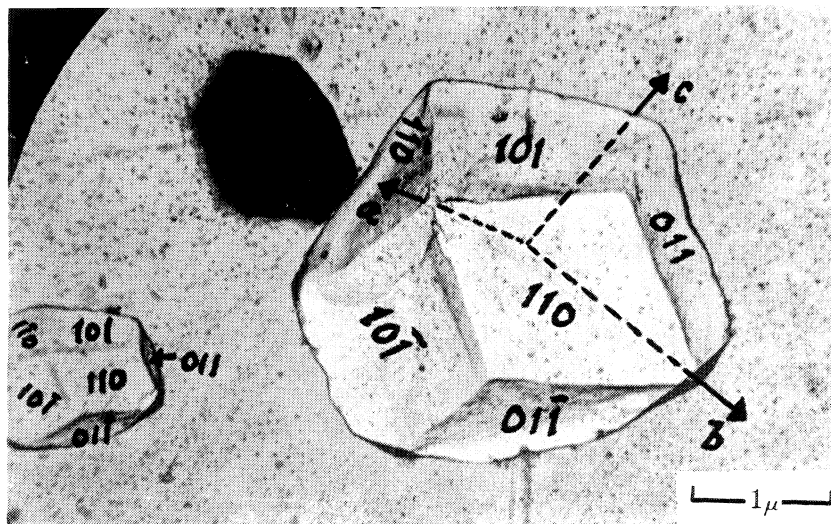


Fig. 6.—The etched surface of ferritic Fe-Cr alloy composed of the dodecahedral (110) and its equivalent planes.

formed over the metal surface. When the corrosion products on metals are exfoliated from the substrate ("erosion"), the corrosion of the first step takes place again. The dissolution of sodium in water is the typical corrosion, in which the first step is held until the end of corrosion. The formation of passive state, which is realizable on iron in nitric acid, is the typical corrosion of the second step.

Summary

1. It has been demonstrated in the present study that the single crystal of pure iron can be oriented by means of electron microscopy and diffraction in order to cut the single crystal along the desired planes. The single crystal of iron was oriented hitherto only by x-ray and optically⁽⁷⁾.

2. The (110) faces of the cubic body-centred ferritic alloys was most inert among their surface lattices. Chromium in 13 Cr stainless steel should be added to iron in order to give rise to the inert (110) planes on the substrate surface.

3. The etched surface of iron single crystal was composed of the (111) and its equivalent planes. The (102) planes of Fe_3O_4 crystals formed on this surface were parallel to the (111) planes of substrate. And the (010) direction of the former was parallel to the (110) direction of the latter. This fact signified that the (102) planes composed of Fe^{++} might be soldered to the (111) planes of iron by exchanging of residual valency electrons. As a matter of fact, the Fe_3O_4 film formed on iron under the given conditions serves as protective coating for substrate.

4. The corrosion of metals depends either on the activities of surface lattice planes of metals or on the properties of the corrosion products formed on surfaces.

I desire to thank Prof. N. Kameyama, Prof. I. Iitaka and Prof. S. Mizushima, who have always given the author encouragement in carrying out this study.

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(7) J. G. Walker, H. J. Williams and R. M. Bozorth,
Rev. Sci. Instr., **20**, 947 (1949).

Synthetic Studies on Thiothreonines. II

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Several investigations that have been carried out recently in our laboratory were motivated by a desire to study the method for the preparation of certain thiothreonine derivatives via threonines. In a previous paper⁽¹⁾, it was shown that ethyl DL- α -benzamido- β -chlorobutyrate, m. p. 84.5-86.5°, was obtained from DL-threonine, when the methyl ester of the latter was chlorinated with phosphorus pentachloride in acetyl chloride, hydrolyzed, benzoylated and finally esterified with ethanol. On the other hand, from DL-allothreonine another diastereoisomer of ethyl DL-benzamido- β -chlorobutyrate, m. p. 99-100°, was obtained by an analogous process. Recently D. F.

Filliot⁽²⁾ reported on the formation of these substances from ethyl α -benzamido- β -hydroxybutyrate. The present study⁽³⁾ deals with the chlorination of DL-N-benzoylallothreonine ethyl ester and the formation of thiothreonine derivatives.

Chlorination of DL-N-benzoylallothreonine ethyl ester with thionyl chloride in benzene in the presence of pyridine afforded the lower-melting isomer of ethyl DL- α -benzamido- β -chlorobutyrate in a yield of 57%, while on the contrary, chlorination with phosphorus pentachloride in chloroform afforded the higher-melting isomer. Thus we found⁽⁴⁾ that

(1) M. Kinoshita and S. Umezawa, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **72**, 382 (1951).

(2) D. F. Elliott, *J. Chem. Soc.*, **1949**, 589-594.

(3) The present paper was read by one of the authors (M. K.) at the 4th Annual Meeting of the Chemical Society of Japan in Tokyo held on April 6, 1951.

one of the two diastereoisomers of ethyl DL- α -benzamido- β -chlorobutyrate was obtained depending on the experimental conditions, apparently one of these chlorinating agents causing the Walden inversion.

Replacement of the chlorine atom of the two diastereoisomers of ethyl DL- α -benzamido- β -chlorobutyrate by the sulfhydryl group could be accomplished by the action of benzyl mercaptan. We found that the reaction of the two isomers of ethyl DL- α -benzamido- β -chlorobutyrate with benzyl mercaptan in absolute ethanol in the presence of sodium ethylate gave a separable mixture of the two isomers of α -benzamido- β -benzylmercaptobutyric acid. The benzene-soluble isomer melted at 136-141° and gave β -phenylethylamine salt, m. p. 166-168°, which afforded a pure free acid, melting at 145-147°, namely, N-benzoyl-S-benzylthiothreonine A. The benzene-insoluble isomer melted at 181-185° and this corresponded to the N-benzoyl-S-benzylthiothreonine B. These preparations showed no mixed melting point depression with the specimens prepared by the azlactone synthesis as reported by Carter *et al.*⁽⁴⁾. The replacement reaction under the above conditions caused apparently some inversion. In contrast, a single racemic thiothreonine derivative was obtained when the reaction was carried out in such a non-polar or less polar solvent as benzene or ether. The reaction of benzyl mercaptan with the two isomers of ethyl α -benzamido- β -chlorobutyrate in benzene or ether led to the same N-benzoyl-S-benzylthiothreonine A as the sole product isolated. From the two isomers of α -benzamido- β -benzylmercaptobutyric acid were obtained thiothreonine A and B as Carter has described already.

Experimental

DL-N-Benzoylallothreonine Ethyl Ester.—A suspension of DL-N-benzoylallothreonine (5 g., m. p. 176°) in a solution of absolute ethyl alcohol (100 cc.) and conc. sulfuric acid (0.76 cc.) was refluxed for 3 hours. After the addition of water (0.7 cc.) solid sodium bicarbonate was added until the mixture became neutral to Congo red. The filtered solution was concentrated to a syrup under reduced pressure, and the residue was taken up in benzene. The benzene extract was concentrated again to a viscous oil. The crude ethyl ester of DL-N-benzoylallothreonine was dissolved in a small amount of dry benzene, and petroleum ether was added to this solution. The separated oil solidified after standing for several hours,

yielding crude ester (5.4 g.). The recrystallization of the crude material from benzene-petroleum-ether yielded colourless needles, m. p. 84-86° (2.7 g.). Recrystallization twice from benzene raised the melting point up to 87-89.3°. By further repetition of recrystallization the melting point could not be raised further, elementary analysis showing a fair coincidence with the theoretical value (Found: N, 5.54. Calculated for $C_{13}H_{17}O_4N$: N, 5.58 %). J. Attemburrow *et al.*⁽⁵⁾ have described this substance as having a higher melting point of 98.5-101.5°.

Ethyl α -Benzamido- β -chlorobutyrate. (i) Chlorination of N-benzoyl-DL-allothreonine ethyl ester with thionyl chloride.—A solution of dry pyridine (0.49 cc.) and thionyl chloride (0.74 cc.) in dry benzene was added to a suspension of DL-N-benzoylallothreonine (1.7 g.) ethyl ester in dry benzene (11 cc.). The mixture was heated on a boiling water-bath for 20 minutes. After cooling, the mixture was washed with water, dil. hydrochloric acid, a saturated sodium bicarbonate solution in turn, and finally with water. The benzene was removed under reduced pressure. A red-brown crystalline mass (1.3 g.) was obtained. Recrystallization from petroleum ether with charcoal gave colourless plates of ethyl α -benzamido- β -chlorobutyrate, m. p. 84.5-86.5° (1 g., yield 57 %); the mixed melting point with an authentic sample (cf. the previous report⁽⁵⁾) showed no depression.

(ii) Chlorination of DL-N-benzoylallothreonine ethyl ester with phosphorus pentachloride.—Phosphorus pentachloride (0.85 g.) was dissolved in a solution of DL-N-benzoylallothreonine ethyl ester (1 g.) in chloroform (10 cc.) cooled with ice-water. After refluxing several minutes on a water-bath, the mixture was cooled and then washed with water, dil. hydrochloric acid, a sodium bicarbonate solution in turn, and finally with water again. The chloroform was distilled off, leaving a syrup. The syrup was extracted with hot petroleum ether. When the extract was cooled, colourless prisms, m. p. 98-99°, were obtained, and recrystallization from the same solvent gave colourless prisms of ethyl α -benzamido- β -chlorobutyrate, m. p. 99-100°. The melting point was not depressed on admixture with the higher-melting specimen obtained from DL- α -benzamido- β -chlorobutyric acid (cf. the previous report⁽⁵⁾).

α -Benzamido- β -benzylmercaptobutyric Acids. (A) The reaction of the two isomers of ethyl α -benzamido- β -chlorobutyrate with sodium benzyl mercaptide in absolute alcohol.—(i) A solution of benzyl mercaptan (0.19 g.) in a 12 % sodium ethoxide solution (0.86 cc.) was added to a solution of the higher-melting ethyl DL- α -benzamido- β -chlorobutyrate (0.4 g., m. p. 99-100°) in absolute alcohol (0.6 cc.). After heating on a water-bath for 30 minutes, the precipitated sodium chloride

(4) H. E. Carter, C. M. Stevens and L. F. Ney, *J. Biol. Chem.*, **139**, 247-254 (1941).

(5) J. Attemburrow, D. F. Elliott and G. F. Penny, *J. Chem. Soc.*, **1948**, 310-18.

was filtered off, and the alcohol was distilled under reduced pressure. The residue was taken up in ether and evaporated, leaving ethyl α -benzamido- β -benzylmercaptobutyrate as a syrup. The syrup was dissolved in a hot mixture of glacial acetic acid (3.8 cc.), conc. hydrochloric acid (1.1 cc.), and water (2.3 cc.). The solution was refluxed for 50 minutes and allowed to cool overnight. The crystalline precipitate was filtered and washed with 50 % acetic acid and then with water, yielding a mixture of the two isomers of α -benzamido- β -benzylmercaptobutyric acid (230 mg., yield 47 %). The mixture was extracted with two portions of boiling benzene (1.8 cc. and 1 cc.). From the residue was obtained the crude material melting at 176-183° (25 mg.). Recrystallization from benzene-alcohol gave colourless crystals, m. p. 181-185°, not depressed by mixing with the S-benzyl-N-benzoylthiothreonine B obtained by Carter's azlactone method. (Found: N, 3.95. Calculated for $C_{18}H_{19}O_3NS$: N, 4.26 %). The combined benzene extract was cooled and a material melting at 136-141° was obtained (100 mg.). This material was converted into the β -phenylethylamine salt, m. p. 166-8°, by treating with β -phenylethylamine in hot ethyl acetate. By the decomposition of the salt we obtained, colourless plates, m. p. 145-7°, which were not depressed by mixing with S-benzyl-N-benzoyl thiothreonine A obtained by Carter's method (Found: N, 3.95. Calculated for $C_{18}H_{19}O_3NS$: N, 4.26 %).—(ii) The lower-melting ethyl DL- α -benzamido- β -chlorobutyrate (m. p. 84-86°) was treated with benzyl mercaptan in sodium ethoxide under the same conditions as described above, giving crude S-benzyl-N-benzoyl thiothreonine A melting at 136-141° (107 mg.) and S-benzyl-N-benzoyl thiothreonine B melting at 176-183° (20 mg.).

(B) The reaction of the two isomeric ethyl α -benzamido- β -chlorobutyrate with sodium benzylmercaptide in absolute benzene. — (i) Sodium (0.02 g.) in absolute methanol (0.18 cc.) was treated with benzyl mercaptan (0.098 g.) and the solvent was removed *in vacuo*. The white sodium benzylmercaptide was covered with dry benzene, and a solution of ethyl α -benzamido- β -chlorobutyrate (0.2 g., m. p. 99-100°) in dry benzene was added. The mixture was refluxed for 2 hours on a water-bath. The mixture was filtered and the benzene was distilled under reduced pressure. The residue was extracted with ether, and ether evaporated, leaving ethyl α -benzamido- β -benzylmercaptobutyrate as a syrup. The syrup was dissolved in a hot solution of glacial acetic acid (1.87 cc.), conc. hydrochloric acid (0.57 cc.) and water (1.13 cc.). The solution was refluxed for 50 minutes and allowed to cool overnight. The crystalline precipitate was washed with 50 % acetic acid and with water, yielding a crude material melting at 134-141°

(110 mg., 45 %). Almost all portions of this product were soluble in boiling benzene. From the benzene extract crystals melting at 136-141° were obtained (70 mg.), and the melting point was not depressed by mixing with the crude S-benzyl-N-benzoyl thiothreonine A (m. p. 136-141°) described in (A). (ii) The lower-melting ethyl DL- α -benzamido- β -chlorobutyrate (0.2 g., m. p. 84-86°) was treated with sodium benzylmercaptide in dry benzene under the same conditions, and hydrolyzed as described above, giving a crude product melting at 130-136° (65 mg.). S-benzyl-N-benzoyl thiothreonine A melting at 136-141° (41 mg.) was obtained from the benzene-soluble part.

(C) The reaction of ethyl α -benzamido- β -chlorobutyrate with sodium benzylmercaptide in absolute ether. — Sodium benzylmercaptide, which was prepared by the same method as described in (B), was covered with dry ether and an ethereal solution of lower-melting ethyl DL- α -benzamido- β -chlorobutyrate (0.2 g., m. p. 84-86°) was added. The mixture was refluxed in a water-bath at 60° for 15 minutes, and the subsequent treatment was accomplished as mentioned above. A crude product (112 mg.) melting at 128-138° was obtained. From benzene extract, S-benzyl-N-benzoyl thiothreonine A (75 mg.) melting at 136-141° was obtained.

Summary

(1) Chlorination of DL-N-benzoylallothreonine ethyl ester with thionyl chloride in benzene in the presence of pyridine gave the lower-melting isomer of ethyl DL- α -benzamido- β -chlorobutyrate, m. p. 84.5-86.5°, in a yield of 57 %. On the other hand, chlorination with phosphorus pentachloride in chloroform gave the higher-melting isomer, m. p. 99-100°.

(2) Two isomers of α -benzamido- β -benzylmercaptobutyric acid (derivatives of thiothreonine A and B) were synthesised. The chlorine atom of ethyl DL- α -benzamido- β -chlorobutyrate could be replaced by a sulfhydryl group by the action of benzyl mercaptan. A remarkable effect of different solvents on this replacement reaction was described.

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Calculation of the Diamagnetic Anisotropy of Benzene by the Method of Antisymmetric Molecular Orbitals

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Introduction

Cyclic molecules⁽¹⁾ composed of conjugated double bonds, such as aromatic compounds,⁽²⁾ have a remarkable degree of diamagnetic anisotropy in the directions perpendicular to the molecular planes. For instance, the observed value of the anisotropy for benzene is about -54×10^{-6} ergs per gauss per mole⁽³⁾. This phenomenon is generally recognized to be caused by the free migration of the resonating $p\pi$ -electrons along the molecular network under an external magnetic field. The quantum mechanical theories of the effect in aromatic molecules have been worked out by F. London⁽⁴⁾ and by H. Brooks,^{(5), (6)} who calculated the ratio of the anisotropies of the various condensed ring compounds to that of benzene. In London's theory⁽⁴⁾ based on the simple method of molecular orbitals the calculated results are in good agreement with experiments, but his theory neglects the Pauli's exclusion principle and also the correlation effects between electrons. On the other hand H. Brooks⁽⁶⁾ treated anisotropy from the standpoint of the Heitler-London-Pauling-Slater approximation including ionic structures and amended the weakness of London's method, but his results are not better than London's in spite of his great labor. Furthermore both theories can not calculate the absolute value of the anisotropy for benzene.

The present paper is an effort to treat the diamagnetic anisotropy of benzene from the standpoint of the method of antisymmetric molecular orbitals (Goepfert-Mayer and Sklar's method⁽⁷⁾) and to calculate the absolute value of the anisotropy. The G-M-S method has given a satisfactory result in the calculation of the lower excited levels of benzene and

therefore it is interesting to see what results we can get from this method for the present purpose.

The Orbitals

When the magnetic field $\mathbf{H}$ is applied in the direction perpendicular to the plane of benzene molecule, the orbital of the ν -th π -electron in the l -th energy level may be described according to London's method:

$$\phi_l = (6\sigma_l)^{-\frac{1}{2}} \sum_{k=1}^6 e^{\frac{2\pi i}{6}(kl+f)} \times e^{i[\vec{\alpha}(k) \cdot \vec{r}_\nu]} \times U_k(\nu), \quad (1)$$

$$l=0, \pm 1, \pm 2, 3, \quad \phi_l^* = \phi_{-l}^{(8)},$$

where $U_k(\nu)$ is the $2p\pi$ wave function of the k -th carbon atom at $\mathbf{H}=0$ and σ_l the normalization factor ($\sigma_l=1$ in London's paper). Also $\vec{\alpha}(k) = \frac{2\pi e}{\hbar c} \vec{A}(r_k)$, $\vec{A}(r_k)$ ⁽⁹⁾ being the vector potential in the position of the k -th nucleus; $f = \frac{e}{\hbar c} \mathbf{S} \cdot \mathbf{H}$, S being the area of the benzene ring. Here the orbitals ϕ_l are mutually orthogonal and $U_k(\nu)$ assumed to be normalized.

If the treatment for the vector potential is similar to that in London's paper, the normalization factors σ_l are then determined by the relation:

$$\sigma_l = 1 + 2S_1 \cos \frac{2\pi}{6}(l+f) + 2S_2 \cos \frac{2\pi}{6}(2l+f) + (-1)^l S_3, \quad (2)$$

where

$$S_i = \int U_{1(\nu)} \cdot U_{1+i(\nu)} d\tau_\nu$$

(overlap integrals at $\mathbf{H}=0$).

The energy of the molecule is the lowest if the

(1) Cyclooctatetraene C_8H_8 is excepted: see S. Shida and S. Fujii, This Bulletin, **24**, 173 (1951).

(2) K. Lonsdale, *Reports on Progress in Physics*, **4**, 368 (1937).

(3) K. Lonsdale and K. S. Krishnan, *Proc. Roy. Soc. London*, **156 A**, 597 (1937).

(4) F. London, *J. phys.*, **8**, 397 (1937).

(5) H. Brooks, *J. Chem. Phys.*, **9**, 463 (1941).

(6) H. Brooks, *J. Chem. Phys.*, **8**, 939 (1940).

(7) M. Goepfert-Mayer and A. L. Sklar, *J. Chem. Phys.*, **6**, 645 (1938).

(8) ϕ_l^* is the complex conjugate of ϕ_l . $\phi_l^* = \phi_{-l}$ for $\mathbf{H}=0$.

(9) If the direction perpendicular to the molecular plane is chosen to be Z-axis,

$$\vec{A} = (A_x, A_y, A_z) = \left(-\frac{1}{2}yH, \frac{1}{2}xH, 0 \right).$$

orbitals $\phi_0, \phi_1, \phi_{-1}$ contain two electrons each; the perturbation energy caused by the magnetic field is usually very small. Therefore it is not necessary, for the present purpose, to consider the excited levels $l = \pm 2, 3$. Then the eigenfunction of the lowest state in this order of approximation is represented by

$$\psi_0 = \phi_0(1)\phi_0(2)\phi_1(3)\phi_1(4)\phi_{-1}(5)\phi_{-1}(6).$$

Also the total spin function in this state is the product

$$\chi_0 = \alpha(1)\beta(2)\alpha(3)\beta(4)\alpha(5)\beta(6),$$

for the lowest state is experimentally diamagnetic.

The totally antisymmetric eigenfunction for this state is then obtained as follows,

$$\Psi_0 = (6!)^{-1/2} \sum_p (-1)^p \mathbf{P}(\psi_0 \chi_0), \quad (3)$$

where $\mathbf{P}$ is the permutation operator.

The Calculation of Energy in a Magnetic Field

The Hamiltonian for the benzene molecule in the magnetic field may be written^{(4), (7)}:

$$\mathcal{H} = \sum_{\nu} \left\{ \frac{\hbar^2}{8\pi^2 m} \left(\frac{1}{i} \vec{\nabla}_{\nu} + \vec{\alpha}_{\nu} \right)^2 + \sum_k V_{\nu k} \right\} + \sum_{\substack{\nu=1 \\ \mu < \nu}}^6 \frac{e^2}{r_{\nu\mu}}, \quad (4)$$

where $\vec{\alpha}_{\nu} = \frac{2\pi e}{\hbar c} \vec{\mathbf{A}}_{\nu}$, $\vec{\mathbf{A}}_{\nu}$ being the vector potential which acts in the ν -th electron. $V_{\nu k}$ is the potential of the k -th carbon nucleus acting on the ν -th electron and may be represented as follows,

$$V_{\nu k} = \mathbf{H}_{\nu k} - \int \frac{e^2}{r_{\nu\mu}} U_k^2(\mu), \quad (5)$$

where $\mathbf{H}_{\nu k}$ is the potential of the neutral carbon atom. The average value of the Hamiltonian $\mathcal{H}$ in this state is given by

$$E = \int \dots \int \Psi_0^* \mathcal{H} \Psi_0 d\tau_1 d\tau_2 \dots d\tau_6. \quad (6)$$

If we put

$$\left. \begin{aligned} \mathcal{E} &= \int \phi_i^*(\nu) \left\{ \frac{\hbar^2}{8\pi^2 m} \left(\frac{1}{i} \vec{\nabla}_{\nu} + \vec{\alpha}_{\nu} \right)^2 + \sum_k V_{\nu k} \right\} \phi_i(\nu) d\tau_{\nu}, \\ \gamma_{ll'} &= \int \frac{e^2}{r_{\nu\mu}} [\phi_l(\nu) \phi_l^*(\nu)] [\phi_{l'}(\mu) \phi_{l'}^*(\mu)] d\tau_{\nu} d\tau_{\mu}, \\ \delta_{ll'} &= \int \frac{e^2}{r_{\nu\mu}} [\phi_l(\nu) \phi_{l'}^*(\nu)] [\phi_{l'}(\mu) \phi_l^*(\mu)] d\tau_{\nu} d\tau_{\mu}, \end{aligned} \right\} \quad (7)$$

then the total energy in the magnetic field $\mathbf{H}$ is

$$\begin{aligned} E &= (2\mathcal{E}_0 + 2\mathcal{E}_1 + 2\mathcal{E}_{-1}) \\ &+ \int \dots \int \Psi_0^* \left(\sum_{\substack{\nu=1 \\ \mu < \nu}}^6 \frac{e^2}{r_{\nu\mu}} \right) \Psi_0 d\tau_1 d\tau_2 \dots d\tau_6 \\ &= (2\mathcal{E}_0 + 2\mathcal{E}_1 + 2\mathcal{E}_{-1}) + (\gamma_{00} + 4\gamma_{01} + 4\gamma_{0-1} \\ &+ 4\gamma_{1-1} + \gamma_{11} + \gamma_{-1-1} - 2\delta_{01} - 2\delta_{0-1} - 2\delta_{1-1}). \end{aligned} \quad (8)$$

In the expansion of the integrals $\mathcal{E}$, γ , δ in terms of $\mathbf{H}$ and integrals over the atomic eigenfunctions U_k , we must treat the integrals of the form

$$\int \int e^{i[\vec{\alpha}(k) - \vec{\alpha}(l) \cdot \vec{r}_{\nu}]} U_k(\nu) U_l(\nu) \frac{e^2}{r_{\nu\mu}} e^{i[\vec{\alpha}(m) - \vec{\alpha}(n) \cdot \vec{r}_{\mu}]} \times U_m(\mu) U_n(\mu) d\tau_{\nu} d\tau_{\mu}. \quad (9)$$

The rigorous calculations of these integrals are complicated. Therefore, for the first approximation, $\vec{r}_{\nu}$ is replaced by $\frac{1}{2}(\vec{R}_k + \vec{R}_l)$ where the product $U_k(\nu) U_l(\nu)$ has the maximum value, and $\vec{r}_{\mu}$ by $\frac{1}{2}(\vec{R}_m + \vec{R}_n)$ in the similar manner.

Here $\vec{R}_k$, $\vec{R}_l$, $\vec{R}_m$ and $\vec{R}_n$ represent the position vectors of the correspondingly numbered nuclei. This approximation⁽¹⁰⁾ may be adequate, because $e^{i[\vec{\alpha}(k) - \vec{\alpha}(l) \cdot \vec{r}_{\nu}]}$, $e^{i[\vec{\alpha}(m) - \vec{\alpha}(n) \cdot \vec{r}_{\mu}]}$ do not make large changes in the ranges of $\vec{R}_k \sim \vec{R}_l$ and $\vec{R}_m \sim \vec{R}_n$ respectively. Using this approximation, we then obtain

$$\begin{aligned} \gamma_{ll'} &= \frac{1}{6\sigma_l \sigma_{l'}} \left[(A_0 + 2A_1 + 2A_2 + A_3) \right. \\ &+ 2(B_1 + B_2 + B_3) \left\{ \cos \frac{2\pi}{6}(l+f) + \cos \frac{2\pi}{6}(l'+f) \right\} \\ &+ 2(C_1 + 2C_2 + 2C_3 + C_4) \left\{ \cos \frac{2\pi}{6}(l+l'+2f) \right. \\ &\quad \left. + \cos \frac{2\pi}{6}(l-l') \right\} \\ &+ 2(F_1 + 2F_2 + 2F_3 + F_4) \left\{ \cos \frac{2\pi}{6}(2l+f) \right. \\ &\quad \left. + \cos \frac{2\pi}{6}(2l'+f) \right\} \end{aligned}$$

(10) This approximation is analogous to the one used by F. London in the calculation of the resonance integral of π -electron in a magnetic field.

$$\begin{aligned}
& +4\{J_1+J_2+J_3\}\left\{\cos\frac{2\pi}{6}(2l+l'+2f)\right. \\
& +\cos\frac{2\pi}{6}(l+2l'+2f)+\cos\frac{2\pi}{6}(2l-l') \\
& \left. +\cos\frac{2\pi}{6}(2l'-l)\right\}+6\{(-1)^l+(-1)^{l'}\}\cdot D\}, \quad (10)
\end{aligned}$$

$$\begin{aligned}
\delta_{ll'} &= \frac{1}{6\sigma_l \cdot \sigma_{l'}} \left[\left\{ A_0 + 2A_1 \cos\frac{2\pi}{6}(l-l') \right. \right. \\
& \quad \left. \left. + 2A_2 \cos\frac{4\pi}{6}(l-l') + (-1)^{l-l'} A_3 \right\} \right. \\
& + 4B_1 \left\{ \cos\frac{2\pi}{6}(l+f) + \cos\frac{2\pi}{6}(l'+f) \right\} \\
& + 4B_2 \left\{ \cos\frac{2\pi}{6}(2l-l'+f) + \cos\frac{2\pi}{6}(2l'-l+f) \right\} \\
& + 4B_3 \left\{ (-1)^{l-l'} \cos\frac{2\pi}{6}(l+f) \right. \\
& \quad \left. + (-1)^{l'-l} \cos\frac{2\pi}{6}(l'+f) \right\} \\
& + 2 \left\{ C_1 + 2C_2 \cos\frac{2\pi}{6}(l-l') + 2C_3 \cos\frac{4\pi}{6}(l-l') \right. \\
& \quad \left. + (-1)^{l-l'} \cdot C_4 \right\} \left\{ 1 + \cos\frac{2\pi}{6}(l+l'+2f) \right\} \\
& + 4 \{ F_1 + (-1)^{l-l'} F_4 \} \cos\frac{2\pi}{6}(l+l'+f) \\
& + 4 \{ F_2 + (-1)^{l-l'} \cdot F_3 \} \left\{ \cos\frac{2\pi}{6}(2l+f) \right. \\
& \quad \left. + \cos\frac{2\pi}{6}(2l'+f) \right\} \\
& + 4 \{ J_1 + (-1)^{l-l'} \cdot J_3 \} \left\{ \cos\frac{2\pi}{6}(2l'+l+2f) \right. \\
& \quad \left. + \cos\frac{2\pi}{6}(2l+l'+2f) + \cos\frac{2\pi}{6}l + \cos\frac{2\pi}{6}l' \right\} \\
& + 4J_2 \left\{ (-1)^l \cos\frac{4\pi}{6}f + (-1)^{l'} \cos\frac{4\pi}{6}f \right. \\
& \quad \left. + \cos\frac{2\pi}{6}(2l-l') + \cos\frac{2\pi}{6}(2l'-l) \right\} \\
& + D \cdot \{ (-1)^l + (-1)^{l'} \} \cdot \left\{ 1 + 2 \cos\frac{2\pi}{6}(l-l') \right. \\
& \quad \left. + 2 \cos\frac{4\pi}{6}(l-l') + (-1)^{l-l'} \right\} \Big], \quad (11)
\end{aligned}$$

where

$$\begin{aligned}
A_i &= \iint U_1^2(\nu) \frac{e^2}{r_{\nu\mu}} U_{1+i}^2(\mu) d\tau_\nu d\tau_\mu, \\
B_i &= \iint U_1(\nu) U_6(\nu) \frac{e^2}{r_{\nu\mu}} U_i^2(\mu) d\tau_\nu d\tau_\mu, \\
C_i &= \iint U_1(\nu) U_2(\nu) \frac{e^2}{r_{\nu\mu}} U_i(\mu) U_{1+i}(\mu) d\tau_\nu d\tau_\mu,
\end{aligned}$$

$$\begin{aligned}
D^{(11)} &= \iint U_1(\nu) U_4(\nu) \frac{e^2}{r_{\nu\mu}} U_i^2(\mu) d\tau_\nu d\tau_\mu, \\
F_i &= \iint U_1(\nu) U_3(\nu) \frac{e^2}{r_{\nu\mu}} U_{1+i}^2(\mu) d\tau_\nu d\tau_\mu, \\
J_i &= \iint U_1(\nu) U_2(\nu) \frac{e^2}{r_{\nu\mu}} U_i(\mu) U_{2+i}(\mu) d\tau_\nu d\tau_\mu,
\end{aligned} \quad (12)$$

Also, since $e^{i[\vec{\omega}(k) \cdot \vec{r}]} U_k(\nu)$ is taken to be an atomic eigenfunction in the magnetic field $\mathbf{H}$, the relation

$$\begin{aligned}
& \left\{ \frac{\hbar^2}{8\pi^2 m} \left(\frac{1}{i} \vec{\nabla}_\nu + \vec{\alpha}_\nu \right)^2 + V_{\nu k} \right\} e^{i[\vec{\omega}(k) \cdot \vec{r}_\nu]} U_k(\nu) \\
& = W_{2p'} e^{i[\vec{\omega}(k) \cdot \vec{r}_\nu]} U_k(\nu) \quad (13)
\end{aligned}$$

holds, where $W_{2p'}$ is the energy of a $2p$ electron which is in the valence state and in the magnetic field $\mathbf{H}$. Hence ε_l , the energy of the orbital in (1), is expanded in the form

$$\begin{aligned}
\varepsilon_l &= W'_{2p} - \frac{2}{\sigma_l} \left[\left(Q + A_1 + A_2 + \frac{1}{2} A_3 \right) \right. \\
& \quad + (R_1 + 2R'_1 + B_1 + 2B_2 + 2B_3) \cos\frac{2\pi}{6}(l+f) \\
& \quad + (R_2 + R'_2 + F_1 + F_2 + 2F_3 + F_4) \cos\frac{2\pi}{6}(2l+f) \\
& \quad \left. + (-1)^l \cdot \left(2R'_3 + \frac{5}{2} D \right) \right], \quad (14)
\end{aligned}$$

where

$$\begin{aligned}
Q &= - \int \mathbf{H}_\nu U_2^2(\nu) d\tau_\nu, \\
R_i &= - \int \mathbf{H}_\nu U_1(\nu) U_{1+i}(\nu) d\tau_\nu, \\
R'_i &= - \int \mathbf{H}_\nu U_2(\nu) U_{2+i}(\nu) d\tau_\nu.
\end{aligned} \quad (15)$$

The functions U_k used for the numerical calculation of the integrals are $2p\pi$ hydrogen-like functions

$$U(r, \theta, \varphi) = \sqrt{\frac{Z^5}{32\pi}} \cdot r \cdot \sin \theta \cdot \cos \varphi \cdot e^{-\frac{Zr}{2}},$$

where the effective nuclear charge Z is chosen to be 3.18⁽¹²⁾ as usual. The distance between neighboring carbon atoms is 1.39 Å. The numerical values of $A_i, B_i, C_i, D_i, F_i, J_i, R_i, R'_i$, and S_i are collected in Table 1. These adopted

(11) Here D represents D_i , but the values of D_i for all of i are the same.

(12) C. Zener, *Phys. Rev.*, **36**, 51 (1930).

data are selected by U. Mori⁽¹³⁾, who has recalculated the numerical values of the above integrals from Parr-Crawford's⁽¹⁴⁾ and Kotani-Amemiya-Simose's⁽¹⁵⁾ tables and with A. London's approximation method⁽¹⁶⁾.

Table 1

$A_0 = 16.9301$ e.V.	$D = 0.1622$ e.V.
$A_1 = 9.0232$ e.V.	$J_1 = 0.1354$ e.V.
$A_2 = 5.6669$ e.V.	$J_2 = 0.0911$ e.V.
$A_3 = 4.9744$ e.V.	$J_3 = 0.0725$ e.V.
$B_1 = 3.3184$ e.V.	$Q = 0.8542$ e.V.
$B_2 = 1.8681$ e.V.	$R_1 = 1.8880$ e.V.
$B_3 = 1.4227$ e.V.	$R_2 = 0.1080$ e.V.
$C_1 = 0.9516$ e.V.	$R_1' = 0.0387$ e.V.
$C_2 = 0.6769$ e.V.	$R_2' = 0.0318$ e.V.
$C_3 = 0.4357$ e.V.	$R_3' = 0.0316$ e.V.
$C_4 = 0.3831$ e.V.	
$F_1 = 0.5208$ e.V.	$S_1 = 0.2600$
$F_2 = 0.3888$ e.V.	$S_2 = 0.0388$
$F_3 = 0.2790$ e.V.	$S_3 = 0.0179$
$F_4 = 0.2503$ e.V.	

The Calculation of Anisotropy

When the magnetic field $\mathbf{H}$ is applied in the direction parallel to the molecular plane, neither $\gamma_{ll'}$ nor $\delta_{ll'}$ depends on $\mathbf{H}$, and in the expansion of ε_l only the term $W'_{2p'}$ remains unchanged as the function of $\mathbf{H}$, since $f=0$ in this case. Therefore the anisotropy in the direction perpendicular to the molecular plane may be written:

$$\begin{aligned} \Delta\chi_{\perp} = & - \left[\frac{\partial^2}{\partial H^2} (E - E^0) \right]_{H \rightarrow 0} \\ = & - \left[\frac{\partial^2}{\partial H^2} (2\varepsilon_0 + 2\varepsilon_1 + 2\varepsilon_{-1} - 6W'_{2p}) \right]_{H \rightarrow 0} \\ & - \left[\frac{\partial^2}{\partial H^2} \left(\int \int \dots \int \psi_0^* \left(\sum_{\mu < \nu}^6 \frac{e^2}{r_{\nu\mu}} \right) \right. \right. \\ & \quad \left. \left. \times \psi_0 d\tau_1 d\tau_2 \dots d\tau_6 \right) \right]_{H \rightarrow 0}, \quad (16) \end{aligned}$$

where E^0 is E in the case of which $\mathbf{H}$ is

Table 2

	A	B	C
$-\left[\frac{\partial^2}{\partial H^2} (\varepsilon_0 - W'_{2p}) \right]_{H \rightarrow 0}$	$+4.157 \left(\frac{2\pi eS}{6hc} \right)^2$	$-2.092 \left(\frac{2\pi eS}{6hc} \right)^2$	$-2.456 \left(\frac{2\pi eS}{6hc} \right)^2$
$-\left[\frac{\partial^2}{\partial H^2} (\varepsilon_{\pm 1} - W'_{2p}) \right]_{H \rightarrow 0}$	$+8.221$ "	-5.160 "	-5.712 "
$-\left[\frac{\partial^2 r_{00}}{\partial H^2} \right]_{H \rightarrow 0}$	-1.675 "	$+0.034$ "	$+0.034$ "
$-\left[\frac{\partial^2 r_{0+1}}{\partial H^2} \right]_{H \rightarrow 0}$	-2.664 "	$+0.041$ "	$+0.041$ "
$-\left[\frac{\partial^2 r_{1-1}}{\partial H^2} \right]_{H \rightarrow 0}$	-3.158 "	$+0.110$ "	$+0.110$ "
$-\left[\frac{\partial^2 r_{11}}{\partial H^2} \right]_{H \rightarrow 0} = -\left[\frac{\partial^2 r_{-1-1}}{\partial H^2} \right]_{H \rightarrow 0}$	-7.231 "	-0.512 "	-0.512 "
$-\left[\frac{\partial^2 \delta_{0+1}}{\partial H^2} \right]_{H \rightarrow 0}$	$+0.109$ "	-0.225 "	-0.225 "
$-\left[\frac{\partial^2 \delta_{1-1}}{\partial H^2} \right]_{H \rightarrow 0}$	$+0.665$ "	-0.319 "	-0.319 "
$-\left[\frac{\partial^2}{\partial H^2} (2\varepsilon_0 + 2\varepsilon_1 + 2\varepsilon_{-1} - 6W'_{2p}) \right]_{H \rightarrow 0}$	$+41.198$ "	-24.824 "	-27.760 "
$-\left[\frac{\partial^2}{\partial H^2} \left(\int \int \dots \int \psi_0^* \left(\sum_{\mu < \nu}^6 \frac{e^2}{r_{\nu\mu}} \right) \psi_0 d\tau_1 d\tau_2 \dots d\tau_6 \right) \right]_{H \rightarrow 0}$	-51.853 "	$+1.840$ "	$+1.840$ "
$-\left[\frac{\partial^2}{\partial H^2} (E - E^0) \right]_{H \rightarrow 0}$	-10.65 "	-22.98 "	-26.00 "
Calculated anisotropy. (ergs per gauss per mole)	-16.2×10^{-6}	-35.1×10^{-6}	-40.0×10^{-6}
Calculated value Experimental value $\times 100, \%$	30	65	74

(13) One of the members in our laboratory.

(14) R. G. Parr and B. L. Crawford, *J. Chem. Phys.*, **16**, 1049 (1948); C. C. J. Roothaan and R. G. Parr, *J. Chem. Phys.*, **17**, 1001 (1949).

(15) M. Kotani, A. Amemiya and T. Shimose, *Proc. Phys.-Math. Soc. Japan*, **20**, extra number I (1938); **22**, extra number I (1940).

(16) A. London, *J. Chem. Phys.*, **13**, 396 (1945).

applied in the direction parallel to the molecular plane. The results of numerical calculations are given in Table 2. Column A in Table 2 represents the result obtained when only the types of integrals used in Goeppert-Mayer and Sklar's paper⁽⁷⁾ are adopted. Column B is the result when all the remaining types of integrals except R_2 , R'_1 , R'_2 , and R'_3 in Table 1 are used. Column C is derived by the use of all the integrals in Table 1.

Considerations

The best result obtained in this manner is -40×10^{-6} ergs per gauss per mole, it being about 74 percent of the experimental value -54×10^{-6} . The physical contradiction appears in the case of column A, where the contribution of $\mathcal{E}_i$ to the anisotropy is paramagnetic and that of repulsions between electrons diamagnetic, in spite of the fact that the former and the latter must be physically diamagnetic and paramagnetic respectively. But this contradiction is removed in columns B and C by the use of the integrals neglected in column A, and the numerical results become better. It is natural that the calculated result approaches more and more to the experimental value as the approximation used becomes of higher order. If the approximate methods used in this paper are not unreasonable, the above considerations may be useful in the criticism of the ground states calculated by the G-M-S method and it may be concluded that the energy level $^1A_{1g}$ in their original paper is unsuitable. On the other hand we have been also taught the fact that the anisotropy is largely enhanced by the orbital effects and slightly diminished by the correlation effects between π -electrons. Thus, the reason why good results were obtained by F. London's method neglecting the correlation

effects between π -electrons may be understood to some extent.

Recently the conception of configurational interaction has been introduced by Craig⁽¹⁷⁾ into the antisymmetric molecular orbital treatment of the absorption spectra of benzene. According to his paper there are four A_{1g} states including the ground state (at $\mathbf{H}=0$), described in the present paper, and the interactions among this set of A_{1g} states depress the lowest of them by about 2 e.V. Therefore it is interesting and may be valuable to note that the problems of anisotropy are treated with the introduction of configurational interaction.

Summary

The absolute value of the diamagnetic anisotropy of benzene was calculated by the method of antisymmetric molecular orbitals. The value obtained was about -40×10^{-6} ergs per gauss per mole, it being about 74 percent of the experimental value.

It was found that the anisotropy was largely enhanced by orbital effects and slightly diminished by correlation effects between π -electrons.

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(17) D. P. Craig, *Proc. Roy. Soc. London*, **200 A**, 747 (1950).

On the Mechanism of Evaporation in Vacuum. II. Vapor Pressure and Evaporation Velocity.⁽¹⁾

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It is suggested in the preceding paper⁽²⁾ that the estimation of vapor pressure is valuable when discussing the evaporation of various substances. The phase diagram of one component system is composed, in the simplest case, of three curves, that is sublimation, evaporation and fusion curves. These curves are described by Clapeyron-Clausius' equation:

$$d \ln p / d T = L / RT^2 \quad (1)$$

where p is pressure, T is absolute temperature, L is the latent heat of the phase transition, and R is the gas constant. This is integrated after expanding the latent heat L in power series, according to Nernst, and obtained,

$$\log p(\text{mm.}) = 2.88 - L_0 / 4.59 T + 1.75 \log T - \varepsilon T / 4.59 + \kappa \quad (2)$$

where p (mm.) is the pressure expressed in mm. Hg., ε is a parameter determined from some experimental data, and κ is the conventional chemical constant. The latter is calculated for monoatomic gases by the following equation:

$$\kappa = -1.587 + 1.5 \log M \quad (3)$$

where M is the molecular weight. All three curves in the phase diagram cross at one point, named a triple point. At this point, in general, the heat of sublimation and the heat of evaporation are not equal, while the relationship:

$$L_{\text{sub.}} = L_{\text{fus.}} + L_{\text{eva.}} \quad (4)$$

is obtained thermodynamically⁽³⁾. As for many metals, it is seen that,

$$L_{\text{fus.}} / L_{\text{sub.}} \simeq 0.015 \sim 0.058 \quad (5)$$

The following approximation is, therefore, used:

$$L_{\text{sub.}} \simeq L_{\text{eva.}} \quad (6)$$

Under this approximation sublimation and evaporation curves are described by one curve. Moreover, the melting point curve is often approximated by a straight line parallel to the pressure axis. Then, a simplified phase diagram is drawn for every metal, using the data tabulated in Table 1. For various metals, atomic weight M , and boiling point T_b inserted in the "Rika-Nenpyo"⁽⁴⁾, and the heat of sublimation at absolute zero temperature L_0 by Slater⁽⁵⁾ are cited in the Table. Among the data of L_0 , those marked with * are values at room temperature by Seitz⁽⁶⁾. The difference of the latent heat at absolute zero and room temperature is, in general, negligible, since it is less than 1 kcal./mole for these metals. The value of conventional chemical constant obtained from equation (3) is cited in the fifth column. The parameter ε is calculated by equation (2), using the fact that the temperature corresponding to the pressure $p = 760$ mm. Hg is the boiling point T_b ; and cited on the sixth column. Then, the vapor pressure curve is drawn, using Eq. (2) and values L_0 , ε , and κ , cited above. By the assumption that the temperature for the triple point is nearly equal to the melting point T_m , given in "Rika-Nenpyo"⁽⁴⁾ and Slater's book⁽⁵⁾, the pressure for the triple point p_t , is obtained. These are cited in the seventh and eighth column. Phase diagrams are depicted in Fig. 1 for various metals. They approximately coincide with curves by Law⁽⁷⁾, excepting Be, Al, Cr and Fe. The disagreements will be studied later.

Yarwood⁽⁸⁾ recorded the temperature of vacuum evaporation T_e . These values are cited in the tenth column of Table 1. The pressure in the vessel was 10^{-5} mm. Hg. The plots of these temperature data on the vapor

(1) These results were presented before the Meeting of Colloid Chemistry held by the Chemical Society of Japan at Osaka, November, 1950.

(2) M. Nakagaki, *This Bulletin*, **24**, 206 (1951).

(3) J. C. Slater, "Introduction to Chemical Physics", New York, 1939, p. 172.

(4) Edited by the Tokyo Astronomical Observatory, "Rika-Nenpyo", 1950, Tokyo.

(5) J. C. Slater, *loc. cit.*, pp. 259 and 454.

(6) F. Seitz, "The Modern Theory of Solid", New York, 1940, p. 3 and 61.

(7) R. R. Law, *Rev. Sci. Instr.*, **19**, 920 (1948).

(8) J. Yarwood, "High Vacuum Technique", London, 1948, pp. 84-90.

Table 1

Substances	Atomic or molecular wt. M	Boiling point T_b , °C.	Latent heat L_0 (kcal./mole)	Parameters in Eq. (2)		Triple point		Vacuum evaporation temp. T_e , °C.	
				κ	ϵ , cal./deg. ²	T_m , °C.	$\log p_t$, mm. Hg	Calcd.	Obsd.
Cs	132.91	670	18.7	1.599	0.0121	28.5	-7.26	200	433
Rb	85.48	700	20.6	1.311	0.0091	38.	-8.06	250	450
Cd	112.41	764	27.0	1.487	0.00487	320.9	-1.78	400	541
Zn	65.38	907	31.4	1.136	0.00288	419.5	-1.69	500	623
Mg	24.32	1110	36.6	0.491	0.00070	651.	-0.48	650	712
Li	6.94	1340	36.0	-0.325	0.00120	186.	-10.70	700	821
Sr	87.63	1150	47.0*	1.327	-0.00113	800.	0.02	700	811
Ca	40.08	1170	47.8*	0.818	-0.00280	810.	-0.15	750	878
Bi	209.00	1450	47.8	1.893	0.00405	271.	-11.00	750	913
Pb	207.21	1620	46.7	1.887	0.00547	327.3	-8.50	800	1000
Sb	121.76	1380	54.4	1.543	0.00000	630.5	-3.79	850	973
Be	9.02	(1500)	75.0*	-0.154	-0.0095	1350.	1.6	1150	—
Al	39.94	1800	67.6	0.815	-0.0011	659.	-6.7	1150	1461
Ag	107.88	1950	69.4	1.463	0.00107	960.5	-2.98	1200	1319
Sn	118.70	2260	68.0	1.526	0.00296	231.9	-21.09	1250	1148
Cu	63.54	2360	81.7	1.117	0.00061	1083.	-3.99	1450	1542
Cr	52.01	2200	89.4	0.987	-0.0018	1580.	-0.2	1500	1190
Si	28.06	2600	85.0*	0.585	0.00028	1420.	-1.94	1550	—
Au	197.2	2680	90.7	1.855	0.0016	1063.	-5.0	1600	1445
Ni	58.69	2900	98.1	1.066	0.00087	1454.	-3.12	1800	1717
Fe	55.85	3200	96.5	1.034	0.00155	1530.	-2.77	1850	1694
Pt	195.23	4300	125.	1.848	0.00231	1765.	-3.98	2400	2332
Mo	95.95	3700	156.	1.386	-0.00100	2620.	-0.87	2600	2755
C	12.01	(4000)	170.*	0.032	-0.0025	3600.	1.7	2900	—
W _o	183.92	5900	210.*	1.810	0.00076	3400.	-2.2	3800	3505
SiO ₂ (A)	60.06	2590	190.8	1.319	-0.01145	1710.	-6.0	2200	—
SiO ₂ (B)	60.06	—	95.4	1.319	-0.01145	—	—	1200	—
SiO ₂ (C)	60.06	—	127.2	1.319	-0.01145	—	—	1550	—

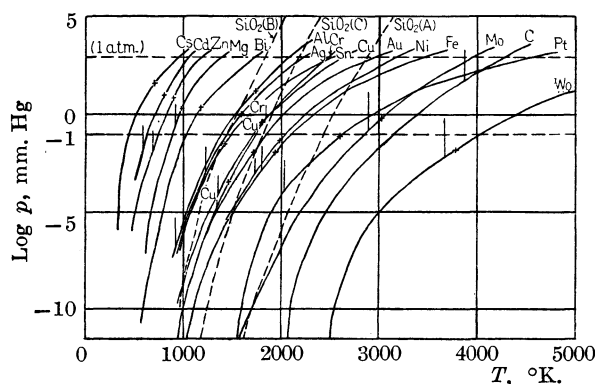


Fig. 1.—Phase diagrams of metals.

pressure curves in Fig. 1 (marked with +) show, however, that these temperatures correspond roughly to 10^{-1} mm. Hg of pressure, though the pressure is somewhat higher than 10^{-1} mm. Hg for volatile metals owing to the "over-heating". According to this fact, it is concluded that the vapor pressure near the specimen (10^{-1} mm. Hg) is usually not equal

to the pressure in the vessel distant from the specimen (10^{-5} mm. Hg). This circumstance will be discussed later in detail. Temperature corresponding to the vapor pressure 10^{-1} mm. Hg is obtained from vapor pressure curve in Fig. 1, and cited on the ninth column as calculated values of vacuum evaporation temperature T_e . These agree well with values by Yarwood, excepting Al, Cr and Wo. It is commonly accepted that aluminum evaporates more easily than silver or chromium. This fact coincides with the calculated evaporation temperature, while Yarwood's values show that aluminum evaporates at higher temperature than

silver or chromium. Some questions remained concerning this point. Data on silica, discussed in the preceding paper⁽²⁾, are also cited in Table 1 and Fig. 1. From the Table and Fig., it is seen that quartz, SiO₂(A), evaporates at 2200°C. or with as great difficulty as platinum, while idealized silica gel, SiO₂(B), evaporates at 1200°C., or as easily as silver. The vacuum

evaporation temperature of actual silica gel, $\text{SiO}_2(\text{C})$, is estimated to be 1550°C ., which is nearly equal to that of chromium or gold, and also coincides with experience.

Although the technique of vacuum evaporation is frequently used in electron microscopy, little has been discussed from the physico-chemical point of view, so that even an approximate estimation will bring forth some contributions. To evaluate the rate of evaporation, the following assumptions are made. The molecules of an evaporating specimen fly away straightly in every direction with the mean square velocity:

$$\bar{v} = \sqrt{3RT/M} = 15800\sqrt{T/M} \text{ (cm./sec.)}. \quad (7)$$

At a point, apart enough from the specimen, collisions between specimen molecules are, therefore, negligible, as long as collisions between specimen molecules and air molecules are negligible. This latter is easily verified as follows. Let the number of collisions with air molecules done by one specimen molecule in unit time be Z , then,

$$Z = \pi \left(\frac{\sigma + \sigma_a}{2} \right)^2 \cdot \sqrt{\bar{v}^2 + \bar{v}_a^2} \cdot n_a, \quad (8)$$

where σ and σ_a are collision diameters of specimen and air molecule, respectively, and both are considered to be nearly equal to $3 \text{ \AA}$. $\bar{v}$ and $\bar{v}_a$ are mean square velocities of specimen and air molecules, the values of which are obtained by the insertion of each value of temperatures and molecular weights into Eq. (7). n_a is the number of air molecules in unit volume and is expressed with the pressure p_a (mm.Hg) in the vessel by the equation:

$$n_a = p_a/kT_a. \quad (9)$$

The mean free path of specimen molecule in this air, λ , is given by

$$\lambda = \bar{v}/Z. \quad (10)$$

Since silica gel, as an example, evaporates at $T_e = 1830^\circ\text{K}$., and its molecular weight is $M_0 = 60$, the mean free path in air, where $T_a = 293^\circ\text{K}$. and $M_a = 28.8$ are calculated by

$$\lambda = 0.96 \times 10^{-2}/p_a \quad (11)$$

If $p_a = 10^{-4}$ or 10^{-5} mm.Hg, then $\lambda = 96$ or 960 cm., respectively. Under the usual experimental conditions, therefore, the probability of collision between specimen molecule and the air is safely omitted.

The number of specimen molecules in unit

volume, n , placed at a distance r from the specimen is to be calculated as follows. Imagine a spherical shell of radius r , thickness dr , and volume $4\pi r^2 dr$. Then the time required to pass through this shell by a molecule of velocity $\bar{v}$ is $(dr/\bar{v})$. The number of molecules evaporated in unit time is $-(N_A/M) \times (dw/dt)$, where w is the weight of specimen (g.), and N_A is Avogadro's number, so the number of specimen molecules in the shell is $-(N_A/M)(dw/dt) \times (dr/\bar{v})$. Therefore,

$$n = -(N_A/M) \times (dw/dt)/(4\pi r^2 \bar{v}). \quad (12)$$

Let the temperature of a specimen be T_0 and the vapor pressure corresponding to it be p_0 . The density of this vapor, n_0 , is

$$n_0 = p_0/kT_0. \quad (13)$$

The specimen is surrounded by the layer of such vapor, but the thickness of the atmosphere is assumed to be very slight. Then, in Eq. (12), $n = n_0$ if $r = r_0$ = the radius of the specimen itself. The rate of evaporation becomes, therefore,

$$-dw/dt = 4\pi r_0^2 \bar{v} n_0 (M/N_A). \quad (14)$$

From Eqs. (12) and (14),

$$n = n_0 (r_0/r)^2. \quad (15)$$

That is to say, the vapor density n at a place distant as r from the specimen is greater when n_0 is greater, r is less, or r_0 is greater. n_0 becomes great when the temperature of specimen is high, since, in Eq. (13), p_0 increases exponentially when T_0 increases. If r_0 is great, the area of evaporation and the vapor density n are great.

When a shadow is cast using some metal as a specimen for electron microscopy, it is generally accepted that the shadow becomes diffuse if the pressure of air in the vessel is not low enough. Let us consider a unit area, of the distance l from the evaporating specimen, and of the angle of inclination θ to the direction of flying of a specimen molecule. Since the mean kinetic energy of a gas molecule is $(3/2)kT$, the sum of kinetic energy of a specimen molecule hitting this unit area per unit time, K_0 , is

$$K_0 = (3/2)kT_0 n \bar{v} \sin \theta \quad (16)$$

where Eq. (15) is used for n , with $r = l$. While the sum of kinetic energy of air molecule hitting this area, K_a , is

$$K_a = (3/2)kT_a n_a (RT_a/2\pi M_a)^{1/2}. \quad (17)$$

It may be assumed that a shadow is clearly cast if $K_0 > K_a$, while the shadow becomes diffuse by the disturbance of air if $K_0 < K_a$. The value of l corresponding to $K_0 \approx K_a$ is written as l_e :

$$l_e \approx \left(6\pi \frac{T_0 M_a}{M_0 T_a} \right)^{1/4} (\sin \theta)^{1/2} r_0 (p_0/p_a)^{1/2}. \quad (18)$$

If the distance between the evaporating specimen and the area, where the shadow is to be cast, l is smaller than l_e , then a clear shadow will be obtained, and if l is greater than l_e , a diffuse shadow will be obtained. Let us assume, following ordinary experimental conditions, that $T_a = 293^\circ\text{K}$., $M_a = 28.8$, $\sin \theta = 1/5$, $r_0 \approx 10^{-1}\text{cm}$., and $p_0 \approx 10^{-1}\text{mm.Hg}$. The calculated value of l_e is cited in Table 2 for some metals. It is seen that the value of l_e is about 1 cm. when the pressure of air in the vessel p_a equals 10^{-3}mm.Hg , and l_e is about 10 or 14 cm. for $p_a = 10^{-5}\text{mm.Hg}$. In ordinary conditions, that is l is 6 cm. or so, a clear shadow will be obtained if the vacuum in the vessel is more than 10^{-4}mm.Hg , while the shadow will be disturbed if the vacuum is less than 10^{-4}mm.Hg . According to Eq. (18), it is understood that a clear shadow is easily obtained, if p_a is small by a sufficient preliminary evacuation, if p_0 is great by the high temperature of evaporating specimen, and if angle θ is not too small. These conclusions coincide with common experiences.

The rate of evaporation of a specimen has been given by Eq. (14). This is integrated with the equation:

$$(4/3)\pi r_0^3 \rho = w \quad (19)$$

and the time τ (sec.) required to evaporate $w_0(\text{g.})$ of the specimen completely is obtained as

$$\tau = \left(\frac{3\rho^2}{4\pi} \right)^{1/3} \left(\frac{RT_0}{Mv p_0} \right) w_0^{1/3} \quad (20)$$

where ρ is the density of the specimen. In the case of silica gel, it is assumed that $\rho = 2.2$, $M = 60$, $T_0 = 1830^\circ\text{K}$., $\bar{v} = 8.73 \times 10^4\text{cm./sec}$. and $p_0 = 10^{-1}\text{mm.Hg}$, and

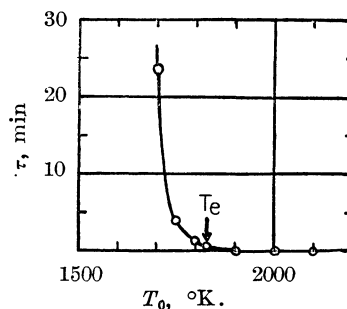
Table 2

Metals	M_0	T_0 , °K.	l_e , cm.		
			$p_a = 10^{-3}$ mm. Hg.	10^{-4} mm. Hg.	10^{-5} mm. Hg.
Al	27	1410	1.4	4.4	14
Ag	108	1440	1.0	3.2	10
Cr	52	1740	1.3	4.1	13
Au	197	1860	0.9	2.7	9
Ni	59	2040	1.3	4.4	13

$$\text{for } w_0 = 5 \text{ mg.}, \quad \tau = 39 \text{ sec.} \quad (21)$$

is obtained. This agrees well with the experimental data cited in the preceding paper⁽²⁾, that is 4~8 mg. of silica gel requires 20~40 sec. for evaporation.

Concerning the Eq. (20), two facts should be emphasized. The one is that the temperature of evaporation in a vacuum is defined as the temperature corresponding to the vapor pressure $p_0 = 10^{-1}\text{mm.Hg}$. This is only a conventional definition and has no theoretical meaning. The time required to evaporate 5 mg. of silica gel is calculated for various temperatures and depicted on Fig. 2. As easily seen from this Figure, time τ increases enormously if the temperature is somewhat lowered from the evaporation temperature $T_e = 1830^\circ\text{K}$. It is, therefore, concluded that the definition of T_e is significant practically. The second is that the rate of evaporation is mainly affected by the temperature of the evaporating specimen T_0 , since the pressure p_0 is only dependent on T_0 for a given substance. The pressure of air in the vessel p_a , as far as $p_a < p_0$, is of least importance for evaporation velocity, although the distinctness of the shadow cast is largely affected by p_a .

Fig. 2.—Dependence of τ on temperature.

The temperatures of tungsten filament and silica gel are directly measured by an optical pyrometer under the ordinary experimental condition of evaporation. The temperature obtained by the optical pyrometer is "brightness temperature" or "black body temperature". The emissivity of the substance should be known to recalculate the black body temperature to actual temperature⁽⁹⁾. As for tungsten, the data necessary to this correction are given for $0.665\ \mu$ of wave length of light⁽¹⁰⁾. As for silica gel, no data are given on its

(9) Edited by American Institute of Physics, "Temperature; Its Measurement and Control in Science and Industry," 1941, p. 1129.

(10) International Critical Tables, Volume V, pp. 243 and 245.

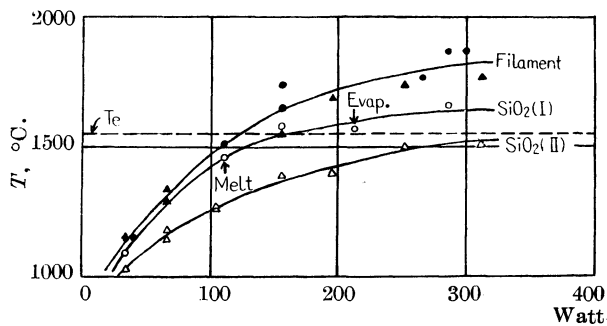


Fig. 3.—Temperature of filament and specimen.

emissivity. For a convention, the calibration curve for tungsten is also used for silica gel. The relation between electric power (watt) used and temperature observed are depicted in Fig. 3. The apparatus for evaporation and tungsten filament used are the same as reported in the preceding paper⁽²⁾. The relation between the temperature of tungsten filament and electric power used varies with the length of tungsten wire and the manner of its coiling. The data cited are examples. Five mg. of silica gel are used. When a piece of silica gel is placed in the bottom of a tungsten basket, it melts at about 1450°C. and evaporates at 1600°C., as shown in the Fig. 3 as SiO₂(I). This agrees with the estimated evaporation temperature cited in Table 1. While the piece is placed on the upper part of the basket, it cannot be made to evaporate by less than 300 watts heating as shown as SiO₂(II). This fact should be remembered when an evaporation experiment is done.

Whether the substance evaporates after fusion or sublimates without fusion may have some significance in the rate of evaporation, since the melted substance adheres to the filament, and high temperature will readily be obtained. For example, the evaporation of silver is far easier than that of chromium. The main reason for this will be that the evaporation temperature shown in Table 1 of silver is even 300°C. lower than that of chromium. However, there may also be another reason that silver evaporates after fusion while chromium sublimates without fusion.

Summary

Phase diagrams are drawn for many metals under some approximations, and "vacuum evaporation temperature" is estimated as the temperature corresponding to 10⁻¹ mm.Hg of vapor pressure. This temperature agrees well with that given by Yarwood. The rate of evaporation is calculated, and the result agrees well with experience, at least, for silica gel. As for shadow casting, it is concluded that high temperature of specimen and low pressure of air in the vessel are the necessary conditions to obtain clear shadow. The temperature of evaporating silica gel is measured with optical pyrometer, and a satisfactory result is obtained.

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Gehalt an Molybdän in Japanischen Vulkanischen Gesteinen

Von Tomitaro ISHIMORI

(Eingegangen am 12, Juni 1951)

Über den Gehalt an Molybdän in europäischen Eruptivgesteinen wurden schon einige Untersuchungen ausgeführt^{(1)·(2)}. Einige Bestimmungen des Molybdäns wurden auch ausgeführt über verschiedene Tiefseetone⁽³⁾ und Kohlenaschen⁽⁴⁾. Vor kurzem versuchte I.

Iwasaki⁽⁵⁾ die Bestimmungen des Gehaltes an Molybdän in mehreren japanischen Gesteinen. Aber, aus dieselben Untersuchungen erkannte er dass man die grössere Menge der Gesteinsprobe braucht um die genaueren Zahlen zu gewinnen, denn das Gehalt an Molybdän sind

(1) I. und W. Noddack, *Z. Physik. Chem.*, A **154**, 207 (1931).

(2) G. von Hevesy und R. Hobbie, *Z. anorg. allgem. Chem.*, **121**, 142 (1933).

(3) S. Oona, *J. Chem. Soc. Japan*, **59**, 1234 (1938); K. Kuroda, *ibid.*, **63**, 496 (1942).

(4) I. Iwasaki, unveröffentlicht.

(5) I. Iwasaki, "Chemistry of Volcanoes" 1948, S. 182.

sehr niedrig in japanischen vulkanischen Gesteinen (0.0001~0.0002 % MoO_3). In vorliegender Mitteilung berichte ich über die experimentellen Resultate meiner Bestimmung über den Gehalt an Molybdän in japanischen vulkanischen Gesteinen mit grösserer Menge der Probe (5~10 g.).

Durchschnittsmischung von 15 japan. intermediären Ergussgesteinen	0.00017
Durchschnittsmischung von 10 japan. Lipariten	0.00045
Olivinbasalt (Shimo-Oimura, Shizuoka)	0.00008
Hypersthendazit (Yugawara, Kanagawa)	0.00027
Nephelinbasalt (Nagahama, Shimane)	0.00026

Methode der Bestimmungen

Sandellsche kolorimetrische Methode⁽⁶⁾ für die Bestimmung von Molybdän in Silikatgesteinen wurde mit einigen Modifizierungen angewendet.

Etwa 5-10g. feingepulverte Probe wurde in einem Platintiegel mit fünfmalen Natriumkarbonat genug geschmolzen. Die Schmelze wurde mit Wasser digeriert unter Zusatz von einigen Tropfen des Äthylalkohols. Der Niederschlag wurde dann abfiltriert und mit Wasser verdünnt zum definierten Volum um je 100 cc. Lösung 1 g. Probe zu enthalten.

Je 100 cc. Lösung wurde in Scheidetrichter mit 16 cc. konzentrierter Salzsäure, 6 cc. 5-prozentigem Kaliumrhodanat und 6 cc. 10-prozentigem Zinn-(II)-chlorid behandelt, dann mit 20 cc. Äther (behandelt mit Kaliumrhodanat und Zinn-(II)-chlorid) geschüttelt. Das Molybdän geht in die Schicht von Ätherlösung über. Die Ätherlösung wurde abgetrennt und verdünnt zum 20 cc. Volum unter Zusatz von neuem Ätherreagens.

Die zweite 100 cc. Lösung der Probe wurde nach gleicher Behandlung wieder mit oben-erwähnter 20 cc. Ätherlösung geschüttelt. Nach einer Reihe von dieselben Behandlungen wurde alles Molybdän in Form von $\text{K}_2[\text{MoO}(\text{ONS})_3]$ in einem kleinem Volum von Ätherlösung gesammelt. Die rote Färbung der Ätherlösung wurde mit der Färbung der Lösung des bekannten Gehaltes an Molybdän kolorimetrisch vergleicht.

Resultat

Die Bestimmung über drei Durchschnittsmischungen und drei Gesteinsproben wurden ausgeführt. Die Resultate sind in Tabelle 1 zusammengefasst.

Tabelle 1	
Probe	% MoO_3
Durchschnittsmischung von 10 japan. Basalten	0.00014

(6) E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.* **8**, 336 (1936).

(7) Y. Uzunasa und K. Doi, *Dies Bulletin*, **14**, 337 (1939).

Tabelle 2

	g. Mo/g.
Sauer Schluchsee Granit (Schwarzwald)	1.2×10^{-3}
Mischung von 282 Eruptivgesteinen	1.5×10^{-3}
Gemisch aus 67 Gabbros und Noriten	
sehr verschiedener Herkunft	0.3×10^{-3}

Aus Tabelle 1, wissen wir dass die vorliegenden Resultate mit den Iwasakischen Resultaten⁽⁵⁾ genau übereinstimmen.

V. M. Goldschmidt⁽⁸⁾ gab 15 g. Mo/ton für Eruptivgesteinen an und I. und W. Noddack⁽¹⁾, in 1931, 0.00 n % Mo für europäische Basalte. In der Vergleichung mit diesen Resultaten, sind die Werte an Molybdän in japanischen vulkanischen Gesteinen sehr niedrig. Es sei noch erwähnenswert dass die Bestimmungen von Olivinbasalt und Durchschnittsmischung von japanischen Basalten nur niedrige Werte des Gehaltes ermittelten, während sich die von Nephelinbasalt einen bemerkbaren grossen Gehalt ergaben. Hier muss man berücksichtigen, dass das Nephelinbasalt die grossen Verschiedenheiten, vergleicht mit den normalen japanischen vulkanischen Gesteinen, auch in anderen mehreren chemischen Bestandteilen zeigt.

Die Resultate der Untersuchung von G. von Hevesy und seiner Mitarbeiter⁽²⁾ zeigten die Anreicherung des Molybdäns in saueren Eruptivgesteinen (Tabelle 2). Die Neigung stimmt mit der Resultaten meiner Untersuchung überein.

Herrn Prof. I. Iwasaki bin ich für die Anregung zu dieser Arbeit und für seine zahlreichen Ratschläge zu grossem Dank verpflichtet.

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(8) V. M. Goldschmidt, "Geochemische Verteilungsgesetze der Elemente," IX (1938).

Structure of the "Structureless" Replica Film for Electron Microscopy

By Shigeto YAMAGUCHI

(Received August 8, 1951)

Introduction

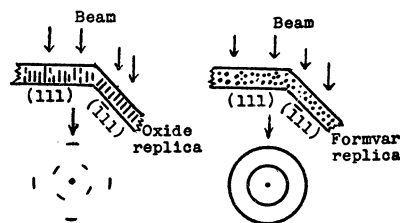
The thin films, which reprint faithfully the elevations and depressions of the surfaces of substances, are called "structureless" replica in electron microscopy. It is known that the oxide replica⁽¹⁾ and electrodeposited films⁽²⁾ formed on metal surfaces give more resolved images than Formvar replica. It has been demonstrated in the present study that the structureless oxide replica has a crystallographic structure distinguishable from that of Formvar or collodium replica. The reason why the oxide, sulphide and electrodeposited replica films give the resolved images in electron microscopy are to be explained in the present study.

Experimental

The specimen of iron single crystal used here was a piece of wire (diameter, 2 mm.; length, 10 mm.). This was etched with C_2H_5OH -Br (10:1 by vol.) solution for 10-30 seconds. The oxide replica was formed on this etched surface by the author's method⁽³⁾ and it was stripped from the substrate by Mahla-Nielsen's method⁽⁴⁾. The micrograph of this replica film is shown in Fig. 2. In Fig. 2 there are octahedral crystals oriented parallel to each other and the (001) planes of these crystals are inclined by 25-30° to the replica film. The electron diffraction pattern from the etched surface of the specimen showed the same inclination of (001) plane to the macroscopic surface as that in microscopic observation. This coincidence verified the faithfulness of the oxide reprint performed here.

The electron beam running perpendicular to the replica film of Fig. 2 gave the diffraction pattern of Fig. 1, which verified the existence

of regularly oriented Fe_3O_4 crystals. The oxide crystals formed on metal single crystals orientate themselves according to the orientation of the substrate⁽⁵⁾. On the contrary, Formvar replica gives the diffraction pattern consisting of diffuse haloes. The orientation of the oxide particles formed on the boundary plane (*e. g.*, (111) plane in Fig. 2) of single crystal should be distinguishable from the orientation of oxide particles of another face (*e. g.*, $(\bar{1}11)$ plane in Fig. 2). Therefore, the diffraction spots obtained from the oxide replica appear in the separated positions on a back focal plane of objective lens, which are determined by the orientation of the oxide particles to the incident beam (*vid.* Fig. 3).



Diffraction pattern on focal plane

Fig. 3.—The diffraction pattern of oriented oxide replica and that of Formvar replica.

Discussion

The diffraction pattern obtained on a focal plane of a microscope behaves as a new diffraction lattice for the observable image (Abbe's principle); as a matter of fact, this was demonstrated with the electron microscope in three stages⁽⁶⁾. It is, therefore, reasonable that the sharp diffraction spots obtained from oxide replica on a focal plane lead to more resolved images than Formvar replica giving diffuse haloes.

According to the diffraction experiment, the oxide particles formed on the polycrystalline

(1) "Metallurgical Application of Electron Microscope" Monograph and Report Series No. 8, Institute of Metals, London, 1950.

(2) R. Well and H. J. Read, *J. Appl. Phys.*, **21**, 1068 (1950); G. M. Corney, *J. Appl. Phys.*, **22**, 682 (1951).

(3) S. Yamaguchi, *J. Appl. Phys.*, **22**, 680 (1951).

(4) E. M. Mahla and N. A. Nielsen, *J. Appl. Phys.*, **19**, 378 (1948).

(5) H. R. Nelson, *J. Chem. Phys.*, **5**, 262 (1937).

(6) A. C. van Dorsten, H. Nieuwdorp and A. Verhoeff, *Philips Tech. Rev.*, **12**, 33 (1950); M. E. Haine, P. S. Page and R. G. Garfitt, *J. Appl. Phys.*, **21**, 173 (1950).

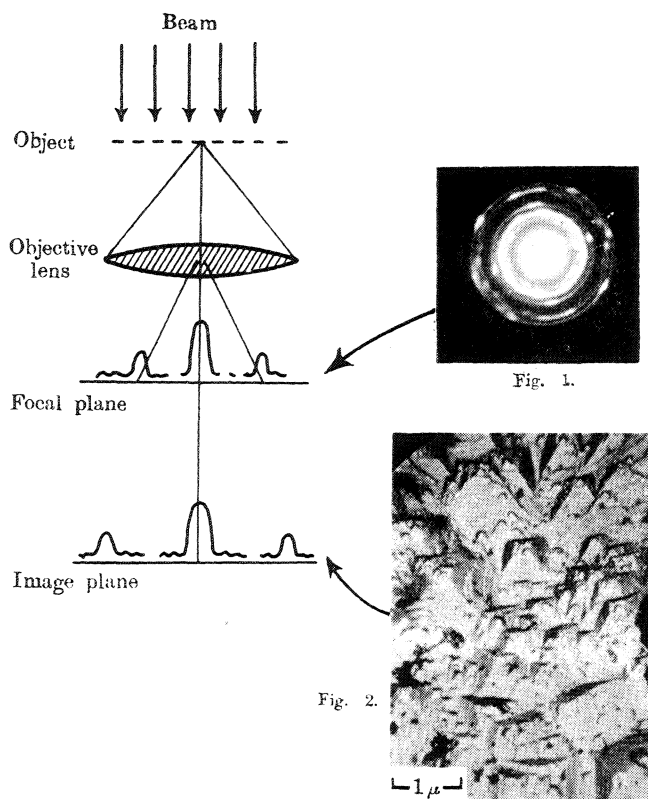


Fig. 1.—Diffraction pattern obtained by the electron beam running perpendicular to the replica film of Fig. 2.

Fig. 2.—Micrograph of the oxide replica formed on iron single crystal.

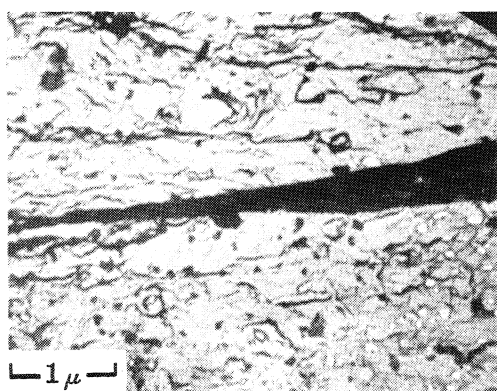


Fig. 4.—Micrograph of the sulphide replica formed on silver plate.

[To face page 253.

metals are arranged at random. The orientation of the oxide particles to their substrate can be recognized with the oxidized surface of a single crystal, as is shown in Fig. 2. It is, therefore, plausible that the small oxide particles formed on the individual crystals of polycrystalline metal surface orientate themselves in a small area. This fact makes it possible that the oxide replica gives a resolved image and is suitable for dark-field illumination in microscopy. The same results as for the oxide replica should be applicable to the electrodeposited films on metal surfaces.

It is impossible for silver to obtain oxide replica film for microscopy. This metal gives the stable sulfide film on its surface, which is formed with sodium sulfide solution and can be stripped off the substrate with nitric acid. This sulfide film gave a more resolved image (Fig. 4) in the present study than Formvar replica. It is concluded here that the films on metals formed chemically give more resolved images than Formvar replica of metal surface mechanically prepared.

Summary

The reason the oxide replica gives a more resolved image in electron microscopy than Formvar or collodium replica is because the small oxide particles (50-100 Å.) composing replica film are oriented according to the orientation of the metal crystals of substrates. The electrodeposited replica and sulphide film formed on metals give the resolved images in microscopy. This is explained in the same way as for oxide replica.

Prof. N. Kameyama, Prof. S. Mizushima and Mr. K. Sakatani (director of Scientific Research Institute Ltd.) have constantly given the author encouragement in pursuing this study, and his thanks are extended to them.

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New Method of Preparation of Reduced Strychnine Reagent for the Nitrate Determination in Seawater

By Yoshihiro MATIDA

(Received February 28, 1951)

The determination of nitrate is the essential work in the oceano-chemical studies. Since H. W. Harvey⁽¹⁾ applied the G. Deniges's reduced strychnine method⁽²⁾ to the colorimetric determination of nitrate in sea water, this reagent has been used universally in such studies.⁽³⁾ The writer has reported with regard to the Harvey's method applied to his oceano-chemical studies of Tokyo Bay.⁽⁴⁾ As the Harvey's method of preparation presents some trouble and inconvenience, he has devised a newly preparing reduced strychnine reagent by the use of liquid amalgam.

Inconvenient points of Harvey's method are as follows: (1) The time of reduction is so long as from several hours to more than

twenty hours. (2) The extent of the reduction is not constant every time. (3) Zinc of high purity is necessary. Even if amalgamation of zinc is perfect, iron and lead are occasionally dissolved and on account of these impurities this reagent shows pink color even in the absence of nitrite or nitrate in the sample water. (4) Zinc is unnecessarily consumed in mere hydrogen generation. (5) When concentrated sulfuric acid is added after the reduction, a large quantity of zinc sulfate crystallizes out and also the generation of heat and hydrogen chloride is so violent that the operation is very troublesome. (6) Reduced strychnine is oxidized by oxygen or nitric oxide in the atmosphere.

The application of liquid amalgam to analytical chemistry was made by Prof. M. Kobayashi.⁽⁶⁾ Of the excellent characteristics of

(1) H. W. Harvey, *J. Mar. Biol. Assoc., N. S.*, **14**, 71-88 (1926).

(2) G. Deniges, *Bull. soc. chim.*, **9**, 544-546 (1911).

(3) D. Echford, *Commonwealth of Australia, Council for Scientific and Industrial Research, Bull.*, No. 220 (1947).

(4) Y. Matida, in press.

(5) Y. Miyake, "Water Analysis," Tokyo, 1949, p. 102.

(6) K. Nakazono, *J. Chem. Soc. Japan*, **42**, 526 (1921).

this application, the following points⁽⁷⁾ are worthy of special notice: (1) Reduction velocity is accelerated by shaking. (2) Wasteful consumption of zinc is avoided. (3) By the substitution of the air in the reductor with suitable inactive gas (carbon dioxide is the most convenient) the reoxidation of reduced strychnine is avoided.

Experiment and Discussion

I. Operation.—(1) Method of reduction. Into the reductor (Fig. 1) the acid solution of

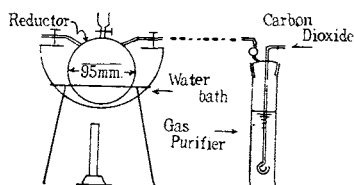


Fig. 1.

strychnine sulfate (0.27 g./20 cc.) and 150 g. liquid amalgam were added, then carbon dioxide was vigorously passed from Kipp's apparatus. The reductor was heated on a water-bath for three minutes. Hereafter it was heated and shaken for two and three minutes respectively. When the sum of shaking periods attained to the definite time, zinc amalgam was taken out into a beaker, carbon dioxide having been passed slowly through the reductor. Then 120 cc. of concentrated sulfuric acid was added and thoroughly mixed.

The purpose of passing carbon dioxide is to protect the reduced strychnine from reoxidation by the oxygen in the atmosphere as D. Rochford's indication, and also by this operation the contamination due to nitrate or nitrite in the laboratory air is preserved.

(2) Colorimetry. In a small test tube with glass-stopper, 5 cc. of sample water or standard solution was taken, then about 0.2 g. of purified sodium chloride or two drops of concentrated hydrochloric acid were added. After the dissolution of sodium chloride, 5 cc. of the reagent were slowly poured on the sample water along the inner side of the tube. After stirring, the tube was preserved in a dark and cold place for definite time. The extinction coefficient of the colored solution was determined with the Pulfrich's photometer or compared with the standard color solution (aqueous solution of safranin red was used). The usefulness of the addition of chloride ion is already found⁽⁸⁾

and the writer recognized that the above mentioned quantity of sodium chloride was necessary and sufficient.

II. Preliminary Experiment.—In the first place the suitable acid and its concentration for reduction were studied. From the results, 9 N sulfuric acid solution was adopted.

III. Criticism on Shaking Period, Reserving Time and Reproducibility by the Method of Variance Analysis.—The difference of color developing power due to change in shaking period and preserving time was tested. Also the reproducibility—whether two reagents prepared by strictly identical procedure have the same color developing power or not—was investigated. Simultaneously by this factorial analysis the interrelations of these factors were tested.

Table 1*

	D1				D2			
	H1		H2		H1		H2	
B1	1.7,	2.3	2.8,	1.1	-0.6,	-0.7	0.8,	3.2
B2	0.2,	1.4	0.0,	0.4	2.0,	1.7	0.2,	1.3
Sum	1.9,	3.7	2.8,	1.5	1.4,	1.0	1.0,	4.5

	D3				Sum
	H1		H2		
B1	0.4,	-1.0	2.8,	3.5	16.3
B2	-0.6,	-0.5	0.1,	3.1	9.3
Sum	-0.2,	-1.5	2.9,	6.6	25.6

D: Reduction time (D1...24 minutes, D2...18 minutes, D3...12 minutes).

H: Preserved time (H1...Immediately after reduction, H2...after 30 days).

B: Repetition...B1 and B2 were prepared strictly by the same method.

* The values of this table were obtained as follows. The colored solution (NO₃-N 500 microgram/1.) was compared with safranin red solution (0.005 %), then the constant value deduced from the observed value.

Table 2

Factor	Variance	Degree of freedom	Mean square
D	0.36	2	0.18
H	7.48	1	7.48*
B	2.04	1	2.04
DH	9.61	2	4.81*
HB	4.79	1	4.79*
BD	4.71	2	2.36
DBH	3.24	2	1.62
R(DHB)	11.59	12	0.97
DHBR	43.82	23	

(7) S. Isimaru, "Experimental Studying Method of Chemistry" Analytical Chemistry, 2 (1942), Tokyo.

(8) B. M. G. Zwickler and P. J. Robinson, *J. Mar. Res.*, 5, 214 (1944).

In Table 1, the results of the experiment are shown. Table 2 is the results of variance analysis, in which the mark (*) shows that the factor is significant when the level of significance is 0.05. From this analysis the following conclusions have been obtained: (1) Color developing power changed in preservation. (2) The interrelation of shaking period and reproducibility, and also that of preservation and reproducibility were recognized.

VI. Characteristics of this New Reagent.—(1) **Absorption Curve.** The curve observed with the Pulfrich's photometer is shown in Fig. 2. From this result the filter S 53 is adopted for the colorimetric determination of nitrate in sea water. Also it was recognised that the aqueous solution of safranine red, used as an artificial standard by L. H. N. Cooper,⁽⁹⁾ can be used.

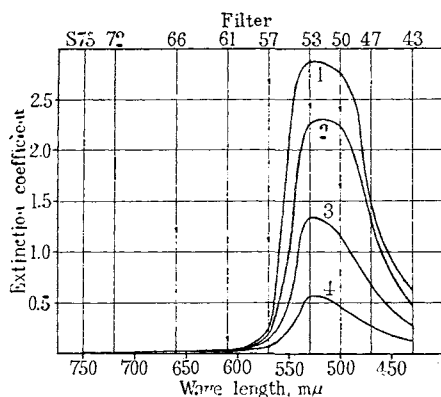


Fig. 2.—Absorption curves of the colored solutions produced by the reactions of reduced strychnine reagents and aqueous solutions of nitrate: curve 1, the product of the new reagent and the aqueous solution containing 200 γ /l. nitrate nitrogen; curve 2, 0.003% aqueous solution of safranine red; curve 3, the product of Harvey's reagent and the aqueous solution containing 200 γ /l. nitrate nitrogen; curve 4, the product of the new reagent and the aqueous solution containing 50 γ /l. nitrate nitrogen.

(2) **The Time for Developing the Maximum Intensity of Coloration.** After the addition of the reagent, the time for developing the maximum coloration differed with the change in the nitrate concentration. But, twelve hours' standing is enough for any concentration (Fig. 3). The colored substance was easily decomposed by the action of light, so the

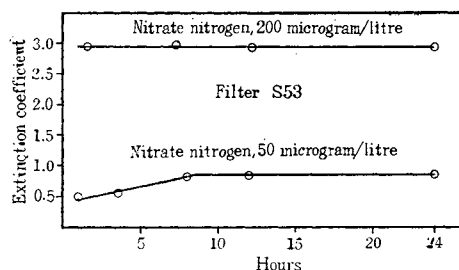


Fig. 3.—A figure to show the time of color development.

colorimetric observation needs rapid operation and much care should be taken to protect the colored solution from the light.

(3) **The Relation Between the Extinction Coefficient and the Concentration of Nitrate Nitrogen.** Ordinarily in natural sea water, nitrate nitrogen concentration is about 500 microgram per litre or less. So in Fig. 4 the calibration curve between extinction coefficient and nitrate nitrogen concentration is shown in this range.

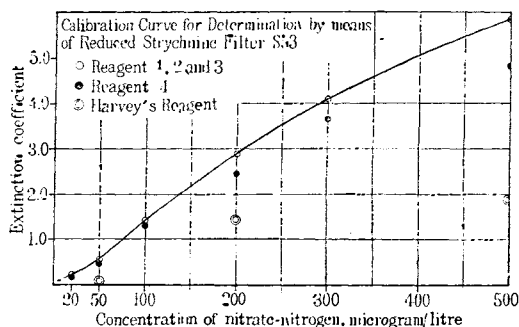


Fig. 4.—A figure to show the relation between the extinction coefficient and the concentration of nitrate. The reduction times to prepare the reagent 1, 2, 3 and 4 are 24, 18, 12 and 5 minutes respectively.

(4) **Application to Sea Water.** To portions of sea water, various quantities of nitrate were added, then the concentrations thereof in the waters were determined. The results were additive, so there might be no considerable salt error larger than the experimental error. Nitrate nitrogen shows the same color, so the correction of this salt was made as follows: In the first place the corresponding extinction coefficient of the nitrite, obtained from the calibration curve thereof (Fig. 5), was subtracted from the measured extinction coefficient of the sample. Nitrite was determined by the use of Griess-Romijn's reagent.

(5) **Sensitiveness of the New Reagent.** The

(9) L. H. N. Cooper, *J. Mar. Biol. Assoc., N. S.*, 18, 161 (1932).

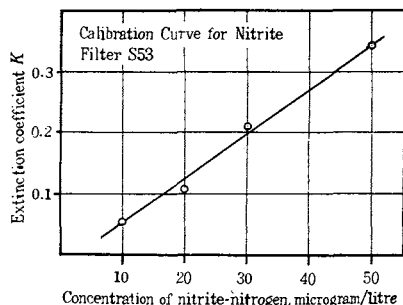


Fig. 5.—A figure to show the relation between the extinction coefficient and the concentration of nitrite.

concentration of this reagent is 1.93 g. per litre as strychnine sulfate. In B. M. G. Zuwicker's report 6 milli-molar strychnidine solution (1.92 g./l.) showed the extinction coefficient 3.48 in the presence of 280 microgram nitrate nitrogen per litre. The new reagent's extinction coefficient in the same concentration of nitrate nitrogen was higher than 3.8, so the new reagent and Zuwicker's one may be of nearly equal sensitiveness. Harvey's reagent aged thoroughly showed considerably lower value than the new one as shown in the fourth figure.

Cooper reported that 0.0008 per cent safranin red solution equaled nitrate nitrogen from 90 to 130 microgram. Also Rochford's reagent showed that 0.0025 per cent solution of the dye equaled 100 or 200 microgram of the nitrate nitrogen. The writer's showed the following relation: 0.005 per cent safranin red solution equaled 150 microgram nitrate nitrogen per litre. So the new reagent is considered to be an excellent one.

Conclusion

Preparation of the Reagent.—(1) 4 g. strychnine sulfate were dissolved in 150 cc. of 18 N sulfuric acid. (2) Into the reductor 10 cc. of the strychnine solution, 10 cc. of water and 150 g. liquid amalgam were added. Then the strychnine was reduced for 15 minutes by the method stated above. (3) After the reduction 120 cc. concentrated sulfuric acid were added and they were preserved in a glass bottle of good quality, cleaned with bromine water. It was better to let it stand in a dark and cool place.

Convenient Points of this Method.—(1) The time of preparation is shortened. (2) Reproducibility of the reagent is enhanced. (3) Zinc of high purity is not necessary. (4) Wasteful consumption of zinc is avoided completely, so the operation of adding sulfuric acid is very easy. (5) There is no need of aging. (6) By the replacement of the air in the reductor with carbon dioxide the reoxidation of the reduced strychnine is avoided.

The writer wishes to express his hearty thanks to Prof. H. Goto for his valuable criticisms and desires to acknowledge the helpful suggestions given by Mr. K. Tanii throughout the investigation. He also wishes to thank Mr. S. Tanaka for the suggestions concerning statistical treatment of the results.

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Research on Activation Energy. II. Some Applications of the Empirical Rule

By Sanshiro KUME and Kiyoteru OTOZAI

(Received May 18, 1951)

Introduction

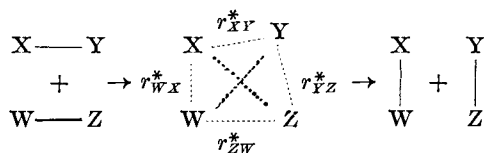
One of the authors has previously proposed a new empirical rule for the calculation of the activation energy and shown that the rule holds well for triatomic and tetratomic re-

actions.⁽¹⁾ The present report concerns further applications of the rule for the more complicated reactions. If we denote the distance

(1) K. Otozai, this Bulletin, **24**, 218 (1951). Details will be published in the Scientific Papers from Osaka University.

corresponding to the inflexion point on the potential-energy curve or to the maximum point on the attractive force curve between two atoms "the activated internuclear distance" and the bond, which appears only in the activated complex "the activated bond," the present rule can be expressed as follows: among all the possible structures, which can be constructed by the use of the fixed values of the activated internuclear distances of the bonds to be broken as well as to be formed, such a structure, in which the sum of the energies of the activated bonds becomes minimum, represents the structure of the activated complex and this minimum sum of the energies of the activated bonds gives the activation energy of the reaction, when it proceeds in the exothermic direction.

Thus for the tetratomic reaction of the type:



the bonds to be broken are X-Y and W-Z, those to be formed are X-W and Y-Z and the activated bonds, which appear only in the activated complex, are X...Z and Y...W. Hence according to the present rule, among all the possible structures, which can be constructed by the use of the fixed values of the activated distances r_{XY}^* , r_{YZ}^* , r_{ZW}^* , and r_{WX}^* , such a structure, in which the sum of the energies of the activated bonds X...Z and Y...W becomes minimum, represents the structure of the activated complex, and this minimum sum of the energies gives the activation energy of the reaction, when it proceeds in the exothermic direction.

As the potential-energy function $U(r)$, which is necessary to carry out the calculations according to the present rule, Rydberg's equation:⁽²⁾

$$U(r) = -D_e \{a(r - r_e) + 1\} e^{-a(r - r_e)}$$

is adopted, where D_e represents the equilibrium dissociation energy, and r_e represents the equilibrium internuclear distance. And the constant a , which is characteristic of the pair of atoms, can be calculated by means of the equation:

$$a = 9.28 \times 10^{-3} \times \omega_e \sqrt{\mu/D_e} = 38.3 \times \sqrt{k_0/D_e},$$

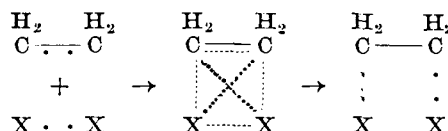
where ω_e is the frequency of vibration (cm^{-1}),

μ the reduced mass per mole, and k_0 the force constant (megadyne/cm.). So it can readily be shown that the activated distance r^* is given by the equation:

$$r^* = r_e + 1/a.$$

Addition of Hydrogen and Halogen to Ethylene

The addition reaction of hydrogen or halogen to ethylene:



can be treated by means of the present method, if one of the double bonds of ethylene is assumed to be independent of the reaction. The data necessary for the calculation are tabulated in Table 1, where D_e of C...C bond was assumed as the difference between that of C=C and C—C, r^* of C...C bond the arithmetical mean of the internuclear distance of C=C and C—C, and r_e of C-Cl, C-Br and C-I the sum of the covalent radii of respective atoms.

Table 1

Fundamental Data Necessary for the Calculation for the Addition of Hydrogen and Halogen to Ethylene

Bond	$D = D_e$, kcal.	r_e , Å.	ω_e , cm^{-1}	μ	a , Å. ⁻¹	r^* , Å.
C...C 41						1.44
Cl-Cl ⁽³⁾ 57						2.32
Br-Br ⁽³⁾ 46						2.64
I-I ⁽³⁾ 36						3.04
C-Cl	66.5 ⁽⁴⁾	1.76	712 ⁽⁵⁾	8.95	2.42	2.19
C-Br	54.0 ⁽⁴⁾	1.91	603 ⁽⁵⁾	10.42	2.46	2.32
C-I	45.5 ⁽⁴⁾	2.10	534 ⁽⁵⁾	10.96	2.44	2.51
H-H ⁽³⁾ 103						1.12
C-H	{ 87 ⁽⁴⁾ 80 ⁽⁶⁾	1.09 ⁽⁷⁾	2988 ⁽⁵⁾	0.923	2.86 2.98	1.44 1.43

The results of the calculation are given in Table 2 and compared with the observed values as well as those calculated by the semi-empirical method of Eyring. From Table 2

(3) Cf. the preceding paper.

(4) L. Pauling, "The Nature of Chemical Bonds," Cornell University Press, New York, 1940, p. 53.

(5) R. A. Ogg, Jr., and M. Polanyi, *Trans. Faraday Soc.*, **31**, 604 (1935).

(6) H. Sponer, "Molekülspektren und ihre Anwendungen auf chemische Probleme," Julius Springer, Berlin, 1935.

(7) L. Pauling, "The Nature of Chemical Bonds," p. 168.

(8) I. Nitta, "The Structure of the Molecule," Tokyo, 1942, p. 126.

(2) R. Rydberg, *Z. Phys.*, **73**, 381 (1932).

Table 2

Activation Energies for the Addition of Hydrogen and Halogen to Ethylene

Reaction	Activation energy					
	Addition			Reverse reaction		
	obs.	i	ii	obs.	i	ii
$\text{CH}_2:\text{CH}_2 + \text{H}_2 =$ $\text{CH}_3\cdot\text{CH}_3 + 30$	43	54.8 (46.4) ⁽¹⁰⁾	43 (48) ⁽¹¹⁾	—	84.8 (62.4) ⁽¹⁰⁾	—
$\text{CH}_2:\text{CH}_2 + \text{Cl}_2 =$ $\text{CH}_2\text{Cl}\cdot\text{CH}_2\text{Cl} + 36$	—	34.8	25.2	—	70.8	80.4
$\text{CH}_2:\text{CH}_2 + \text{Br}_2 =$ $\text{CH}_2\text{Br}\cdot\text{CH}_2\text{Br} + 21$	(30) ⁽⁹⁾	31.0	24.4	—	52.0	50.2
$\text{CH}_2:\text{CH}_2 + \text{I}_2 =$ $\text{CH}_2\text{I}\cdot\text{CH}_2\text{I} + 15$	—	20.2	22.4	(36) ⁽⁹⁾	35.2	30.0

i. According to the present method.

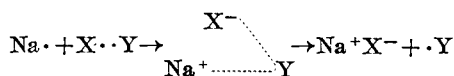
ii. According to the semi-empirical method of Eyring.

we can see that the present rule holds well for the addition of halogen but somewhat unsatisfactorily for the addition of hydrogen, while just the reverse is the case for the semi-empirical method of Eyring. But it may be worth noting to point out that the difference between the observed and calculated values according to the present method for the addition of hydrogen is remarkably reduced if $D_e = 80$ kcal. is used for the C-H bond as is shown in the table.

Atomic Reactions Involving Sodium and Halogen Atoms

Since the bond between sodium and halogen atoms can not be expressed in the usual manner by a single potential-energy curve, the present method can not be applied for the reaction involving these atoms without any additional assumptions. Polanyi *et al.* ⁽¹²⁾ have previously calculated the activation energies of the reactions of the sodium atom with methyl and phenyl halogenides by constructing the so-called potential-energy profile. But according to Eyring *et al.* ⁽¹³⁾ these calculated values may be in error, because no allowance is made for the resonance at the activated state.

If we assume for the reaction:



(9) Somewhat uncertain.

(10) $D_e = 80$ kcal. was used.(11) $\rho = 10\%$ was used, while for all the other cases $\rho = 14\%$.(12) R. A. Ogg and M. Polanyi, *Trans. Faraday Soc.*, **31**, 1375 (1935); M. G. Evans and E. Warhurst, *ibid.*, **35**, 593 (1939).

(13) G. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Company, New York and London, 1941, p. 322.

(14) L. Pauling, *ibid.*, p. 338.

the energy of the activated bond $\text{Na}^+\cdots\text{Y}$ in the same way as for the bond $\text{Na}\cdots\text{Y}$, we can apply the present rule for this type of reaction, where X denotes halogen and Y the hydrogen atom etc. The data necessary for the calculation are tabulated in Table 3, where D_e

Table 3

Fundamental Data Necessary for the Calculation for the Reactions Involving Sodium and Halogen Atoms

Bond	$D = D_e$, kcal.	r_e , Å.	ω_e , cm. ⁻¹	μ	α , Å. ⁻¹	r^* , Å.
Na+Cl ⁻	98 ⁽¹⁵⁾					2.88
Na+Br ⁻	88 ⁽¹⁵⁾					3.03
Na+I ⁻	72 ⁽¹⁵⁾					3.26
H-Cl ⁽¹⁶⁾	102					1.65
H-Br ⁽¹⁶⁾	87					1.80
H-I ⁽¹⁶⁾	71					2.05
Na-H	44	1.88 ⁽⁶⁾	1170.8 ⁽⁶⁾	0.96	1.60	2.50
C-Cl ⁽¹⁷⁾	67					2.17
C-Br ⁽¹⁷⁾	54					2.32
C-I ⁽¹⁷⁾	46					2.51
Na-C	33	2.31			1.63	2.92
Cl-Cl ⁽¹⁶⁾	57					2.32
Br-Br ⁽¹⁶⁾	46					2.64
I-I ⁽¹⁶⁾	36					3.04
Na-Cl	32	2.53			1.60	3.16
Na-Br	28	2.68			1.64	3.29
Na-I	25	2.87			1.68	3.47

of Na-H, Na-C, Na-Cl, Na-Br and Na-I were calculated as a geometrical mean of Na-Na and H-H, C-C, Cl-Cl, Br-Br and I-I respectively, r_e of Na-C, Na-Cl, Na-Br and Na-I as the sum of covalent radii of respective atoms, and α of Na-Br as the arithmetical mean of

(15) R. G. Pearson, *J. Chem. Phys.*, **17**, 969 (1949).

(16) Cf. preceding report.

(17) Cf. Table 1.

Na-Cl and Na-I. The activated distance r^* of Na^+Cl^- , Na^+Br^- and Na^+I^- was calculated by means of the equation:

$$r^* = 1.04 \times (r_{\text{Na}^+} + r_{\text{X}^-}),$$

derived as the distance corresponding to the inflexion point on the potential-energy curve of Na^+X^- given by Pauling:⁽¹⁴⁾

$$U(r) = 331 \times \left\{ -1/r + 296 \times 10^{-4} \right. \\ \left. \times (r_{\text{Na}^+} + r_{\text{X}^-})^8 / r^9 \right\},$$

where r_{Na^+} and r_{X^-} are the so-called standard radii of sodium and halogen ions respectively. The force constant k_0 for Na-C, Na-Cl and Na-I, which is necessary for the computation of a by means of the above-mentioned equation:

$$a = 38.3 \times \sqrt{k_0 / D_e},$$

was calculated according to the empirical rule of Badger:⁽¹⁸⁾

$$k_0 = c_{ij} / (r_e - \delta_{ij})^3,$$

where c_{ij} and δ_{ij} are the constants dependent on the rows of the periodic table containing the two atoms.

The results of the calculation for some reactions involving sodium and halogen atoms are tabulated in Table 4 and compared with the experimental results. The observed values enclosed in brackets are the mean[†] for several reactions with varying sorts of organic halides. From Table 4 it may be said that the present rule holds equally well for the reactions involving the heteropolar bonds under the

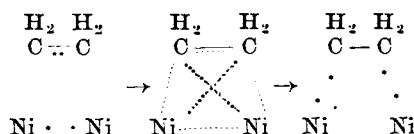
appropriate assumptions as for the ordinary reactions.

Adsorption of Hydrogen and Ethylene on Nickel

Since the dissociative adsorption of hydrogen on Nickel:



and the so-called associative adsorption of ethylene on Nickel:



are important processes relating to the heterogeneous catalytic reactions, we have applied the present rule for these processes. The data used for the calculation are tabulated in Table 5, where the data for H-H and C $\cdots$ C are the

Table 5
Fundamental Data Used for the Calculation of the Adsorption on Nickel

Bond	$D = D_e$, kcal.	r_e , Å.	ω_e , cm. ⁻¹	μ	a , Å. ⁻¹	r^* , Å.
H-H	103					1.12
Ni-H	60 ⁽¹⁹⁾	1.48 ⁽⁶⁾	1900 ⁽⁶⁾	0.983	2.25	1.93
C $\cdots$ C	41					1.44
Ni-C	38 ⁽²⁰⁾	1.92 ⁽²¹⁾			2.74	2.29

same as in Table 1, and the constant a of Ni-C was computed by means of Badger's rule. The result of the calculation are given in Table 6 and graphically shown in Fig. 1, together with the results of the calculations by other authors. The values of the Ni-Ni distance given in the second column of Table 6 are chosen, taking into consideration the actual structure of the nickel crystal surface as is shown in Fig. 2, where the radii of the two circles, *i. e.*, 4.98 Å. and 6.02 Å. represent the length of the linear form of the activated complexes:

Table 4
Activation Energies for the Atomic Reactions Involving Sodium and Halogen Atoms

Reaction	Activation energy	
	obs.	calc.
$\text{Na} \cdot + \text{Cl} \cdot \text{H} \rightarrow \text{Na}^+\text{Cl}^- + \text{H} - 4$	6	7.3
$\text{Na} \cdot + \text{Br} \cdot \text{H} \rightarrow \text{Na}^+\text{Br}^- + \text{H} + 1$	0	2.2
$\text{Na} \cdot + \text{I} \cdot \text{H} \rightarrow \text{Na}^+\text{I}^- + \text{H} + 1$	0	1.2
$\text{Na} \cdot + \text{Cl} \cdot \text{CR} \rightarrow \text{Na}^+\text{Cl}^- + \text{CR} + 31$	(5.5)	2.1
$\text{Na} \cdot + \text{Br} \cdot \text{CR} \rightarrow \text{Na}^+\text{Br}^- + \text{CR} + 34$	(3.0)	1.4
$\text{Na} \cdot + \text{I} \cdot \text{CR} \rightarrow \text{Na}^+\text{I}^- + \text{CR} + 26$	(1.2)	0.8
$\text{Na} \cdot + \text{Cl} \cdot \text{Cl} \rightarrow \text{Na}^+\text{Cl}^- + \text{Cl} + 41$	0	2.4
$\text{Na} \cdot + \text{Br} \cdot \text{Br} \rightarrow \text{Na}^+\text{Br}^- + \text{Br} + 42$	0	1.2
$\text{Na} \cdot + \text{I} \cdot \text{I} \rightarrow \text{Na}^+\text{I}^- + \text{I} + 36$	0	0.5

(18) R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934); *ibid.*, **3**, 710 (1935).

(19) G. Okamoto, J. Horiuchi and K. Hirota, *Scient. Papers Inst. Phys. Chem. Res. Tokyo*, **29**, 223 (1936).

(20) J. Horiuchi, *Catalyst*, **2**, 1 (1947).

(21) A. Sherman, C. E. Sun and H. Eyring, *J. Chem. Phys.*, **3**, 49 (1935).

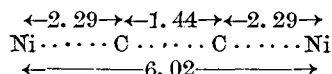
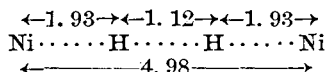


Table 6

Activation Energies for the Adsorption of Hydrogen and Ethylene on Nickel

Ads. of	Ni-Ni distance, Å.	Activation energy			
		i	ii	iii	iv
H ₂	2.38				24
	2.49	37.0	34		
	3.52	26.4	16		
	4.32	19.7			
	4.98	16.0			
C ₂ H ₄	2.49	16.1		3.5	
	3.52	10.1		3.3	
	4.32	6.9			
	5.56	3.9			
	6.02	3.2			

- i. According to the present method.
- ii. Calculated by Okamoto *et al.*⁽¹⁹⁾ according to the semi-empirical method of Eyring, putting $\rho_{\text{HH}}=11\%$, $\rho_{\text{NH}}=24\%$, $\rho_{\text{NIN}}=37\%$.
- iii. Calculated by Keii⁽²²⁾ according to the semi-empirical method of Eyring, putting $\rho_{\text{CC}}=14\%$, $\rho_{\text{NC}}=26\%$, $\rho_{\text{NIN}}=37\%$.
- iv. Calculated by Sherman *et al.*⁽²¹⁾ according to the semi-empirical method of Eyring, putting $\rho_{\text{HH}}=14\%$, $\rho_{\text{NH}}=20\%$, $\rho_{\text{NIN}}=30\%$; the Ni-Ni distance 2.38 Å. is not present on the crystal surface of nickel.

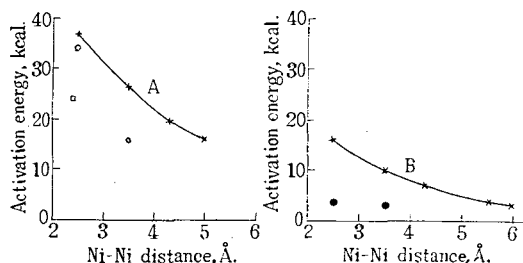
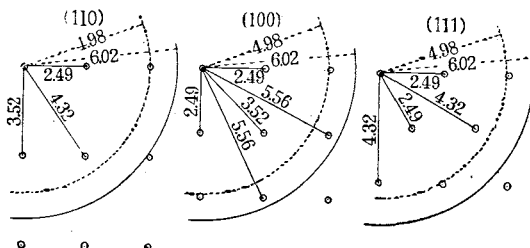
Fig. 1.—Activation energies for the adsorption of hydrogen (curve A) and ethylene (curve B) on nickel: x, Kume *et al.*; o, Okamoto *et al.*; □, Sherman *et al.*; ●, Keii.

Fig. 2.—Ni-Ni distances on the surface of nickel.

respectively, since according to the present theory no longer forms than these can be considered by the fixed values of each activated internuclear distance. But as the activation energy decreases with the increasing length of the activated complex, the Ni-Ni distance, which is actually present on the crystal surface of nickel and for which the activation energy becomes minimum is 4.32 Å. for the adsorption of hydrogen and 5.56 Å. for the adsorption of ethylene.

Although we have no observed value for the activation energy, which are accurate enough to be directly compared with these calculated values, the rate of adsorption of ethylene on nickel has been measured by Steacie and Stovel.⁽²³⁾ By extrapolating the observed values of these authors Keii has obtained the value $3.39 \times 10^{12} \text{ sec.}^{-1} \text{ cm.}^{-2}$ as the initial rate at 293°K. and 19.25 mm. Hg of initial pressure. If we calculate the same rate under the same conditions according to the statistical method presented by Keii by the use of our calculated value of the activation energy, *i. e.*, 3.9 kcal., we obtain the value $7.73 \times 10^{13} \text{ sec.}^{-1} \text{ cm.}^{-2}$

Summary

1. The empirical rule for the calculation of the activation energy previously proposed has been applied for some more complicated reactions.
2. For the addition reaction of halogen to ethylene the calculated values agree very well with the observed values, but for that of hydrogen the calculated value was somewhat greater than the observed.
3. For the atomic reactions involving sodium and halogen atoms the calculated values agree well with the observed under the appropriate assumptions.
4. The activation energies for the adsorption of hydrogen and ethylene on nickel have been calculated, and the initial rate of adsorption of ethylene calculated by the use of the obtained value of the activation energy was compared with the experimental value of Steacie and Stovel.

The authors wish to express their sincere thanks to Prof. T. Titani for his interest to this research.

Faculty of Science, Osaka University, Osaka

(22) T. Keii, *Catalyst*, **3**, 47 (1948).(23) Steacie and Stovel, *J. Chem. Phys.*, **2**, 581 (1934).

Research on Activation Energy. III. On Activation Energy for the Adsorption of Hydrogen on Reduced Copper

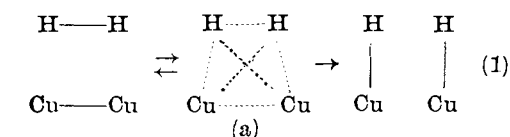
By Sanshiro KUME and Kiyoteru OTOZAI

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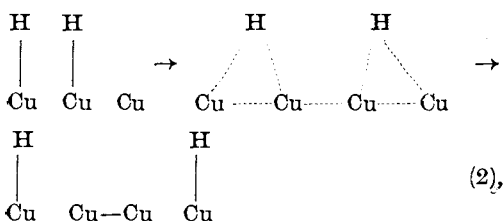
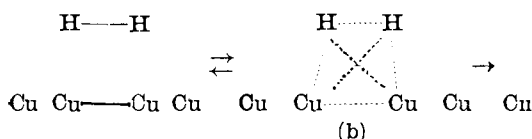
Introduction

Because of experimental difficulties most of the hitherto observed values of the activation energy for the adsorption of hydrogen on metals are not fully reliable. T. Kwan⁽¹⁾ has recently obtained, however, the reliable value for the activation energy of the adsorption of hydrogen on reduced copper, since in this case the velocity of adsorption has a moderate value. So we intend to calculate the activation energy for this process by means of the empirical rule which we have previously proposed,⁽²⁾ as a typical example of the heterogeneous reaction.

In order to calculate the activation energy for a reaction we must have clear knowledge of the mechanism of the given reaction. Since the velocity of the adsorption of hydrogen on reduced copper was found by the experiment of Kwan⁽¹⁾ to be the first order with respect to hydrogen, the mechanism of the reaction must be either



or



if we assume the hydrogen molecule to be

adsorbed dissociatively.⁽³⁾ So long as no information is given on the adsorption isotherm, it is not possible to decide which of the above given mechanisms is the correct one. But if it is assumed that the configuration of the activated complex (a) of the mechanism (1) and that (b) of the mechanism (2) are the same, the activation energy must be the same for both mechanisms. The activation energy for the reaction has been calculated under this assumption, and compared with the observed value of Kwan.

Calculation of Activation Energy

The method of the calculation refers to the previous paper.⁽²⁾ The fundamental data used for the calculation are given in Table 1, where

Table 1

Fundamental Data Used for the Calculation

Bond	D_e (kcal./mole)	r_e (Å.)	ω_e (cm. ⁻¹)
H—H	109.2 ⁽⁴⁾	0.75 ⁽⁴⁾	4276 ⁽⁴⁾
Cu—H	62.2 ⁽⁵⁾	1.46 ⁽⁴⁾	1940.1 ⁽⁴⁾

D_e is the equilibrium dissociation energy, r_e the internuclear distance and ω_e the frequency of the vibration of the given bond.

If we calculate the activated distance r^* , the distance between two atoms in the activated state, for H—H and Cu—H from the data given in Table 1 by the use of the equations⁽²⁾

$$r^* = r_e + 1/\alpha$$

$$\alpha = 9.28 \times 10^{-3} \omega_e \sqrt{\mu/D_e}$$

we obtain $r^* = 1.12$ Å. and $\alpha = 2.68$ Å.⁻¹ for H—H and $r^* = 1.90$ Å. and $\alpha = 2.27$ Å.⁻¹ for Cu—H. But since the activated distance has a fixed

(3) G. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Company, New York and London, 1941, p. 356.

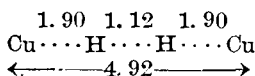
(4) H. Sponer, "Molekülspektren und ihre Anwendungen auf chemische Probleme," Julius Springer, Berlin, 1935. D_e (109.2 kcal.) is sum of the ordinary dissociation energy (103 kcal.) and the zero point energy (6.2 kcal.).

(5) A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall, London, 1947. In the calculation of D_e the zero point energy was neglected in view of the uncertainty of the spectroscopic value itself.

(1) T. Kwan, *J. Research Inst. Catalysis (Hokkaido Univ.)*, 1, 95 (1949); T. Kwan, *This Bulletin*, 23, 73 (1950).

(2) K. Otozai, *This Bulletin*, 24, 218 (1951); K. Otozai, *Collected Papers from the Faculty of Science, Osaka Univ.*, No. 20; S. Kume and K. Otozai, *This Bulletin*, 24, 257 (1951).

value for the respective sort of bond, the maximum possible distance between Cu-Cu for which the dissociative adsorption of hydrogen can occur, must be equal to the total length, i. e., 4.92 Å., of the linear or stretched form of the activated complex:



On the other hand there are seven possible inter-atomic distances between the adjacent atoms on the surfaces of the copper crystal as is shown in Fig. 1, because copper crystallizes in a face-centered cubic lattice having a

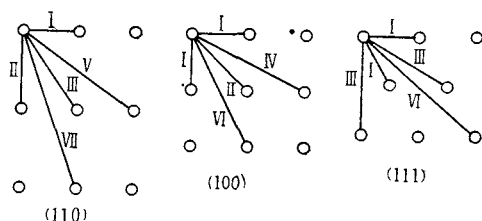


Fig. 1.—Inter-atomic distances on the surface of copper crystal: I = $\sqrt{1/2}a = 2.56$ Å.; II = $a = 3.61$ Å.; III = $\sqrt{3/2}a = 4.42$ Å.; IV = $\sqrt{5/2}a = 5.71$ Å.; V = $\sqrt{3}a = 6.25$ Å.; VI = $\sqrt{7/2}a = 6.74$ Å.; VII = $\sqrt{9/2}a = 7.65$ Å.

lattice constant $a = 3.609$ Å. But since, as pointed above, no dissociative adsorption of hydrogen can occur on a pair of copper atoms, whose inter-atomic distance is larger than 4.92 Å., only three sorts of inter-atomic distances I, II and III need to be considered for the calculation of the activation energy for the adsorption. Furthermore, the adsorption of hydrogen on copper is clearly an exothermic process.⁽⁶⁾ Then the energy of activation in question can readily be calculated by means of our empirical rule, according to which the activated complex must have a symmetrical form as shown in Fig. 2 for the present case, and the sum of the energies of the two diagonal Cu-H bonds which appear only in the activated complex and hence have been called the “activated bonds,” represents the energy of the activation for the reaction. For instance, when

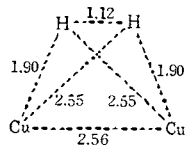


Fig. 2.—The activated complex for the adsorption on the Cu-Cu distance of 2.56 Å.

hydrogen is adsorbed on the pair of copper atoms, whose mutual distance is equal to 2.56 Å., the length of the two activated bonds becomes 2.55 Å. as is shown in Fig. 2. Hence, the energy of each activated bond has been calculated as 18.3 kcal. by putting $r = 2.55$ Å. in Rydberg's equation⁽²⁾ and twice this value, i. e., 36.6 kcal./mole represents the activation energy for the given adsorption.

Similar calculations have been made for the other two Cu-Cu distances and the results are presented in Table 2 and Fig. 3.

Table 2

The Activation Energies of Adsorption of H_2 on Cu

Cu-Cu distance, Å.	Activation energy, kcal./mole
I: 2.56	36.6
II: 3.61	25.4
III: 4.42	19.4

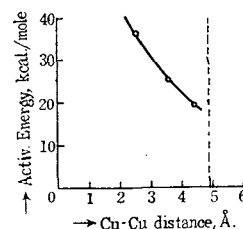


Fig. 3.—The activation energies of adsorption of H_2 on Cu.

Discussion

As will be seen from Table 2 and Fig. 3, the energy of activation for the adsorption of hydrogen on copper decreases considerably as the Cu-Cu distance increases. Hence, if the copper metal in question contains no amorphous parts and the rate of adsorption on various parts of the copper surface is mainly determined by the magnitude of the activation energy, the surfaces (110) and (111), which contain the largest Cu-Cu distance III (cf. Fig. 1), will be adsorbed preferentially by hydrogen and the surface (100), which contains only I and II distances, may be ignored. The activation energy, which will be observed, will thus be equal to 19.4 kcal. corresponding to the adsorption at the largest Cu-Cu distance III. This value agrees, however, very well with the observed value 20 kcal./mole of Kwan, although this agreement may be to some extent an accidental one, when it is taken into consideration that the general accuracy of the present

(6) The heat of adsorption was computed by Kwan as larger than 35 kcal./mole.

rule is ± 3 kcal. and the estimation of the fundamental data may contain some errors. The above obtained conclusion that hydrogen can be adsorbed more easily on the surfaces (110) and (111) than (100) of copper crystal has not yet been experimentally ascertained. But it may be worth pointing out the fact that according to the experiment of Leidheiser and Gwathmey⁽⁷⁾ the catalytic reaction between hydrogen and oxygen takes place more quickly on the surface (111) than on the surface (100) of copper.

(7) H. Leidheiser, Jr., and A. T. Gwathmey, *J. Am. Chem. Soc.*, **70**, 1200, 1206 (1948); H. Leidheiser, Jr., and A. R. Meelheim, *ibid.*, **71**, 1122 (1949).

Summary

The activation energy for the activated adsorption of hydrogen on copper metal has been calculated by the use of the empirical rule previously proposed. The calculated value 19.4 kcal./mole agrees very well with the observed value 20 kcal./mole of T. Kwan. It has been concluded that hydrogen will be adsorbed more quickly on the surfaces (110) and (111) than on the surface (100) of copper crystal.

The authors wish to express their sincere thanks to Prof. T. Titani for his interest in this research.

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Statistical Thermodynamics of Solution of Rigid Rod-like Molecules

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Introduction

Recent theories of polymer solutions may be classified into two types, namely, the one based on the lattice model which was developed by Flory,⁽¹⁾ Huggins,⁽²⁾ and others, and the other represented by Zimm's treatment⁽³⁾ formally equivalent to that of imperfect gas theory. These two, however, include many questions to be discussed. The former involves a somewhat paradoxical situation in the separate evaluation of the entropy and energy terms in the partial molal free energy expression, although the success of the semi-empirical free energy expression justifies considerable confidence being placed in its application to thermodynamic properties of polymer solutions. Namely the statistical configurations of polymer molecules in solution must be influenced by the energetical interaction between polymer and solvent, and the heat of dilution must be determined by these configurations. The latter is more reasonable on

this point, but often its calculation is not so easy as applicable to the practical cases. Furthermore, polymer-solvent interaction is not taken up explicitly, although the "average force potential" between segments involves it implicitly.

Now in the case of rigid large molecules circumstances are extremely simplified because the configurations are not affected by the energetical interaction. Thus the separate evaluation of the energy and entropy terms will be possible in this case. From this point of view, the above two methods were discussed in the present paper in relation to the most simple model for rigid rod-like molecules.

Discussion of Zimm's Result

In spite of its great simplicity, the theory of solution of rigid rod-like molecules has not been presented except by Zimm, who obtained the following result⁽³⁾

$$A_2 = \pi N_0 d l^2 / 4M^2, \quad (1)$$

where A_2 ⁽⁴⁾ is the second coefficient in the

(1) P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942); **9**, 680 (1941).

(2) M. L. Huggins, *J. Chem. Phys.*, **9**, 440 (1941); *J. Phys. Chem.*, **46**, 151 (1942).

(3) B. H. Zimm, *J. Chem. Phys.*, **14**, 164 (1946).

(4) The A_2 values characterize the most important deviation from Raoult's law.

equation expressing osmotic pressure as power series in concentration analogous to the virial expression for gases, N_0 Avogadro's number, d the diameter, l the length, and M the molecular weight of the rod-like molecules. Employing the relationship $\pi d^2 l / 4 = M / N_0 \rho$, Eq. (1) reduces to

$$A_2 = 1 / \rho^2 (\pi / 4) d^3 N_0, \quad (2)$$

where ρ is density of the solute. This result shows that Eq. (1) is not adequate in distinguishing the nature of actual polymer-solvent systems, since A_2 is a function of only ρ and d , and these values will not differ so much for various cellulose derivatives which are supposed to be rod-like molecules.⁽⁵⁾

In recent theories osmotic pressure expression involves one or two parameters which were introduced through some approximate treatments. These parameters are insufficient to account for experimental data or are not of theoretical significance (for example, the well used μ is merely an empirical one characterizing a given system). Actually, the partial molal free energy of dilution is a function of size and shape of solvent and solute molecules (spacial factors) and energetical interaction between solvent and solute. But even if the above factors were introduced in the osmotic pressure expression through amplification and refinement of the existing theory, we cannot compare them with osmotic data without estimating some of these factors in some other

way. It may be said, however, that the approximate treatments in current theories must be improved by knowledge of the actual polymer. Now it must be noted that Zimm's treatment (the "rigid body approximation" for large molecules) is obviously an approximation applicable only to the case of long rigid rod-like molecules suspended in an effectively continuous and structureless solvent. Thus the effect of the above spacial factors on the entropy term must be investigated theoretically as well as experimentally. For this purpose, we adopted a lattice model consistent with the information obtained from the molecular constructions of solute and solvent.

Eq. (2) may be written

$$A_2 = \{V_1 / (\pi / 4) d^3 N_0\} / V_1 \rho^2 \\ = \frac{1}{2} \{ (V_1 / N_0) / (\pi / 8) d^3 \} / V_1 \rho^2 \quad (3)$$

where V_1 is molal volume of solvent. Thus Zimm's result coincides with Flory's⁽¹⁾, based on lattice model as seen in his first paper on polymer solutions, when the volume of the segment equals $(\pi / 8) d^3$. It is interesting that

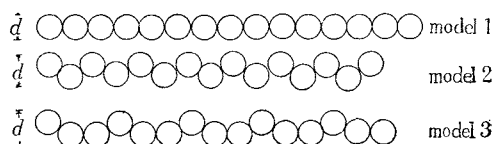


Fig. 1.—Hypothetical model of long rigid rod-like molecules.

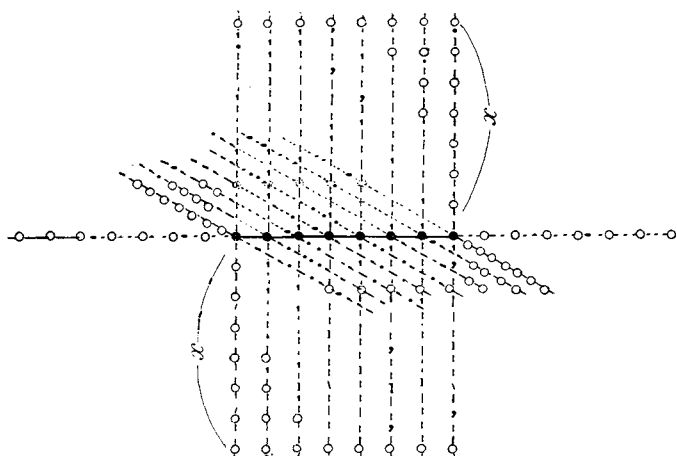


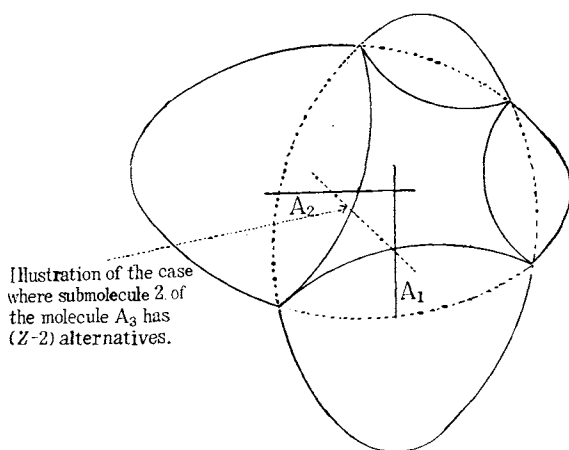
Fig. 2.—Illustration of the region v (cubic lattice): $\cdots\cdots\cdots$ indicates the first molecule A_1 .

(5) It is supposed from the information on viscosity and light scattering etc., that the molecules of cellulose derivatives are not entirely rigid rods, but are somewhat flexible especially when they are long. Our procedure may also be applicable to such cases if the effect of energetical interaction on configurations of polymer molecules can be neglected, since it involves little bending of successive submolecules (See Fig. 1).

this volume equals that of the submolecule assumed in the following section.

New Treatment of Solution of Rigid Rod-like Molecules

Let us consider a hypothetical model of the

Fig. 3.—Illustration of the region v' .

rod-like molecules consisting of x spherical submolecules as illustrated in Fig. 1. For model 1 the volume of the submolecule is $\pi(d/2)^3$ and agrees with that mentioned above. The following procedure may be allowed for models 2, 3, etc.,⁽⁶⁾ although somewhat different values must be adopted for the volume of the submolecule.⁽⁶⁾ Now we assume N_0 lattice sites throughout the solution and make the above submolecule correspond to one lattice site. The type of lattice must be determined by the relative position of the submolecules in solution (accordingly by coordination number z). The solute molecules are first added one at a time, then the solvent molecules, counting the number of different ways setting each molecule in the lattice sites one after another in order to obtain the total number of configurations.

Submolecule 1 of molecule A_1 (the first solute molecule) can be placed in any of N_0 sites. Submolecule 2 of this molecule has a number of alternatives, z , equal to the coordination number. The position of the molecule A_1 is fixed when that of its first two submolecules is, because the successive submolecules must be connected linearly.⁽⁶⁾ Thus the number of the configuration for the molecule A_1 is zN_0 . Next, the second molecule A_2 is added. Here we consider linearly connected x sites starting from each submolecule of the first molecule for all coordinations in the circumference of the molecule, as illustrated in Fig. 2. The total number of these sites is given by⁽⁶⁾

(6) The v values given by Eq. (4) are a little larger than what we need, owing to overlapping of some of the v sites in a certain type of lattice, but are approximately available to such cases. One of the most simple cases where Eq. (4) holds strictly (cubic lattice) is illustrated in Fig. 2.

$$v = (z-2)(x-1)x + 3x - 2 \doteq (z-2)x^2 - (z-5)x. \quad (4)$$

When submolecule 1 of the molecule A_2 is added in these sites, the number of configurations for the molecule A_2 is $v(z-1)$.⁽⁷⁾ When it is added in other (N_0-v) sites, the number of configurations is $(N_0-v)z$.

Similarly for the third molecule A_3 , we may write $(N_0-v')z + (v'-2x)(z-1)^*$ when the molecule A_3 was added in the above v sites, and $(N_0-2v)z + 2(v-x)(z-1)$ when it was added in other (N_0-v) sites. Here the meaning of v' may be seen from Fig. 3, and $(z-1)^*$ is not strictly equal to $(z-1)$, although the difference between them is negligibly small.⁽⁸⁾

Proceeding in this manner to the N -th solute molecule, making the product of corresponding factors, and summing up all of them, a great number of terms are obtained. When concentration of solute is very small, these terms can be arranged as follows, assuming that the terms containing more than two of $(v-x)$ or $(v'-2x)$ etc. may be neglected, and that $v' \doteq 2v$ ⁽⁹⁾:

$$\begin{aligned} & N_0(N_0-v)(N_0-2v) \cdots \{N_0-(N-1)v\} z^N \\ & + [N_0(N_0-v) \cdots \{N_0-(N-2)v\} (N-1)(v-x) \\ & + N_0(N_0-v) \cdots (N-2)(v-x) \{N_0-(N-1)v\} \\ & + N_0(v-x)(N_0-2v) \cdots \\ & \quad \{N_0-(N-1)v\}] z^{N-1} (z-1) \\ & = z^N \{N_0(N_0-v) \cdots [N_0-(N-1)v]\} \times \\ & \quad [1 + (v-x)/(N_0-v) \times (z-1)/z + \cdots \\ & \quad (N-1)(v-x)/[N_0-(N-1)v] \times (z-1)/z] \quad (5) \end{aligned}$$

Thus the total number of configurations for N solute molecules is given by⁽¹⁰⁾

$$W = z^N / 2^N N! \times \{N_0(N_0-v) \cdots [N_0-(N-1)v]\} \times \{1 + (v-x)/(N_0-v) \times (z-1)/z + \cdots$$

(7) The second molecule overlaps with the first in any one of z linearly connected sites starting from submolecule 1 of the second molecule A_2 for one coordination of it.

(8) When one of certain sites on the plane containing the previously added two molecules with in the range v' is occupied by submolecule 1 of the molecule A_3 , the number of alternatives of its second submolecule is $Z-2$, but the number of these sites are very small in this range (see Fig. 3).

(9) Obviously from Fig. 3, this approximation is unsatisfactory, but the calculation is tedious and it is almost hopeless to think of getting results without employing it.

(10) This procedure is formally equivalent to Ichimura's on dilute solutions of coiled polymer (*J. Phys. Soc. Japan*, 3, 308 (1948)).

$$\times (N-1)(v-x)/[N_0 - (N-1)v] \times (z-1)/z \quad (6)^{(11)}$$

$$\begin{aligned} & \div z^N / 2^N N! \times (N_0/v)! / (N_0/v - N)! \\ & \times \{1 + (z-1)/z \times N^2 / 2N_0 \\ & \times (v-x - 2vxN/3N_0)\}, \quad (6') \end{aligned}$$

where the value 2 is the symmetrical number. Here N_0 is replaced by its equivalent $n+xN$ and n is regarded as the number of solvent molecules when each of them equals the submolecule in size and shape. After addition of all the solute molecules, the remaining sites are filled with the solvent molecules. This introduces no increase in the number of distinguishable configurations. Introducing the relationship $\Delta S/R = \ln W$ and replacing factorial terms with Stirling's approximation, the entropy of the system is obtained. Then, deriving the entropy of mixing by the usual manner and differentiating it with respect to n , the partial molal entropy becomes

$$\begin{aligned} \Delta \bar{S}_1 &= R \{ 1/v \times \ln [1 - vN/(n+xN)] \\ & - (z-1)/2z \times (v-x)[N/(n+xN)]^2 \\ & + vx(z-1)/6z \times [N/(n+xN)]^3 + \dots \} \\ & = R \{ v_2^2/x + [v/2x^2 - (z-1)/2z \\ & \times (v-x)/x^2] v_2^2 + \dots \}, \quad (7) \end{aligned}$$

where $v_2 = xN/(n+xN) =$ volume fraction of solute.

In our case, formulation of the energy term is simplified because we can evaluate it apart from the configurations of the system. Thus the heat of mixing may be written⁽¹²⁾

$$\Delta H = K(z-2)xN(1-v_2), \quad (8)$$

where $K = \varepsilon_{12} - (\varepsilon_{11} + \varepsilon_{22})/2$.

$$\text{Or } \Delta \bar{H}_1 = K(z-2)v_2^2 = \alpha v_2^2 \quad (9)$$

(these notations are similar to those employed usually).

Combining Eq. (9) with Eq. (7), there is obtained for partial molal free energy

$$\begin{aligned} \Delta \bar{F}_1 &= \Delta \bar{H}_1 - T\Delta \bar{S}_1 = -RT \{ v_2/x + [v/2x^2 \\ & - (z-1)/2z \times (v-x)/x^2 - \alpha/RT] v_2^2 \}. \quad (10) \end{aligned}$$

Hence, according to the definition of A_2 ,

$$\begin{aligned} A_2 &= 1/V_1 \rho^2 \times \{ v/zx^2 + (1-1/z)/x - \alpha/RT \} \\ &= 1/V_1 \rho^2 \times \{ (z-2)/2z + (z-3-2/z)/2x \\ & - \alpha/RT \} \div 1/V_1 \rho^2 (1/2 - 1/z - \alpha/RT). \quad (11)^{(13)} \end{aligned}$$

This result coincides with that of Huggins, who derived it on solution of coiled molecules. However, it is possible to point out that the coordination number, z , holds its original significance explicitly in our case, since such approximation averaging the "distribution density" as used by Huggins is not adopted here.

Next, we adopted an approximate method introducing the effect of size and shape of solvent on the viewpoint that Flory's modification⁽¹⁾ for the entropy expression owing to the volume ratio β of segment for solvent may be unsatisfactory and that the spacial factors should be considered in more detail. When the above submolecule is a times larger than the solvent molecule, we assume conventionally a lattice sites in each submolecule, taking the coordination number, z' , determined by the spacial factors of the solvent.

As mentioned above, the operation of packing the solvent molecules which equal in size and shape the submolecule in the remaining sites is exactly equivalent to that of setting solute molecules in the sites without considering the existence of solvent molecules. Therefore, the total number of different configurations W'' in this case will be obtained from W' , which is substituted by aN_0 for N_0 , an for n , and axN for xN , in the above expression for W , multiplying by a factor due to the fact that a solvent molecules must be in a group in the new lattice sites. Hence

$$W'' = W' W_1 \left/ \binom{aN_0}{an} \right., \quad (12)$$

where W_1 is the number of different ways in which n molecules, each occupying a sites, can be packed in aN_0 sites without overlapping. Affording a good approximation for small and spherical molecules, W_1 was evaluated by Ōsawa as follows⁽¹⁴⁾:

$$W_1 = \left\{ \binom{N_0}{n} z'^N \right\}^a \left/ \binom{z'N_0}{n} \right.^{a-1} \quad (13)$$

Entropy of this system is obtained in the

(11) The terms in the latter bracket in Eq. (6) are arranged as seen here, employing the relations: $(N-1)(v-x)/[N_0 - (N-1)v] \div (N-1) \times v/N_0 - (N-1) \times n/N_0 \times [1 + (N-1)v/N_0]$, $(v/N_0 \ll 1, n/N_0 \ll 1)$; $1+2+\dots+(N-1) = N(N-1)/2$; $1^2+2^2+3^2+\dots+N^2 = N(N+1) \times (2N+1)/6$.

(12) This result is the same as that for coiled molecules, since the number of polymer-solvent pairs are expressed as seen here in all cases.

(13) Perhaps employing another procedure, Zimm obtained a similar result (J. H. Hildebrand and R. L. Scott "The Solubility of Non-electrolytes," Reinhold Publishing Corp., New York, 1950).

(14) F. Ōsawa, *Busseiron Kenkyu*, 8, 10 (1947).

same manner as mentioned previously. Differentiating the entropy of mixing with respect to an , there is obtained for the partial molal entropy:

$$\begin{aligned}\Delta\bar{S}_1'' &= \Delta\bar{S}_1 + R\{(a-1)/a \times \ln(1-v_2) \\ &\quad + (z'-1) \ln(1+v_2/(z'-1))\} \quad (14) \\ &= R\{v_2/x + [1/2 - 1/z - (a-1)/2a \\ &\quad + (a-1)/a(z'-1)]v_2^2 + \dots\}. \quad (14')\end{aligned}$$

Hence,

$$A_2 = 1/V_1\rho^2 \times [1/2a - 1/z + (a-1)/a(z'-1) - \alpha/RT]. \quad (15)$$

This procedure may detect the effect of size and shape of solvent on the entropy term approximately, although strictly speaking it can be reasonable only when the types of the above two lattices are one and same ($z=z'$). When $z=z'$, $z \gg 1$, Eq. (15) reduces to

$$A_2 \approx 1/V_1\rho^2 \times (1/2a - 1/az - \alpha/RT). \quad (16)$$

Eq. (16) corresponds to Flory's modification for Eq. (11). The values of entropy terms in Eq. (15) and (16) are estimated for cellulose derivatives-various solvents systems, assuming $z=z'=12$ (closely compacted) and that the volume of the submolecule $= \pi d^3/8 \doteq 1000 \text{ \AA}^3$ ($d \doteq 7 \text{ \AA}$).⁽¹⁵⁾ These values are shown in Table 1, being

Table 1
Estimation of Values of the Entropy
Term for Various Solvents

Solvent	a	$1/2a - 1/az$	$1/2a - 1/z + (a-1)/a(z'-1)$	$1/2a$
Acetone	8.22	0.050	0.058	0.061
Methyl acetate	7.59	0.055	0.062	0.066
Ethyl acetate	6.17	0.068	0.074	0.081
Butyl acetate	4.63	0.091	0.096	0.108
Cyclo-hexanone	5.76	0.072	0.079	0.087
Dioxan	7.07	0.059	0.066	0.071
Chloroform	7.51	0.056	0.063	0.067

compared with the values of $1/2a$. Obviously from our assumption, this procedure is concerned only with dilute solutions. At high concentrations, Flory's result⁽¹⁾ $\Delta\bar{S}_1 = v_2/x + 1/2a \times v_2^2 + \dots$ in his early papers may be also applicable to our case. As is shown in

the preceding section, Zimm's result corresponds to Flory's approximation, if we assume the "segment" as mentioned above. In the commonly used range of concentrations, the true value of A_2 is supposed to be a little greater than that calculated by Eq. (15) owing to the terms neglected in Eq. (5).

Now the well-used parameter μ is usually expressed by the form $\beta + \alpha/RT$. Regarding the correlation of the value of β with molecular details of polymer solutions, Zimm⁽¹⁶⁾ has shown that β would have a value of 0.49 for long rigid rods. When the effect of the size of the solvent is not considered, the value 0.49 for β corresponds to $z \doteq 2.0$, showing that the relation $\beta = 1/z$ is not available to practical cases. On the other hand, our procedure anticipates values of β in the range 0.40~0.44, depending principally on the values of a . The exact values to be assigned to a , however, cannot be deduced theoretically because of the difficulty of bridging the gap between the actual polymer in solution on one hand and the idealized model composed of submolecules arranged in the hypothetical lattice on the other. Namely, the difficulty in our estimation of the entropy terms lies in the estimation of the size of the above submolecule. It is supposed, however, that the values of β estimated here may be rather appropriate from Zimm's evaluation in Hildebrand's book quoted in the footnote (13), although we cannot know his procedure in detail.

Many osmotic data for samples selected systematically and the facts from other physico-chemical measurements will enable us to estimate the entropy and energy terms respectively. As is shown in Table 1, the contribution of the entropy of dilution to A_2 will not differ so much for the systems of cellulose derivatives and various solvents, and especially if more data were available to the systems, in a series of solvents for a given polymer, we could estimate

Table 2
Comparison with Experiments

System	Temp., °C.	$A_2 V_1 \rho^2$ entropy $\times 10^4$ (calc.)	$A_2 \times 10^4$ (exper.)
Nitrocellulose in acetone	{20	0.054	10.89
	{40		10.23
Nitrocellulose in methyl acetate	{20	0.062	11.97
	{40		11.17
Nitrocellulose in ethyl acetate	{20	0.074	11.68
	{40		10.07
Nitrocellulose in butyl acetate	{20	0.096	7.85
	{40		7.32

(15) From our knowledge of viscosity, and light scattering etc. d is supposed to be in the range of 8~15 Å.

(16) B. H. Zimm, Am. Chem. Soc. Meeting, Sept. 1947. (P. Doty, M. Brownstein and W. Schlener, *J. Phys. Coll. Chem.*, **53**, 213 (1949)).

the energy term and solvent power from them. In Table 2, the A_2 values calculated from our experiment⁽¹⁷⁾ on nitrocellulose (N content 10.5 %) are compared with those evaluated above.⁽¹⁸⁾ Table 2 shows that acetone, methyl acetate, and ethyl acetate are alike better solvents than butyl acetate.

Summary

(1) A new thermodynamic relationship applicable to dilute solution of rigid rod-like molecules was derived, employing a lattice model.

(2) Small deviation from Zimm's result for rigid rod was discussed here, considering the

effect of size and shape of solvent and solute.

(3) Although quantitative discussion is impossible because of the difficulty of the estimation of the size of the submolecule, it may be said that the contribution of entropy of dilution to A_2 (the second virial coefficient in osmotic pressure expression as power series in concentration) will be less for rigid rod-like molecules than for coiled molecules, and furthermore, the difference between such systems as cellulose derivatives in a series of solvents will be very small.

The author wishes to thank his director K. Makishima for constant encouragement and many helpful suggestions. This report was presented at the Fourth Meeting of the Chem. Soc. Japan, at Tokyo University, April, 1951.

(17) K. Ishikawa and T. Kawai, paper read at the Fourth Meeting of Chem. Soc. Japan, April, 1951.

(18) The usual relations, $\Delta\bar{S}_1 = (V_1\pi - V_1'\pi')/(T - T')$ and $\Delta\bar{H}_1 = (V_1\pi/T - V_1'\pi'/T')/(1/T - 1/T')$, often give the values of $\Delta\bar{S}_1$ and $\Delta\bar{H}_1$ with error as great as 100–200%.

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Studies on Foams. VII. Theory of Foam Formation of Dyestuff Solution

By Masayuki NAKAGAKI

(Received July 23, 1951)

In the preceding paper⁽¹⁾ the close relation between the foam formation and the work required to remove the unit area of adsorption layer, U_r , has been found for alcohol solutions and electrolyte solutions. The theory will be extended, in the present paper, to dyestuff solutions. The calculation of the work U_r was based, in the preceding paper, upon the observed data of the surface tension, but it is, now, replaced by a molecular kinetic theory.

Let the energy required to remove one mole of solute from the adsorption layer to the bulk solution be U_0 , and the concentration of solute in the solution and in the layer be C and C_r (mole/cc.), respectively. U_0 is such as an adsorption potential. The velocity of desorption, G_a (mole/cm.²/sec.), that is the moles of molecule passing through the unit area in the unit time from the adsorption layer to the bulk solution is calculated as fol-

lows. If the velocity distribution of solute molecules in the adsorption layer obeys to Maxwell-Boltzmann's distribution law, the velocity component in x direction, that is the direction normal to the surface, is in the average,

$$\overline{v_x(0)} = 2\sqrt{\frac{kT}{2\pi m}} \quad (1)$$

If a molecule goes and returns between the upper and lower boundaries of adsorption layer, of thickness d (cm.), with the velocity $\overline{v_x(0)}$, the frequency $\bar{\nu}_0$ is, since the path in one period is $2d$,

$$\bar{\nu}_0 = \frac{\overline{v_x(0)}}{2d} = \frac{1}{d} \sqrt{\frac{kT}{2\pi m}} \quad (2)$$

This is analogous to the well known equation in the statistical mechanics of liquid. As for liquid, two models are often used as the first approximations: "smooth potential model" and "harmonic oscillator model". Free volume

(1) M. Nakagaki, This Bulletin, 23, 127 (1950).

per molecule v in the smoothed potential model and the frequency of molecule ν in harmonic oscillator model are related with each other by the equation⁽²⁾:—

$$\nu = \frac{1}{v^{1/3}} \sqrt{\frac{kT}{2\pi m}} \quad (3)$$

Eq. (2) is the one dimensional analogue of Eq. (3). From this point of view, it will be permitted to apply the kinetic theory of gas to the adsorption layer.

The average x -component velocity of molecules, having the kinetic energy greater than U_0/N_0 , is,

$$\bar{v}_x(U_0) = \frac{kT}{A(U_0)} \exp(-U_0/RT) \quad (4)$$

where

$$A(U_0) = \int_{\sqrt{(2/m)(U_0/N_0)}}^{\infty} \exp(-mv_x^2/2kT) dv_x \quad (5)$$

and N_0 is Avogadro's number. Therefore, from Eq. (2),

$$\bar{\nu} = \frac{\bar{v}_x(U_0)}{2d} = \frac{kT}{2dA(U_0)} \exp\left(-\frac{U_0}{RT}\right) \quad (6)$$

Let the moles of solute contained in the unit area of the adsorption layer be n_0 , and the moles of solute molecule having the kinetic energy greater than U_0 be n , then

$$n/n_0 = 2A(U_0)/\sqrt{2\pi mkT} \quad (7)$$

$$\text{and} \quad n_0 = d \cdot C_R \quad (8)$$

$$\text{Therefore: } n = 2dA(U_0)C_R/\sqrt{2\pi mkT} \quad (9)$$

If all the molecules, colliding to the boundary between the adsorption layer and the bulk solution with the kinetic energy greater than U_0 , desorb, then the rate of desorption G_d is,

$$G_d = n\bar{\nu} = C_R \sqrt{kT/2\pi m} \exp(-U_0/RT) \quad (10)$$

Then, calculate the adsorption velocity. Let the saturation amount of adsorption per unit area be N_a (mole/cm²), the actually adsorbed amount be $I_2^{(1)}$, and the area already occupied be $I_2^{(1)}/N_a$. Among the molecules colliding to the surface already occupied, α is assumed to be adsorbed and $(1-\alpha)$ be repelled, and all molecules colliding to the empty surface $(1-I_2^{(1)}/N_a)$ is assumed to be adsorbed. The total number of molecules colliding to the surface is $(C/2)\bar{v}_x(0) = C\sqrt{kT/2\pi m}$, so the rate of adsorption G_a , that is the moles of solute

adsorbed in unit time per unit area, is

$$G_a = \left\{ \left(1 - \frac{I_2^{(1)}}{N_a}\right) + \alpha \frac{I_2^{(1)}}{N_a} \right\} \cdot C \sqrt{\frac{kT}{2\pi m}} \quad (11)$$

In dynamic equilibrium,

$$G_a = G_d \quad (12)$$

The volume of the adsorption layer per unit area is $N_a V_2$, where V_2 is the mole volume of solute. Then,

$$C_R = I_2^{(1)}/N_a V_2 \quad (13)$$

Therefore,

$$I_2^{(1)} = \frac{N_a k C}{1 + (1-\alpha)kC} \quad (14)$$

$$\text{where} \quad k = V_2 \exp(U_0/RT) \quad (15)$$

$$\text{or} \quad \frac{C_R}{C} = \frac{1}{1 + (1-\alpha)kC} \exp\left(-\frac{U_0}{RT}\right) \quad (16)$$

When the adsorbed molecules occupy definite sites on the adsorption surface, the molecules colliding to the area already occupied are all repelled, that is $\alpha=0$. Then Eq. (14) becomes:—

$$\text{when } \alpha=0, \quad I_2^{(1)} = \frac{N_a k C}{1 + kC} \quad (17)$$

This agrees with Langmuir's equation. When the adsorbed molecule moves freely on the surface and the collision diameter of the molecule is not great, all the molecules colliding to the adsorption surface are thought to be adsorbed. In this case, $\alpha=1$, Eq. (16) becomes:

$$\text{when } \alpha=1, \quad C_R/C = \exp(U_0/RT) \quad (18)$$

which is in agreement with Boltzmann's equation used in the preceding paper,⁽¹⁾ for alcohol solutions.

Eq. (16) is rewritten as:

$$\left. \begin{aligned} C_R/C &= \exp(U_1/RT) \\ \text{where } U_1 &= U_0 - RT \ln\{1 + (1-\alpha)kC\} \end{aligned} \right\} \quad (19)$$

U_1 is the energy required to remove one mole of solute from the adsorption layer to the bulk solution. $RT \ln\{1 + (1-\alpha)kC\}$ is the entropy corresponding to the assumption that, $(1-\alpha)$ of molecules colliding to the surface are repelled. This gives the impression as if the transposition of molecule from the adsorption layer to the bulk solution is easier in the case when the repelling is present. In the case of triphenylmethane dyes, the molecules are considered as plates of about 4 Å. in thickness and 200 Å.² in area, and the adsorbed molecules

(2) R. H. Fowler and E. A. Guggenheim: "Statistical Thermodynamics", Cambridge, 1939, p. 324.

are lying parallel to the liquid surface. Almost all molecules colliding to the "already occupied area" are, therefore, repelled, and α is assumed nearly equal to zero. Eq. (19) then becomes,

$$U_1 = U_0 - RT \ln (1 + kC). \quad (20)$$

Gibbs' equation is, if the activity coefficient of solute is assumed to be equal to unity for the dilute solution,

$$\Gamma_2^{(1)} = -(1/RT)(\partial\sigma/\partial \ln C) \quad (21)$$

Using this and Langmuir's equation (17), and assuming that k or U_0 is independent to concentration,

$$1 - \sigma/\sigma_0 = (N_a RT/\sigma_0) \ln (1 + kC) \quad (22)$$

is obtained. Rewriting the natural logarithms to the common one,

$$1 - \sigma/\sigma_0 = A \log (1 + kC) \quad (23)$$

$$\text{where } \begin{cases} A = 2.303 \times N_a RT/\sigma_0 \\ k = V_2 \exp (U_0/RT) \end{cases} \quad (24)$$

Eq. (24) agrees with the results cited in Freundlich's "Kapillarchemie," Vol. 1, p. 84. Eq. (23) is the well known Szyszkowsky's experimental equation, which is recognized as to fit well with many experimental data.

Size of dye molecule is calculated using van der Waals radii cited by Pauling⁽³⁾. The area of benzene molecule is calculated as 38.7 Å.², if C-C distance is assumed to be 1.39 Å., C-H distance 1.07 Å. and van der Waals radius of hydrogen atom 1.2 Å. The area of benzene molecule is calculated as 39.7 Å.², by the assumption that the density is 0.88, and the thickness is 3.7 Å. These two values of the area of benzene molecule agree well with one another. The radical (X-C₆H₄)₃C may be called as "triphenyl methane nucleus", (where X is hydrogen or nitrogen atom). The triphenyl methane nucleus is generally thought to have a triangular co-planar structure⁽⁴⁾. The area of it is assumed to be equal to about three times as large as that of benzene, 116 Å.² Radii of hydrogen atom and methyl radical are assumed to be 1.2 Å. and 2.0 Å., respectively. Areas of various radicals calculated as above are cited in Table 1. Areas, S , of some dye ions calculated by the summation of data of Table 1 are shown in Table 2. The thickness of ions are assumed to be equal to that of benzene, or 3.7 Å. The saturated adsorption

Table 1
Areas Occupied by Some Radicals

Triphenyl methane nucleus	$X-C_6H_4-C \begin{cases} \diagup C_6H_4-X' \\ \diagdown C_6H_4-X'' \end{cases}$	116 Å. ²
Methyl group	CH ₃ -	12.5 Å. ²
Hydrogen atom	H-	4.5 Å. ²
Ethyl group	C ₂ H ₅ -	19 Å. ²
Benzyl group	C ₆ H ₅ -CH ₂ -	45 Å. ²
Thickness of molecule (equal to that of benzene)		37 Å.

Table 2
Dimensions of Dye Ions

Dye	Formula weight M	Area of ion S , 10 ⁻¹⁶ cm. ²	Saturated adsorption amount N_a , 10 ⁻¹⁰ mole/cm. ²	Mole volume V_2 , cc./mole	Density d
Methyl violet 5B	448	223.5	0.743	498	0.898
Brilliant green	385	192	0.864	428	0.899
Malachite green	329	166	1.000	370	0.889
Crystal violet	372	191	0.868	426	0.873

amount per 1 cm.², N_a (mole/cm.²), is calculated from the value of area, S , by the equation,

$$N_a = 1/(N_0 S) = 1.66 \times 10^{-24}/S \quad (25)$$

where N_0 is Avogadro's number. Mole volume of dye ion in the adsorption layer, V_2 (cc./mole), is obtained, assuming the thickness of the adsorption layer being equal to the thickness of ion,

$$V_2 = 3.7 \times 10^{-8}/N_a \quad (26)$$

The density of it, d , is

$$d = M/V_2 \quad (27)$$

where M is the formula weight of dye ion. These values are also shown in Table 2. The density data cited are 0.8~0.9, which are fairly smaller than the value of solid dye, that is about 1.5, and is rather similar to the value of benzene, 0.88. This is quite plausible, since the molecular interaction in the adsorption layer is fairly weaker than in the crystal state.

Using these values, the coefficient A is calculated from Eq. (24). The value of k is determined so as the experimental values fit the Szyszkowsky's equation (23) best. The value of U_0 is then calculated according to Eq. (24). These are cited in Table 3. In Table 3, E is:

$$E = U_0/SN_0 \quad (28)$$

(3) L. Pauling, "The Nature of the Chemical Bond," New York, 1940, p. 189.

(4) See, e. g., E. Hückel, *Z. Elektrochem.*, **43**, 827 (1937); G. N. Lewis and M. Calvin, *Chem. Rev.*, **25**, 273 (1939).

Table 3
Constants for Adsorption (20°C.)

Dye	A	k, 10 ⁶ cc./mole	U ₀ , 10 ¹⁰ erg/mole	E, erg/cm. ²
Methyl violet 5B	0.0573	90.4	29.5	21.9
Brilliant green	0.0667	6.1	23.3	20.1
Malachite green	0.0771	2.40	21.4	21.4
Crystal violet	0.0670	1.71	20.2	17.6

It should be noticed that E is nearly equal to 20 erg/cm.² for all dyes.

Using these data, U_1 and $I_2^{(1)}$ are obtained from Eqs. (20) and (17), respectively. As the product of them:

$$U_R = I_2^{(1)} U_1 \quad (29)$$

the energy required to remove the unit area of the adsorption layer U_R is calculated. According to the preceding paper⁽¹⁾, U_R should be parallel to the foam formation of the solution. In Fig. 1, calculated values of U_R are plotted along with the foaming ability F

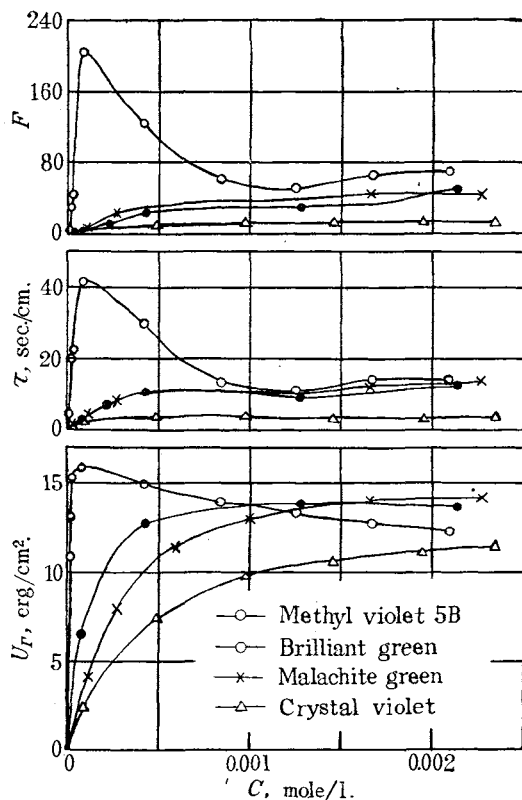


Fig. 1.—The Relation of F and U_R to C .

reported in the third paper of this series.⁽⁵⁾ In these triphenyl methane dyes, only methyl violet 5B has a maximum point in its foaming ability-concentration curve. It has been supposed in that paper that this will be due to the enormously large surface activity of this dye. By the calculation in this paper, it is shown that U_R-C curve has a maximum point for methyl violet 5B, while for other dyes no maximum is obtained. The qualitative discussion done in the former paper has been, therefore, justified in this paper.

The fact that E is nearly equal to 20 erg/cm.² suggests an interesting property of the adsorption layer. As described before, the property of the adsorption layer of triphenyl methane dye is somewhat similar to benzene. This is suggested both from its molecular structure and from its density cited in Table 2. Therefore,

$$E \doteq u_w + u_{w-0} - u_0 \quad (30)$$

where u_w , and u_0 are internal surface energy of water and benzene, respectively, and u_{w-0} is internal interfacial energy of water-benzene interface. According to International critical Tables,⁽⁶⁾

$$\left. \begin{aligned} u_w &= 118.15 \text{ erg/cm.}^2 \\ u_0 &= 67.86 \text{ erg/cm.}^2 \\ u_{w-0} &= 52.00 \text{ erg/cm.}^2 \end{aligned} \right\} \quad (31)$$

at 20°C. From these data,

$$E \doteq 102.3 \text{ erg/cm.}^2 \quad (32)$$

is obtained, which is fairly different from the experimental value: $E \approx 20$ erg/cm.² cited in Table 3. This discrepancy may be ascribed to the fact that the layer of "benzene" is a thin layer of 3.7 Å, so that u_0 and u_{w-0} is different from the value for the bulk of benzene.

Fowler⁽⁷⁾ calculated the adhesion energy and obtained

$$E_{1-2}^{adh} = 2\pi \int_0^\infty n_2(j) dj \int_j^\infty df \int_f^\infty n_1(f-j) \epsilon_{12}(r) r dr \quad (33)$$

where E_{1-2}^{adh} is the adhesion energy between phase 1 and phase 2 per unit area, $\epsilon_{12}(r)$ is the interaction energy between molecules distant as r from each other, n_1 and n_2 are the densities of molecules (number of molecules/cc.) in both phases, and j , f , and r are the distances shown in Fig. 2.

For simplicity, it is taken as

(5) M. Nakagaki, This Bulletin, **22**, 200 (1949).

(6) "International Critical Tables", Vol. IV, p. 436.

(7) Fowler, *Proc. Roy. Soc., A* **159**, 229 (1937).

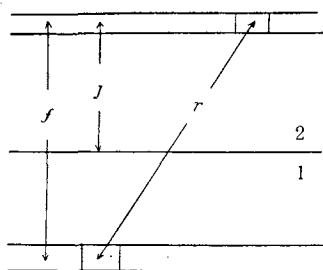


Fig. 2.

$$\left. \begin{aligned} n_1(f-j) &= N_1, \quad n_2(j) = \begin{cases} 0 & \text{if } j < R_{12} \\ N_2 & \text{if } j \geq R_{12} \end{cases} \\ \text{and} \quad \epsilon_{12} &= -\mu_{12}/r^6 \end{aligned} \right\} \quad (34)$$

where, N_1 and N_2 are constants, showing the density in the bulk of phases 1 and 2, respectively, R_{12} is the sum of radii of molecules 1 and 2, and μ_{12} is a constant. Under these assumption, the equation (33) is simplified as,

$$E_{1-2}^{adh} = -(\pi/12)N_1N_2\mu_{12}/R_{12}^2 \quad (35)$$

Then, let u_1 , u_2 and u_{12} be the internal surface energy of phases 1, 2, and the internal interfacial energy between phases 1 and 2, respectively. It is obtained that,

$$\begin{aligned} u_1 &= -E_{1-1}^{adh}/2 = (\pi/24)N_1^2\mu_{11}/R_{11}^2 \\ u_2 &= -E_{2-2}^{adh}/2 = (\pi/24)N_2^2\mu_{22}/R_{22}^2 \\ u_{12} - u_1 - u_2 &= E_{1-2}^{adh} = -(\pi/12)N_1N_2\mu_{12}/R_{12}^2 \end{aligned} \quad (36)$$

The interfacial energy is sometimes schematically explained in a text-book as shown in Fig. 3 a. For a molecule of phase 1, placed at the surface, the lower half of its sphere of action is filled with molecules of phase 1, and

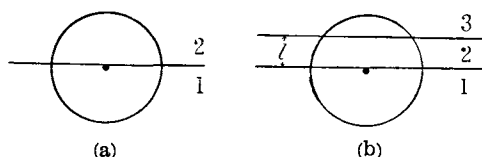


Fig. 3.—A schematic explanation of interfacial energy.

the upper half is filled with molecules of 2, if the thickness of both phases are large enough compared with the radius of the action. The difference of the interactions from two hemispheres causes the interfacial energy between 1 and 2. If, then, the thickness of the layer 2 is smaller than the radius of the sphere, as shown in Fig. 3 b, the interfacial energy between phases 1 and 2 will be different from the

ordinary value corresponding to Fig. 3 a. Modifying Fowler's equation (33), the adhesion energy between the bulk phase 1 and the layer 2, thickness of which is l , (Fig. 3 b), is expressed as:

$$\begin{aligned} E_{1-23}^{adh} &= 2\pi N_1 \int_0^l n_2(j) dj \int_j^\infty df \int_f^\infty \epsilon_{12}(r) r dr \\ &\quad + 2\pi N_1 \int_l^\infty n_3(j) dj \int_j^\infty df \int_f^\infty \epsilon_{13}(r) r dr \end{aligned} \quad (37)$$

This is integrated, besides with assumption (34), under the following additional assumption that

$$n_3(j) = N_3, \quad (\text{if } j \geq l) \quad \text{and} \quad \epsilon_{13}(r) = -\mu_{13}/r^6 \quad (38)$$

and obtained that

$$\begin{aligned} E_{1-23}^{adh} &= -\frac{\pi N_1}{12} \left\{ N_2 \mu_{12} \left(\frac{1}{R_{12(3)}^2} - \frac{1}{l^2} \right) \right. \\ &\quad \left. + N_3 \mu_{13} \frac{1}{l^2} \right\} \end{aligned} \quad (39)$$

As the shortest distance between the centers of gravity of molecule 1 and 2 may be different from the value of R_{12} by the orientation of molecule in the thin layer, it is shown as $R_{12(3)}$. Using Eq. (36),

$$\begin{aligned} E_{1-23}^{adh} &= (u_{12} - u_1 - u_2) \left(\frac{R_{12}^2}{R_{12(3)}^2} - \frac{R_{12}^2}{l^2} \right) \\ &\quad + (u_{13} - u_1 - u_3) \frac{R_{13}^2}{l^2}, \end{aligned} \quad (40)$$

is obtained.

The energy required to bring a dye molecule (per unit area) from the adsorption layer into the bulk solution, E , is expressed

$$E = -E_{w-w}^{adh} + E_{w-ow}^{adh} \quad (41)$$

In Eqs. (36) and (40), let 1 = w , 2 = o , and 3 = w . Then, under the notice that $u_{www} = 0$, Eq. (41) is rewritten:

$$\begin{aligned} E &= 2u_w \left(1 - \frac{R_{ww}^2}{l^2} \right) \\ &\quad + (u_{wo} - u_w - u_o) \left(\frac{R_{wo}^2}{R_{wo(w)}^2} - \frac{R_{wo}^2}{l^2} \right) \end{aligned} \quad (42)$$

If $R_{wo(w)} = R_{wo}$ and $l \gg R_{wo}$, this equation coincides with Eq. (30).

Molecular diameter of water, R_{ww} , is calculated from the density, ρ_w , molecular weight, M_w , and mole volume, V_w , of water and Avogadro's number, N_0 ,

$$R_{ww} = \frac{1}{\gamma} \left(\frac{V_w}{N_0} \right)^{1/3} = \frac{1}{\gamma} \left(\frac{M_w}{\rho_w N_0} \right)^{1/3} \quad (43)$$

γ , a constant determined by the molecular arrangement, is assumed rather arbitrarily,

$$\gamma = 0.935, \quad (44)$$

referring to the facts that $\gamma=1$ for simple cubic lattice, $\gamma=0.916$ for the body centered lattice, and $\gamma=0.890$ for the face centered lattice. Then, R_{wv} is calculated as:

$$R_{wv} = 3.32 \text{ \AA}. \quad (45)$$

For benzene, a similar calculation gives,

$$R_{oo} = 5.64 \text{ \AA}. \quad (46)$$

and

$$R_{vo} = \left(\frac{R_{wv} + R_{oo}}{2} \right) = 4.48 \text{ \AA}. \quad (47)$$

It has already been shown by the assumptions in Eq. (34), the boundary surface between phases 1 and 2 is taken as a plane placed on the centers of the phase 1 molecules nearest to phase 2. Then, using the value of the thickness of benzene molecule, δ , or $3.70 \text{ \AA}$,

$$\left. \begin{aligned} R_{w(u)} &= \frac{1}{2} R_{wv} + \frac{1}{2} \delta = 3.51 \text{ \AA}. \\ l &= \frac{1}{2} R_{wv} + \delta = 5.36 \text{ \AA} \end{aligned} \right\} \quad (48)$$

Then, by Eq. (42),

$$E = 21.0 \text{ erg/cm}^2 \quad (49)$$

is obtained. This agrees well with the values in Table 3, that is $E \approx 20 \text{ erg/cm}^2$.

Summary

Considering the dynamic equilibrium of adsorption and desorption on the surface of water, Szyszkowsky's equation is derived. Using the area of dye molecule calculated from the molecular structure, U_o and $I_2^{(1)}$ are estimated to obtain the best conformity with the measurement of the surface tension. U_r calculated by them is compared with the foam formation of these triphenyl methane dyes. Maximum observed in the foaming ability—concentration curve of methyl violet 5B is explained by its large surface activity. The fact that the energy required to bring the unit area of dye molecule into the bulk solution is about 20 erg/cm^2 is justified using the correction of interfacial energy due to the fact that the thickness of the adsorption layer is nearly equal to the dimension of the range of molecular force.

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Studies on Monomolecular Films. VII. The Effect of Metallic Ions on the Monomolecular Film of Stearic Acid

By Tunetaka SASAKI and Ryôhei MATUURA

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Introduction

It is of great importance in the study of monomolecular films of fatty acids on the surface of water to know precisely the effect of ions in the underlying water on the properties of the monolayers. Harkins and Myers⁽¹⁾ noticed that the decrease in the area per molecule of a fatty acid on the surface of alkaline water is chiefly caused by the con-

tamination of divalent ions (especially calcium ion) which make the chains close-packed ($20.5 \text{ \AA}^2$); in the absence of such ions the molecules may be arranged with their heads close-packed giving approximately the area of $25 \text{ \AA}^2$, the area found on dilute acid solutions. Extensive work on the effect of dissolved salts on insoluble monolayers of stearic acid was carried out by Langmuir and Schaefer,⁽²⁾ who studied

(1) W. D. Harkins and R. J. Myers, *Nature*, **139**, 367 (1937).

(2) I. Langmuir, and V. J. Schaefer, *J. Am. Chem. Soc.*, **59**, 2400 (1937).

in detail the remarkable effect of such metallic ions as calcium, barium and aluminum and proposed a theory of the interaction between ions in the substrate and stearic acid in the film, assuming that the modification of a stearic acid monolayer by the presence of salts is due to the adsorption of salt to the undersurface of the monolayer. It has not been studied systematically, however, how each metallic ion affects the property of a fatty acid monolayer under varying hydrogen ion concentration and, particularly, how the effect can be explained from the standpoint of molecular structure of the resulting metallic soap. Recently studies on metallic soaps have been carried out colloidal chemically by many workers and the interesting results have been obtained concerning the structure as well as the colloidal chemical properties of metallic soaps.^{(3),(4),(5)} It is the purpose of the present work to investigate the effect of the various metallic ions on the monolayer of stearic acid spread on the surface of the solution of varying hydrogen ion concentration and to discuss the result by taking into consideration the recent studies on metallic soaps as well as the characteristic properties of each metallic ion.

Experimental

The monolayer of stearic acid was prepared from benzene solution on the surface of water containing a salt of concentration of 10^{-4} mol/l.. The salts were used as chloride, nitrate and sulfate. They were purified by the repeated recrystallization. From the preliminary experiment the effect of inorganic anion on the monolayer of stearic acid was found negligible. The tray was made of brass and was coated thickly with paraffin. It was found that, when the surface of the tray was covered thickly with paraffin, the effect of the metallic ions which might come from the tray material on the acid monolayer was not measurable at least in the case where pH of the substrate ranged from 2 to 10. The value of pH of the substrate was controlled by hydrochloric acid and ammonium hydroxide. The use of ordinary buffer salts were particularly avoided since the possibility was considered that the buffer salts might frequently cover the remarkable effect usually encountered in the presence of metallic ions for investigation. The pressure~area diagram was measured for each monolayer of stearic acid by the method described already.⁽⁶⁾

Results

Various metallic ions were examined how they affect the pressure~area curve of the monolayer of stearic acid on the surface of the solution and it was found that they can be classified into two groups according to the difference in the effect. One involves those which cause the monolayer to condense on the alkaline solution and the other those which make it expand in a proper pH range of the solution, characteristic of each metallic ion.

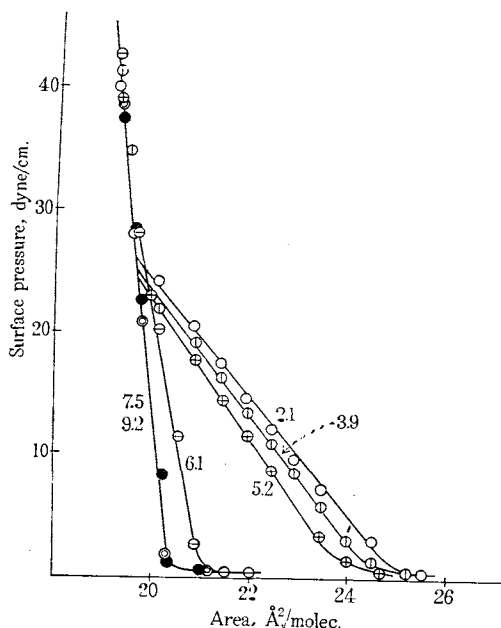


Fig. 1.—Pressure~area curves of the monolayer of stearic acid on water containing calcium ion: The numeral for each curve represents pH of the substrate.

The typical example of the first group is calcium ion. The pressure~area diagram of the monolayer of stearic acid on the surface of water containing calcium ion is shown in Fig. 1. It is obvious from this figure that the effect of calcium ion on the monolayer of stearic acid varies with pH of the substrate. In order to make this relation more distinct, the zero-compression area per molecule of stearic acid is plotted against pH of the substrate as shown by crosses in Fig. 2. The curve shown by small circles in the same figure represents the result of the blank experiment carried out on the surface of water containing no metallic ion. In the absence of metallic ions the monolayer of stearic acid is unstable,

(3) C. G. McGee, *J. Am. Chem. Soc.*, **71**, 278 (1949).

(4) V. R. Gray and A. E. Alexander, *J. Phys. Coll. Chem.*, **53**, 9, 23 (1949).

(5) R. D. Vold and G. S. Hattiangdi, *Ind. Eng. Chem.*, **41**, 2311 (1949); G. S. Hattiangdi, and M. J. Vold, *ibid.*, **41**, 2320 (1949); etc.

(6) T. Sasaki, *J. Chem. Soc. Japan*, **62**, 796 (1941); R.

Matnura and I. Hayasi, *Memoirs of the Faculty of Science, Kyushu University, Ser. C*, Vol. 1, 31 (1948).

presumably a little soluble, on the alkaline substrate and the area per molecule of stearic acid diminishes sometimes to as small as 15

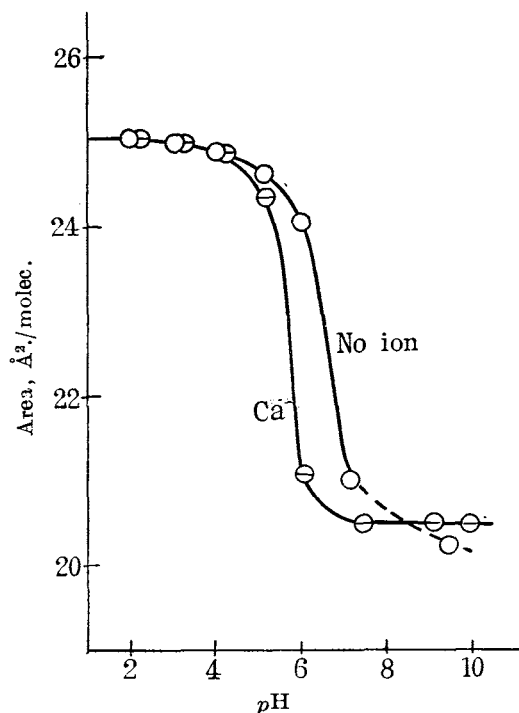


Fig. 2.—Area- pH curve of the monolayer of stearic acid on water containing calcium ion.

or 16 Å^2 . On the contrary when calcium ion is present, the monolayer becomes stable enough even on the alkaline substrate to give a definite area of so-called close-packed chain, 20.5 Å^2 per molecule. On the acid substrate the monolayer of stearic acid is stable irrespective of the presence of calcium ion and gives the area of about 25 Å^2 , the area of so-called close-packed head. The metallic ions which show the similar effect as calcium ion are barium, magnesium, lead and manganese, but the effect of the last two is rather ambiguous. The pressure-area curve of the monolayer of stearic acid affected by these ions is similar, depending little upon the difference in the nature of these metallic ions.

An example of the second group of metallic ions is aluminum. The pressure-area curve of the monolayer of stearic acid spread on the substrate containing AlCl_3 is shown in Fig. 3. It is noticed that aluminum ion remarkably expands the monolayer in a certain range of pH , the maximum expansion occurring at pH near 7. This is more clearly illustrated in Fig. 4, where the zero-compression area per

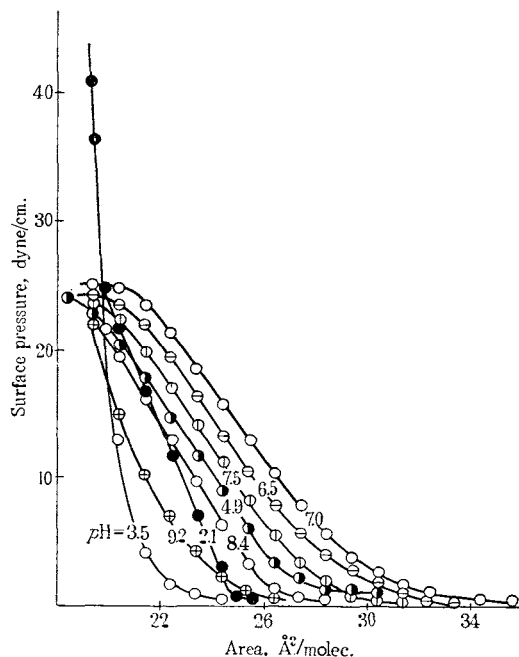


Fig. 3.—Pressure-area curves of the monolayer of stearic acid on water containing aluminum ion.

molecule of stearic acid is plotted against pH of the substrate. When pH increases beyond the value of maximum expansion, the film becomes gradually unstable. It is noteworthy that the monolayer which is made to expand by aluminum ion has a large compressibility and its collapse pressure is rather small compared with that of the film unaffected by metallic ions, as seen in Fig. 3. In this group of the metallic ions copper, zinc, mercury, cobalt, nickel, iron, cerium and thorium ions are included in addition to aluminum ion. The optimum pH of the film expansion is proper for each ion as shown in Fig. 4 in the case of a few metallic ions of this group.

Discussion

It is evident from the experiment of Langmuir and Schaefer⁽⁷⁾ that the metallic soap is formed in the film when stearic acid is spread on the surface of water which contains both metallic ions and a suitable amount of hydrogen ion. Hence the remarkable effect of those metallic ions on the monolayer of stearic acid should be discussed from the standpoint of the resulting metallic soaps.

It was shown that ions of the first group, namely calcium, barium and magnesium,

(7) I. Langmuir and V. J. Schaefer, *J. Am. Chem. Soc.*, **58**, 284 (1936).

were proved to be the case by the present experiment.

It is reasonable to assume that the rest of metallic ions of the second group will also form soaps of similar molecular structure as aluminum soap in a certain pH range characteristic of each ion. The pH value for the maximum of the film expansion seems to depend on the basicity of each ion. It should be emphasized that these metallic ions exhibit a high co-ordination valency and readily form co-ordination compounds with various substances. In presenting a polymer structure of aluminum soap McGee⁽³⁾ also took the linkage by co-ordination valency into consideration. Presumably all the metallic ions classified into the second group in this experiment will form with stearic acid a soap, complex in structure supported by co-ordination valency. In this point they are different from those classified into the first group, *i. e.*, calcium, barium and magnesium. Now, it is to be noted that all the metallic ions of the second group prove to be either transition elements or elements being trivalent or higher. The ionic radius of these elements is known to be generally small and its ionic potential large, which are considered to be favorable conditions for the formation of complex salts. The fact that metallic ions are also classified largely into two groups similar to those in the present experiment according to the difference in some other surface chemical properties was confirmed by the studies on the effect of metallic ions both

on the built-up film of stearic acid carried out by Muramatsu⁽¹⁴⁾ and on the wettability of stearic acid surface carried out by Inaba,⁽¹⁵⁾ both of our laboratory.

Summary

The effect of various metallic ions on the pressure~area curve of the monomolecular film of stearic acid spread on the surface of the solution was studied. It was found that they were classified into two groups; one involves those which make the film condense such as calcium, barium and magnesium and the other those which make it expand such as thorium, aluminum, iron, copper, zinc, mercury, cobalt and nickel. This classification was explained from the standpoint of molecular structure of the resulting metallic soaps. It was suggested that while the soap of the former metals has a simple structure the soap of the latter metals has a complicated polymeric structure. These structures were explained by the characteristic nature of metallic ions of two groups.

The cost of this research has been defrayed from the grant of the Ministry of Education given to one of the authors.

*Chemical Institute, Faculty of Science,
Kyūshū University, Fukuoka.*

(14) M. Muramatsu and T. Sasaki, in press.

(15) A. Inaba, to be published recently.

Studies on Monomolecular Films. VIII.
Rigidity of the Monolayer of Stearic Acid on the Surface
of Salt Solutions

By Ryôhei MATUURA

(Received August 2, 1951)

In the preceding paper⁽¹⁾ the effect of metallic ions on the pressure~area curve of the monolayer of stearic acid spread on the surface of the solution was studied. There the metallic ions were classified into two groups, one con-

densing and the other expanding the film. It was suggested then that the ions of the latter group form, with stearic acid, soaps of a complicated polymeric structure. In order to confirm further this structure the measurement of some rheological properties of the monolayer of stearic acid on the surface of water containing these metallic ions is most desirable.

(1) T. Sasaki and R. Matuura, This Bulletin, **24**, 271 (1951).

In this connection it was found already by Langmuir and Schaefer⁽²⁾ that the monolayer of stearic acid becomes rigid when it is spread on water containing metallic ions. Blodgett⁽³⁾ reported that it is difficult to build up the monolayer of stearic acid formed on water containing copper or aluminum ion because of its high rigidity. Rigidity of a film is closely related to the structure of the film, and it is expected that the metallic ions can also be classified with regards to the measurement of the film rigidity into two groups in the same way as in the preceding paper. Therefore, it is attempted in the present experiment to measure the rigidity of the monolayer of stearic acid formed on the surface of water containing various metallic ions and to find how the result can be accounted for by the structure of the film.

Experimental

For the purpose of the present experiment, it is required merely to know the change of the film rigidity due to the presence of various kinds of metallic ions, and so instead of measuring absolute rigidity it was attempted in this experiment to measure simply relative rigidity of the monolayer of stearic acid with or without metallic ions in the substrate by means of a simple device shown in Fig. 1. In this figure a glass thread,

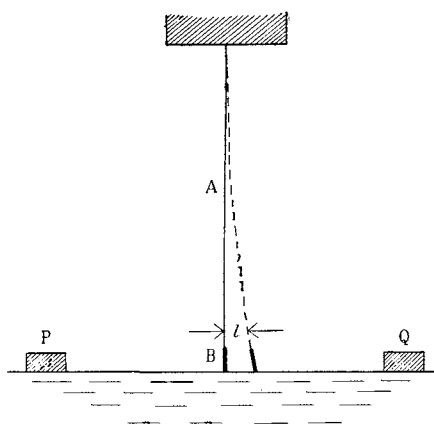


Fig. 1.—Apparatus for measurement of film rigidity.

A, 40 cm. in length and 0.1 mm. in diameter, is suspended vertically over the surface of water in a tray on which the monolayer is to be formed. The top end of the thread is firmly fixed to a

suitable support while to the lower end a small platinum wire, B, is welded which is brought to just touching the surface of water. The monolayer was spread on water between two barriers, P and Q, and the film was compressed by moving the barrier P towards the fixed barrier Q. If the monolayer has any appreciable amount of rigidity, the glass thread will be displaced and take a new position as shown by a dotted line in Fig. 1. It took sometimes several minutes or more to reach this equilibrium position. This displacement of the thread, l , which can be taken as a measure of rigidity of the film, was read at every compression by a cathetometer. Surface pressure of the film was simultaneously measured in the same tray using the surface balance already described.⁽⁴⁾ The procedure of the preparation of a stearic acid monolayer and the salts used were also the same as before.⁽⁵⁾

Besides the measurement of film rigidity, so-called expansion patterns of the monolayer of stearic acid on the substrate containing metallic ions were investigated as follows, according to somewhat modified method of Schaefer's.⁽⁶⁾ The monolayer of stearic acid was prepared on the surface of the solution and a drop of camellia-oil colored red with a dissolved azo dye was placed on it. As the oil spread pushing aside the monolayer of stearic acid, a colored pattern of the various shape was obtained. This pattern, although depending upon the pH value of the substrate, was characteristic of each ion present in the substrate and profoundly affected by the mechanical structure of the monolayer of stearic acid. It was also possible to transfer this pattern from the surface of water to the surface of a filter paper.

Results

It was found that the monolayer of stearic acid formed on the surface of water containing no metallic ion exhibited no rigidity detectable by the present apparatus throughout the whole range of the pH value of the substrate, namely from pH 2 to 10. Likewise, even when calcium, barium, magnesium ion was present in the substrate in the concentration of 10^{-4} mol/l., the monolayer effected so small a displacement of the glass thread even under the high compression that it could hardly be measured accurately.

On the contrary, in the presence of such metallic ions as thorium, aluminium, iron, copper, zinc, mercury, cobalt, nickel, etc. in the substrate the monolayer of stearic acid formed on it revealed a remarkable rigidity which could be measured by a large displacement of the glass thread. In this case the

(2) I. Langmuir and V. J. Schaefer, *J. Am. Chem. Soc.*, **59**, 2400 (1937).

(3) K. B. Blodgett, *J. Am. Chem. Soc.*, **57**, 1007 (1935); *J. Phys. Chem.*, **41**, 975 (1937).

(4) T. Sasaki, *J. Chem. Soc. Japan*, **62**, 796 (1941); R. Matsumura and I. Hayashi, *Memoirs of the Faculty of Science, Kyushu University, Ser. C*, Vol. 1, 31 (1948).

(5) V. J. Schaefer, *J. Phys. Chem.*, **42**, 1089 (1938).

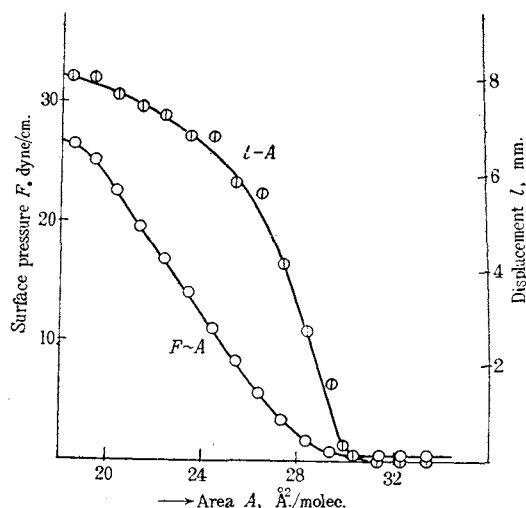


Fig. 2.—Pressure~area and displacement~area curves of the monolayer of stearic acid on water containing aluminum ion.

displacement of the glass thread was intensely dependent upon the degree of compression of the film. The example is shown in Fig. 2 in the case of the substrate containing AlCl_3 of 10^{-4} mol/l., and its pH being 7.6. In the same figure the pressure~area curve of this film is also depicted for reference. It is noteworthy that the film begins to show a measurable rigidity at nearly the same surface area at which the surface pressure of the film begins to increase perceptibly. Rigidity of the film, then, increases with the increase in the surface pressure until the film collapses at about 25 dynes/cm. Rigidity of the film also depends strongly upon the pH value of the substrate. This relation is shown in Fig. 3, where the maximum displacement, *i. e.*, the displacement

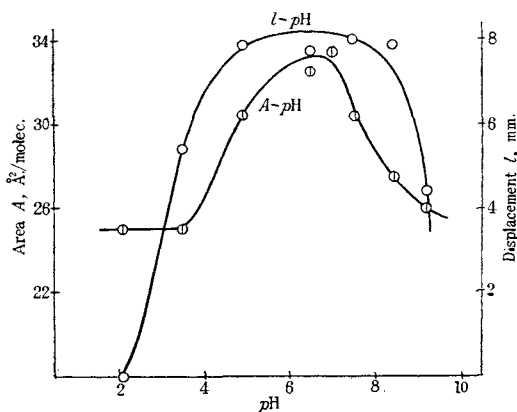


Fig. 3.—Area~pH and Displacement~pH curves of the monolayer of stearic acid on water containing aluminum ion.

just before the collapse of the film, at each pH of the substrate is plotted. In the same figure the area~pH curve as shown in Fig. 4 in the preceding paper is also depicted for comparison. It is seen that both the expansion of the film of stearic acid in the presence of aluminum ion and the remarkable rigidity of the film appear in the same range of pH of the substrate. Thus in the case of the other metallic ions this relation between expansion and rigidity of the film can also be confirmed similarly by comparing Fig. 4 in this paper with Fig. 4 in the preceding paper.

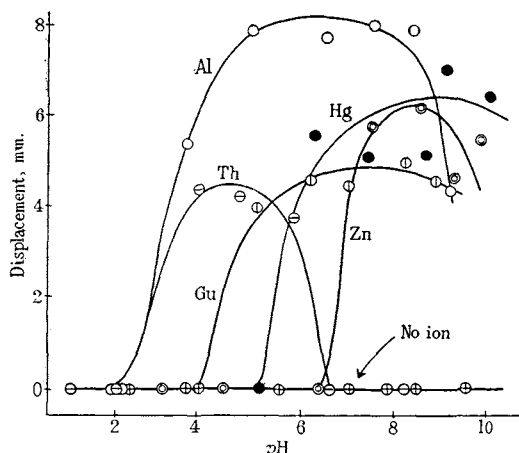


Fig. 4.—Displacement~pH curves of the monolayer of stearic acid on water containing some metallic ions.

The expansion pattern is shown schematically in Fig. 5 in the case of the monolayer of stearic acid formed on the surface of water containing calcium, aluminum and thorium ions, together with the pattern obtained in the absence of metallic ions. The surface pressure of the film was kept constant to 10 dynes/cm.

Discussion

The idea of classification of the metallic ions into two groups as proposed in the preceding paper proves to be applicable also to the result of the present experiment. Ions which cause to condense the film of stearic acid make it no rigid, while ions which make the film expand render it remarkably rigid. Thus, rigidity of the film is, probably, another criterion available for the classification of the metallic ions into two groups which are essentially the same as in the former report. The appearance or absence of the remarkable rigidity mentioned above can also be explained

as follows by a simple and complex type of metallic soaps suggested in the preceding paper. That is, the soaps of calcium, barium or magnesium have a rather simple stoichiometric molecular structure, and the molecules of these soaps are likely to be oriented vertically on the surface of water and closely packed. It is expected from this structure of the film that the film has no perceptible rigidity although it may show a fairly small compressibility. On the contrary, the soaps of thorium, aluminum, iron, copper, zinc, mercury, cobalt and nickel were suggested to have a complicated polymeric structure. It is expected in this case that the film will become rigid by interlocking of the long chain. The result of the present experiment shows that this is practically the case. The expansion of the film, its large compressibility, its remarkable rigidity, and the collapse occurring under a rather small surface pressure, all these properties are intimately related to each other and come from the complexity in molecular structure of these metallic soaps. In these properties the monolayer of stearic acid formed on the surface of water containing such metallic ions as thorium, aluminum, etc. resembles that of proteins well studied by many authors.⁽⁶⁾

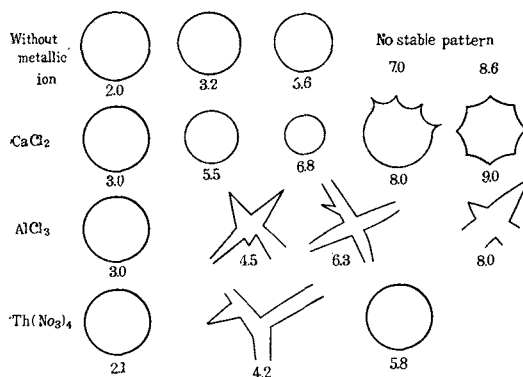


Fig. 5.—Expansion patterns. The numeral for each pattern represents pH of the solution.

The experiment on expansion pattern also makes clear the similar difference between the effect of calcium ion and that of aluminum and thorium ions. Indeed in the presence of calcium ion the pattern is somewhat less round than that obtained in the absence of metallic ion, especially at high pH, but its irregularity is much less marked compared with the pattern in the presence of aluminum or thorium ion, where the pattern consists mainly of sharp lines. Here the sharpness of the pattern becomes most remarkable at a certain pH value of the substrate characteristic of each ion. On both sides of this pH the pattern gradually loses its sharpness until it becomes perfectly round. Here again the maximum of the sharpness of the pattern corresponds just to the maximum of the film expansion and also to the maximum of the film rigidity.

Summary

A relative rigidity of the monolayer of stearic acid on the surface of water containing various metallic ions was measured by the displacement of the glass thread. It was found, as was pointed out in the preceding paper, that metallic ions were classified largely into two groups, namely ions which render the surface film remarkably rigid and those without such effect. Those of the former group are thorium, aluminum, iron, copper, zinc, mercury, cobalt and nickel, while the latter group involves calcium, barium and magnesium. So-called expansion pattern of the film of stearic acid in the presence of these metallic ions was also studied, the result of which also confirmed this conclusion.

In conclusion, the author thanks to Prof. T. Sasaki for his kind guidance in the course of this study. The cost of this research has been defrayed from the grant of the Ministry of Education given to the professor.

*Chemical Institute, Faculty of Science,
Kyushu University, Fukuoka.*

(6) E. Gorter, *Ann. Rev. Biochem.*, 10, 619 (1941); H. B. Bull, *Advances in Protein Chemistry*, 3, 95 (1947); M. Joly, *Research (London)*, Suppl., Surface Chemistry, 1949, 17.

Studies on Monomolecular Films. IX. The Effect of Dissolved Dyes on the Monolayer of Stearic Acid

By Ryôhei MATUURA

(Received August 2, 1951)

Introduction

In the preceding two papers^{(1),(2)} the effect of metallic ions on the monolayer of stearic acid was reported. There it was suggested that such metallic ions as thorium, aluminum, iron, copper, zinc, mercury, cobalt and nickel in the substrate formed stearate of a complicated high-molecular structure in the film. It may be expected that some contribution to the confirmation of this suggestion will be obtained by studying the effect of the substance of a large molecule dissolved in the substrate on the monolayer of stearic acid formed on it. For this purpose dyes are considered suitable because the molecules of the dyes are usually large, sometimes forming micelles in a solution, and, in addition, they have one or more ionizable groups which are expected to interact with a polar group of stearic acid. For this reason it has been attempted in this experiment to investigate the interaction between some dyes in the substrate and stearic acid in the film and to compare the result with the effect of such metallic ions as mentioned above. Furthermore, since some dyes are known to be remarkably surface active and their surface chemical properties have been studied in connection with the adsorbed films,⁽³⁾ foams,⁽⁴⁾ etc., it is interesting also for the purpose of studying the surface chemical properties of dyes with regards to their molecular structure to investigate the interaction between dissolved dyes and insoluble films.

Experimental

Dyes used in this experiment were conventionally classified according to their molecular structure into three groups, namely those of acidic, basic and amphoteric ones. As acidic dyes

scarlet red and phloxine, as basic dyes chrysoidine, crystal violet and night blue and as amphoteric dyes methyl orange, congo red and trypan red were chosen. Of all these dyes crystal violet, methyl orange and congo red were especially purified by salting out⁽⁵⁾ or recrystallization. Comparison of the effect of a commercial dye with that of a purified one on the monolayer of stearic acid gave no essential difference between them, and so the rest of the dyes were used without special purification. Each of these dyes was dissolved in water to the concentration of 10^{-2} mol/l. and aged for about ten days before use. The solution was diluted to 10^{-4} mol/l. when it was used, and the monolayer of stearic acid was spread on the surface of this solution and the pressure-area curve was measured in the same way as described already.⁽⁶⁾ The hydrogen ion concentration of the dye solution was varied from 1.5 to 10 using hydrochloric acid and ammonium hydroxide. Here the use of ordinary buffer salts was avoided for controlling pH because of the disturbing effect produced by buffer ions as mentioned in the preceding paper.⁽¹⁾ The film experiment was carried out at room temperature.

Results

As to the effect on the stearic acid monolayer, some dyes were remarkable in their action in a pH range of the solution proper for each dye, while the effect was imperceptible with other dyes throughout the whole range of pH in the present experiment.

(1) **Acidic Dyes.**—Scarlet red showed no effect on the pressure-area relation of the monolayer of stearic acid spread on the surface of the solution throughout the whole range of pH, covering from 1.5 to 10, while phloxine modified it considerably in the solution of the acid region. In Fig. 1 the area per molecule of stearic acid at the pressure of 2 dynes/cm. with or without the dyes in the underlying

(1) T. Sasaki and R. Matuura, *This Bulletin*, **24**, 274 (1951).

(2) R. Matuura, *This Bulletin*, **24**, 278 (1951).

(3) K. S. G. Doss *Kolloid-Z.* **84**, 138 (1938); **86**, 205 (1939); **87**, 272 (1939).

(4) M. Nakagaki, *This Bulletin*, **22**, 201 (1949); **23**, 48, 105 (1950).

(5) C. Robinson and H. A. T. Mills, *Proc. Roy. Soc. A*, 131 576 (1931).

(6) T. Sasaki, *J. Chem. Soc. Japan*, **62**, 796 (1941); R. Matuura and I. Hayashi, *Memoirs of the Faculty of Science, Kyushu University, Ser. C*, Vol. 1 (1948).

solution is plotted against its pH . It can be seen that in the presence of phloxine the curve shows a sharp maximum at pH 3.5. It was found that even in the absence of the monolayer of stearic acid the phloxine solution formed rigid adsorbed films of its own at the neighborhood of this pH , and they appear practically insoluble, showing rather a large surface pressure. The question arose that the remarkable expansion of a stearic acid monolayer might come from this adsorbed film of the phloxine solution, but the comparison with the blank experiment showed that it was caused considerably by the interaction between phloxine and stearic acid and could not be explained merely by a simple additive effect of both films.

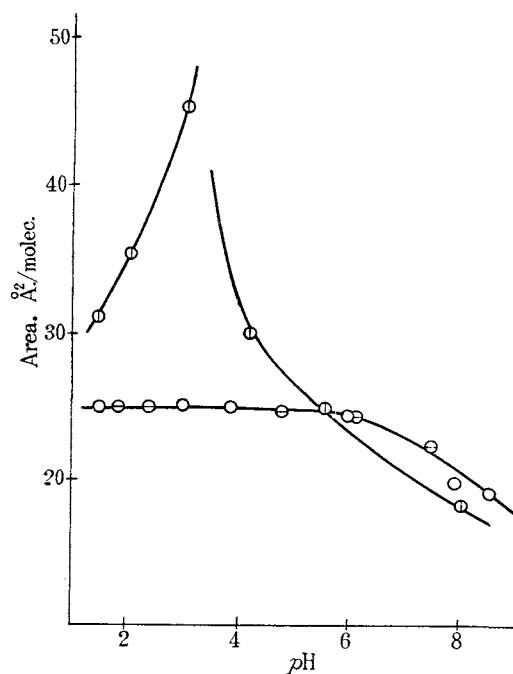


Fig. 1.—Area $\sim pH$ curves of monolayer of stearic acid on water containing acid dyes: $\circ$, without dye; $\odot$, scarlet red; $\oplus$, phloxine.

(2) **Basic Dyes.**—Both chrysoidine and crystal violet made the monolayer of stearic acid expand in the solution of the alkaline region as shown in Fig. 2. In the case of night blue the expansion of the monolayer of stearic acid was very remarkable, but this dye formed rigid adsorbed films of its own from especially the alkaline solution, just as phloxine did from the acid solution. The result with night blue is not shown in Fig. 2. A trouble occurred that the solutions of crystal violet and night

blue remarkably wetted the paraffined wall of the tray so that the water in the tray overflowed from the edges on compression and the film experiment became impossible. This was largely avoided by using the solution whose concentration was 10^{-5} mol/l. The result with crystal violet shown in Fig. 2 is that obtained using this dilute solution, the film area being that at the surface pressure of 15 dynes/cm. In the case of chrysoidins the concentration of the solution was 10^{-4} mol/l, and the film area

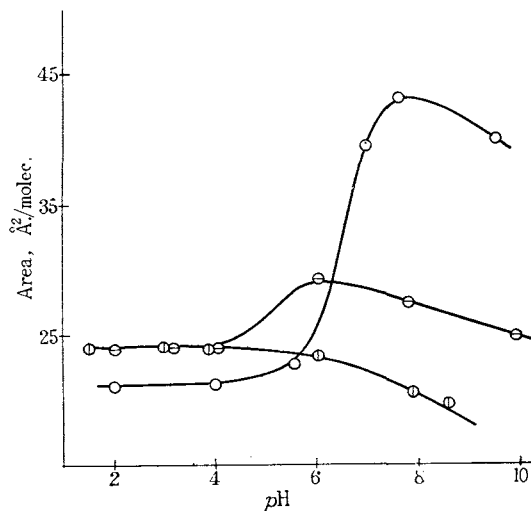


Fig. 2.—Area $\sim pH$ curves of the monolayer of stearic acid on water containing basic dyes: $\circ$, crystal violet (area at 15 dynes/cm.); $\odot$, chrysoidine; $\oplus$, without dye.

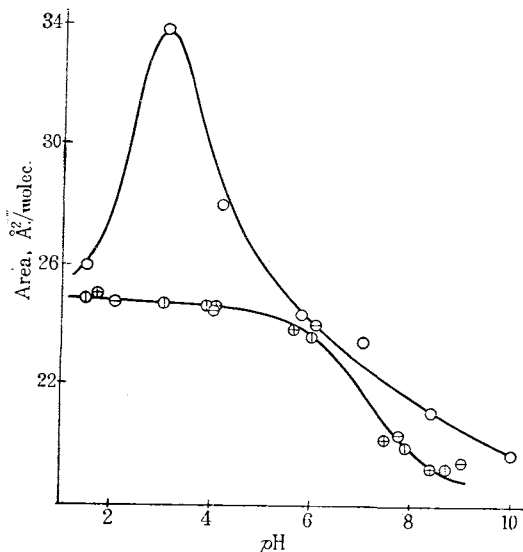


Fig. 3.—Area $\sim pH$ curves of the monolayer of stearic acid on water containing amphoteric dyes: $\circ$, congo red; $\odot$, methyl orange; $\oplus$, trypan red; $\oplus$, without dye.

was that at 2 dynes/cm.

(3) **Amphoteric Dyes.**—It was found that methyl orange and trypan red gave no measurable effect on the monolayer of stearic acid in the pH range from 2 to 10, while congo red affected it remarkably when the substrate solution was acidic, as shown in Fig. 3. The film area in Fig. 3 was that at the surface pressure of 2 dynes/cm. It is seen that the curve for congo red shows a maximum at pH 3. As the solution becomes more acidic, congo red reduces its solubility and finally precipitates.

Discussion

The result of the present experiment shows that some dyes, when dissolved in the substrate, remarkably expand the monolayer of stearic acid spread on it. It is probable that this comes from the interaction between dyes in the substrate and stearic acid in the film. Here it is of importance to seek for the explanation for this interaction in terms of the molecular structure of the dyes. In the interaction between the dye and stearic acid electric forces due to polar and ionic groups and van der Waals force between nonpolar groups will play an important rôle. Electric forces, of course, are affected by the hydrogen ion concentration of the solution, while van der Waals force is independent of pH. Because of the presence of dye ion and stearate ion, both anion, a repulsion will act between the acidic dye and stearic acid in the solution of the alkaline region. This repulsion will disappear in the acid region and the dye will have a possibility of being adsorbed by van der Waals force to the surface of the stearic acid film. This may perhaps be taken as the explanation of the remarkable expansion of the monolayer of stearic acid on the acid solution of phloxine. In the case of scarlet red the ionic repulsion will be much greater because of its strongly ionizable $-\text{SO}_3\text{Na}$ group and weak van der Waals attraction due to a small size of the molecule. This leads to the failure in adsorption to the monolayer of stearic acid throughout the whole range of pH in the present experiment. The remarkable expansion of the monolayer of stearic acid in the presence of congo red at pH 3 may also be explained by van der Waals adsorption of the dye to the monolayer. That is, at this pH, being the isoelectric point of congo red, the electric repulsion will be the least between the dye and stearic acid due to the lack of the electric charge as a whole, and the van der Waals force will become the dominant one. In case of trypan red, although the molecule is large, five sulfonic

groups will act to shift its isoelectric point towards more acidic side, which prevents the adsorption from taking place. It might be expected that here the adsorption by the van der Waals force will occur if the solution is rendered much more acidic than that in the present experiment.

The situation is different in the case of basic dyes. They produce dye cations which are, presumably, capable of combining with stearic acid to form stearates. The degree of ionization of the basic dye becomes larger while that of stearic acid becomes smaller as pH of the solution decreases, and, consequently, it is expected that the adsorption becomes most pronounced at a certain pH value of the solution. This is confirmed by the present experiment, as shown in Fig. 2, where it is seen that the maximum expansion of the stearic acid monolayer occurs at pH 6 in the case of chrysoidine and at pH 7.8 in the case of crystal violet. In order to know further the significance of ionic interaction between basic dyes and stearic acid, the effect of crystal violet on the monolayer of cetyl alcohol was investigated. The condition of the experiment was the same as in the case of the monolayer of stearic acid. The result is shown as area~pH curves in Fig. 4. It should be noted that the expansion of the monolayer of cetyl alcohol is much smaller

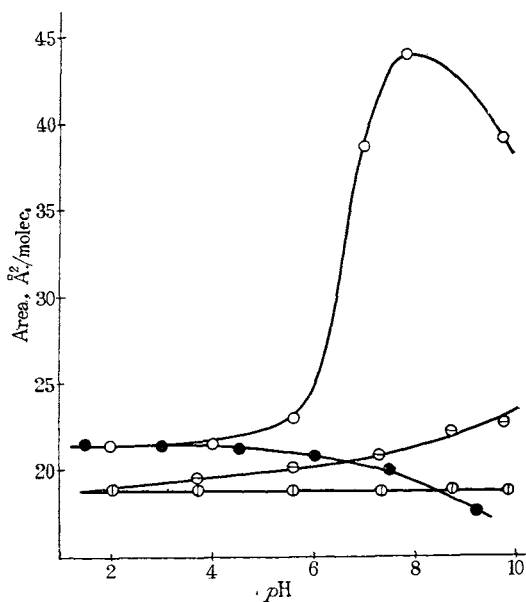


Fig. 4.—Comparison of the effect of crystal violet on the film area (at 15 dynes/cm) of stearic acid with that of cetyl alcohol: ○, stearic acid with dye; ●, stearic acid without dye; ⊙, cetyl alcohol with dye; ⊖, cetyl alcohol without dye.

than that of stearic acid in the presence of crystal violet. This is explained by the fact that cetyl alcohol is much less ionizable than stearic acid and so ionic interaction, a chief factor of the mutual interaction considered above, is much weaker between cetyl alcohol and crystal violet than between stearic acid and crystal violet. Such an ionic interaction has also been confirmed in the case of proteins and some dyes.⁽⁷⁾

It should be emphasized here that the mechanism of the interaction between dyes and stearic acid is fairly complex in nature, involving at least the ionic interaction and van der Waals force. The latter is also considered as a main factor determining the solubilization of dyes by detergents, the phenomenon which became to draw attention of many investigators recently.⁽⁸⁾ The author reported in the preceding paper the special interaction between stearic acid and such metallic ions as aluminum, thorium, etc. Comparing this with that between stearic acid and dyes studied in the present experiment we can find some similarities as well as differences in the mechanism underlying them. It may be mentioned that the basic dyes react with stearic acid in a similar manner as thorium and aluminum ions do with stearic

acid as far as the expansion and the complex structure of the resulting film are concerned. This view can also be confirmed by the experiment of wettability carried out by Inaba⁽⁹⁾ of our laboratory.

Summary

The interaction between the dyes dissolved in water and the monolayer of stearic acid spread on it was studied and discussed. It was shown that a remarkable expansion of the monolayer of stearic acid in the presence of phloxine and congo red was explained chiefly by the van der Waals adsorption, while that in the presence of basic dyes was explained chiefly by the ionic interaction. It was suggested that the interaction between basic dyes and stearic acid was analogous in some respects to the formation of soaps of such metals as thorium, aluminum, etc.

In conclusion the author expresses his hearty thanks to Prof. T. Sasaki for his kind guidance in the course of this study. The cost of this research has been defrayed from the grant of the Ministry of Education given to the professor.

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Kyūshū University, Fukuoka.*

(7) I. M. Klotz and F. M. Walker, *J. Am. Chem. Soc.*, **69**, 1609 (1947).

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On Some Dark-colored Chloroplumbates (II, IV) of the Type $[M^{III}A_6]PbCl_6$

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Introduction

In 1934 Norman Elliott⁽²⁾ determined the magnetic susceptibility of a violet black compound, $(NH_4)_2SbBr_6$, which had for years been generally believed to be a quadrivalent antimony compound, and found that the substance was diamagnetic and therefore could not con-

tain quadrivalent antimony in an ordinary sense. Three years later K. A. Jensen⁽³⁾ analysed the crystal structure of three similar compounds, $(NH_4)_2SbBr_6$, Rb_2SbBr_6 and Rb_2SbCl_6 , by the x-ray powder method and found scarcely any difference between the lattice structure of these compounds and that of ammonium hexabromostannate (IV) etc. except

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(2) N. Elliott, *J. Chem., Phys.*, **2**, 298 (1934).

(3) K. A. Jensen, *Zanorg. Chem.*, **232**, 193 (1937); *ibid.*, **233**, 295 (1937).

in their lattice dimensions, six halogen atoms being arranged around one antimony atom to make an octahedral structure. It is thus probable that these octahedral ions SbBr_6^- are a mixture of Sb Br^{-3}_6 (in which Sb is trivalent) and Sb Br^{-5}_6 (in which Sb is quinquevalent).

Yet another problem remains unsolved: Why do these antimony compounds present a dark violet appearance, which neither trivalent nor quinquevalent antimony compounds do?

While attempting to get some double salts between cobalt(III) or chromium(III) ammine chlorides and chlorides of heavy metals, the present author obtained crystalline compounds of empirical formulas, $[\text{Co}(\text{NH}_3)_6]\text{PbCl}_6$ (violet black), $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{PbCl}_6$ (puce-colored), $[\text{Cr}(\text{NH}_3)_6]\text{PbCl}_6$ (violet black) and $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]\text{PbCl}_6$ (puce-colored). These compounds, which from their formulas alone might be supposed to have trivalent lead atoms, have shown several points of resemblance to the antimony compounds above mentioned,—for example, in their anomalous coloration and magnetic property. In this paper the methods of preparation and magnetic data pertaining to these compounds will be given.

Experimental

Preparation of Chloroplumbates of the Type $[\text{M}^{\text{III}}\text{A}_6]\text{PbCl}_6$.—A solution containing chloroplumbic (IV) acid should first be prepared:

Three and three tenths grams of lead nitrate and 1 g. of potassium chlorate are dissolved in 50 ml. of water and the solution is poured little by little into 50 ml. of concentrated hydrochloric acid containing 1 g. of potassium chlorite. The white precipitate of lead(II) chloride produced at each addition is brought into solution by shaking and mixing, before the next portion is added. The yellow solution thus produced will contain lead(IV) at about 0.1 M in concentration.

In order to prepare a chloroplumbate of the type $[\text{M}^{\text{III}}\text{A}_6]\text{PbCl}_6$ (where M=Co or Cr), a solution of chloroplumbic acid thus prepared is mixed with a solution of a metal ammine, $[\text{M}^{\text{III}}\text{A}_6]\text{Cl}_3$; and the mixture is digested for some time. As starting metal ammine salts, it is recommended that those complex salts should be employed the preparation of which is the easiest. These metal amines, together with proper solvents and modes of digestion, are given in Table 1.

In each case of preparation a chloroplumbate (IV) of a sallow color is first formed, and this, with liberation of chlorine, is quickly changed into a dark-colored chloroplumbate of the type $[\text{M}^{\text{III}}\text{A}_6]\text{PbCl}_6$. It is filtered, and washed with dilute hydrochloric acid and alcohol.

These dark-colored chloroplumbates are hardly soluble in dilute hydrochloric acid but are decomposed by water forming a suspension of lead dioxide. When any of these compounds is warmed

Table 1

Salts to be prepared	Starting metal amines	Dissolved in	Mixed with H_2PbCl_6 aq. and digested
$\text{Co}(\text{NH}_3)_6\text{PbCl}_6$	4 g. of $\text{Co}(\text{NH}_3)_6\text{Cl}_3^{(4)}$	300 ml. of 3N HCl	at 60°C. for 20 min.
$\text{Co}(\text{NH}_3)_5\text{H}_2\text{O-PbCl}_6$	5 g. of $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O-oxalate}^{(5)}$	100 ml. of N/2 HCl	at 40°C. for 5 min.
$\text{Cr}(\text{NH}_3)_6\text{PbCl}_6$	5 g. of $\text{Cr}(\text{NH}_3)_6\text{(NO}_3)_3$	300 ml. of 3N HCl	at 60°C. for 20 min.
$\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O-PbCl}_6$	5 g. of $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O-(NO}_3)_3$	100 ml. of N HCl	at 40°C. for 5 min.

with dilute sulfuric acid and iron(II) sulfate, all the lead is precipitated as lead(II) sulfate, and the supernatant liquid shows the color of the complex ions employed as the cation source.

Of the starting complex salts mentioned above, hexamminechromium(III) nitrate has been prepared by a method modified from one proposed by S. M. Jørgensen, and aquopentamminechromium(III) nitrate by a new method of the present author's, which will be published shortly.

Analyses:

Calcd. for $\text{Co}(\text{NH}_3)_6\text{PbCl}_6$ or $[\text{Co}(\text{NH}_3)_6]_2(\text{Pb}^{\text{IV}}\text{Cl}_6)_2$: Pb(total), 35.64%; Pb(IV), 17.82%; Co, 10.14%; Cl, 36.63%. Found: Pb(total), 35.89%; Pb(IV) (determined by iodometry), 17.96%; Co, 9.76%; Cl, 36.95%.

Calcd. for $\text{Co}(\text{NH}_3)_5\text{H}_2\text{OPbCl}_6$ or $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]_2(\text{Pb}^{\text{IV}}\text{Cl}_6)_2$: Pb(total), 35.60%; Pb(IV), 17.80%; Co, 10.13%; Cl, 36.56%. Found: Pb(total), 35.88%; Pb(IV), 16.85%; Co, 9.62%; Cl, 36.59%.

Calcd. for $\text{Cr}(\text{NH}_3)_6\text{PbCl}_6$: Pb(total), 36.09%; Cr, 9.06%; Cl, 37.05%. Found: Pb, 36.00%; Cr, 8.63%; Cl, 37.46%.

Calcd. for $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{OPbCl}_6$: Pb(total), 36.05%; Cr, 9.04%; Cl, 37.00%. Found: Pb, 35.00%; Cr, 9.30%; Cl, 37.64%.

Magnetic Susceptibility of the Chloroplumbates of the Type $[\text{M}^{\text{III}}\text{A}_6]\text{PbCl}_6$.—In order to test whether the Pb's in such cobalt complex chloroplumbates as $[\text{Co}(\text{NH}_3)_6]\text{PbCl}_6$ have unpaired electrons or not, it is only necessary to determine their magnetic susceptibility; for, in the trivalent cobaltammine complex ions the electrons are known to be all paired.

Measurements by the Gouy's cylinder method have given, as the mass-susceptibility of $[\text{Co}(\text{NH}_3)_6]\text{PbCl}_6$ and $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{PbCl}_6$, values in the neighborhood of -0.3×10^{-6} E. M. U., thus proving that the Pb's in these compounds have no

(4) Hexamminecobalt(III) chloride is easily prepared by bubbling air through a solution of cobalt(II) chloride in aqueous ammonia in the presence of ammonium chloride and adsorption charcoal. J. Bjerrum, "Metal Ammine Formation in Aqueous Solutions," P. Haase and Son, Copenhagen, 1941. See *Chem. Abstr.*, **34**, 6534 (1941) and also W. C. Fernelius et al., "Inorganic Syntheses" Vol. II, McGraw Hill Book Co., New York, N. Y., 1946, p. 216.

(5) S. M. Jørgensen, *J. Prakt. Chem.*, **31** 89 (1985); *Z. anorg. Chem.*, **17**, 461 (1898).

unpaired electrons and therefore cannot be tervalent in an ordinary sense.

The corresponding chromium compounds have shown strong paramagnetism, but this may be due to the presence of unpaired electrons in tervalent chromium complex ions. Considering every point of resemblance between these cobalt (III) and chromium(III) ammine chloroplumbates, it seems quite reasonable to think that in the latter, too, the Pb's do not exist in the tervalent state.

It therefore seems adequate to name these compounds as hexamminecobalt(III) chloroplumbate (II, IV) etc.

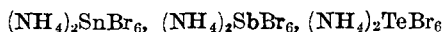
Considerations

Several series of compounds are known which have a characteristic dark color and contain the same element in different valence states.⁽⁶⁾ The chloroplumbates (II, IV) described above appear to be new additions to these series, because:

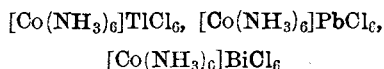
(i) They are all dark colored which is inexplicable from the colors of the component ions. (Double salts between $[Co(NH_3)_6]Cl_3$ etc. and $PbCl_2$ show the color of $Co(NH_3)_6^{+++}$ ions etc.⁽⁷⁾ and so do the chloroplumbates (IV) of these complex cations.)

(ii) The magnetic property of $[Co(NH_3)_6]PbCl_6$ and $[Co(NH_3)_5H_2O]PbCl_6$ denies the existence of any unpaired electrons in Pb's; and it is natural to think that the compounds contain $PbCl_4^{-2}$ and $PbCl_6^{-2}$.

(iii) Two very similar series:



and



are obtained where Sn, Sb and Te as well as

Tl, Pb and Bi are arranged in the order of atomic numbers.⁽⁸⁾

Some hypotheses have been advanced by different authors as to the reason of the coloration of these mixed valence compounds ("Oscillieren" or "resonance" for example); but the experimental evidence is not sufficient for any of them; and anything like a perfect solution of the problem must depend on the fruits of further researches.

Summary

(1) Compounds ranging from violet black to puce in color, $[Co(NH_3)_6]PbCl_6$, $[Cr(NH_3)_6]PbCl_6$, $[Co(NH_3)_5H_2O]PbCl_6$ and $[Cr(NH_3)_5H_2O]PbCl_6$ have been prepared, by mixing a solution of $[Co(NH_3)_6]Cl_3$ etc. (in dil. HCl) and a solution containing H_2PbCl_6 and digesting them at 40° to 60°.

(2) $[Co(NH_3)_6]PbCl_6$ and $[Co(NH_3)_5H_2O]PbCl_6$ are diamagnetic and therefore it seems natural to consider these compounds as hexamminecobalt(III) chloroplumbate (II, IV) and aquopentamminecobalt(III) chloroplumbate (II, IV) respectively.

It is the author's genuine pleasure to acknowledge his indebtedness to Mr. Meitaro Endo without whose wholehearted coöperation in magnetic measurements, these pages could never have been written.

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(8) In a letter to the author, Prof. Tokunosuké Watanabe and Mr. Masao Atoji of the University of Osaka have kindly informed him that the crystal lattice structure of $Co(NH_3)_6PbCl_6$ or $[Co(NH_3)_6](Pb^{II}Cl_6)(Pb^{IV}Cl_6)$ exhibits a close resemblance with a slight deformation to that of $Co(NH_3)_6TiCl_6$, the latter being composed of $Co(NH_3)_6^{+3}$ and $TiCl_6^{-3}$ arranged in a NaCl-type. See *Acta Cryst.*, **3**, 405 (1950).

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