Studies on the Gas-Liquid Interface by Surface Potential Measurements III. The Surface Aging of the Solutions of the Long-chain Dibasic Acids

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When a new surface is formed on the top of a solution by sweeping the surface with a glass barrier, the solute in the solution will begin immediately to be adsorbed on the freshly formed surface. The rate of adsorption depends mainly on the nature of the solute if the other conditions are the same, and is a problem of some interest in regard to the structure of the layer and the mechanism of adsorption. The adsorption equilibrium of polar organic compounds on the surface of its solution can be considered as a result of competition of the hydrophilic nature of polar groups and the hydrophobic nature of the nonpolar part of the amphipathic molecule. In a homologous series the solute of low molecular weight readily reaches a steady state. With the solute of moderate molecular weight, the formation of a completely adsorbed layer needs considerable time. On the other hand, the solute of high molecular weight requires so much longer time for equilibration, that the solution apparently reaches a steady state immediately. In a homologous series of the amphipathic compounds, it is generally expected that the lower the molecular weight of the solute is, the higher the solubility and the larger the mobility of the solute is.

The variation of a surface layer will be reflected on the surface tension and surface potential of the solution. Hence, the rate of adsorption can be readily followed by measuring the surface tension and the surface potential as a function of time. In the course of our previous investigation,(1) the change of surface

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(1) T. Isemura and H. Hotta, *Bull. Chem. Soc. Japan*, **23**, 193 (1950).

potential with time was found with solutions of some ω, ω'-dicarboxylic acids.

In this respect, the measurements of surface tension and surface potential of the solution are the powerful means to study the change of the surface layer of the solution. In order to observe the change of the surface layer and to clarify its cause, we modified the apparatus used in the previous investigation to adapt it for this purpose. The change of the surface tension and the surface potential was determined with some dicarboxylic acids. From such experiments it was concluded that the adsorption may occur in two stages, initial rapid, and later slow adsorption. In our present experiments, the slow adsorption only was studied. The experimental results will be considered on the ground of the kinetic molecular theory.

Experimental

Experimental Methods.—The apparatus used in our present experiment was a combination of a surface balance of hanging plate type and a surface potentiometer of vibrating electrode type. A thick-walled shallow glass trough, 0.7×7.0×15.0 cm. was used for the economy of the solution. The vibrating electrode of the diameter of 20 mm. was hung over the middle of the trough and the glass plate for the surface tension measurement was inserted into the solution by the side of the electrode. The other electrode made of platinum wire was immersed over-night in the same solution prior to the experiment by using such a syphon as shown in Fig. 1. In order to observe the surface aging of the solution, the surface of the solution was cleaned before starting by the paraffined glass barrier.

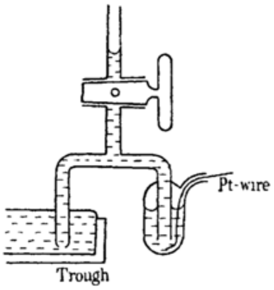

Fig. 1.

The amplifier of the surface potentiometer consists of two parts, *i. e.*, the pre- and main amplifier. The main amplifier is a three-stage tuned amplifier for *ca.* 500 c./s. using three CZ-501 D tubes.

The change of the surface tension was followed by the hanging plate method, and the displacement of the plate was measured by an optical lever.

The level of the surface of the solution was defined by using a telescope.

The materials used in the present experiment were adipic, suberic, azelaic, sebacic and γ, γ'-sulfonyl dibutyric acid. Most of the measurements were made with acidulated solution by hydrochloric acid (in a concentration of 0.015 *N* HCl) if without any special indications. With sebacic acid, a measurement was also made for comparison with aqueous solution. The monolayer of ω, ω'-hexadecadicarboxylic acid was also studied by the technique generally used for insoluble monolayer. All measurements were made at room temperature in a small closed chamber without any special temperature regulation. However, the variation of temperature in the course of measurement to obtain a single curve never exceeded more than 0.4°. At first, it was confirmed that the change of surface tension of pure water with time was not detectable during a course of experiment (within 1.5 hours). The effect of evaporation was also negligible in such a small closed chamber.

Results.—From such experiments as the above it was found that the rate of change of the surface tension was generally parallel to that of the surface potential. However, at the last stage of adsorption of the nearly saturated solution of sebacic acid after 60 minutes, both rates were not parallel to each other. (See curves *f* and *f'* in Fig. 3 and 4.) In this respect, some theoretical consideration will be given in the following section. No appreciable change of the tension and the potential could be observed with nearly saturated solutions of adipic acid (0.095 mol/l.) and of γ, γ'-sulfonyl dibutyric acid (0.017 mol/l.) at 22°.

A part of the experimental results is shown in the following figures (Fig. 2, 3 and 4). The surface tension of suberic acid solution in the concentration of 4.5×10^{-3} mol/l. changed definitely by *ca.* 0.1 dyn./cm. during the first four minutes, although the change can hardly be recognized from the figure. Azelaic acid solution of 2.7×10^{-3} mol/l. showed the gradual change of the tension until after 93 minutes when the experiment was disrupted. On the other hand, azelaic acid solution of 1.35×10^{-3} mol/l. showed no change. Meanwhile, all the solutions of sebacic acid examined changed the tension even in a concentration as dilute as 1.87×10^{-4} mol/l.

From these results it can be concluded that the shorter the dicarboxylic acid is and the more dilute the solution is, the shorter is the time required for equilibration. In the case of sebacic acid, the surface tension and potential of the most dilute solution showed an appreciable change after a considerable time.

The absolute value of surface tension can hardly be determined by our present method without any uncertainty, even though the level of the surface of the solution was adjusted to

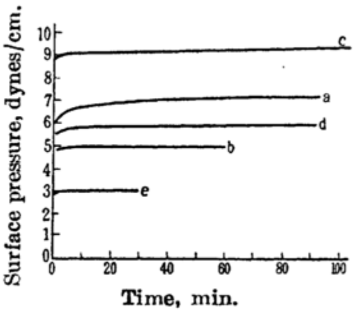

Fig. 2.—The change of surface pressure with time.

(I) Suberic acid solutions in 0.015 N HCl: curve a, 9.03×10^{-3} mol/l. (nearly saturated), 22°C.; curve b, 4.5×10^{-3} mol/l., 22°C.

(II) Azeraic acid solutions in 0.015 N HCl: curve c, 5.4×10^{-3} mol/l., 20.5°C.; curve d, 2.7×10^{-3} mol/l., 20.5°C.; curve e, 1.35×10^{-3} mol/l., 21.0°C.

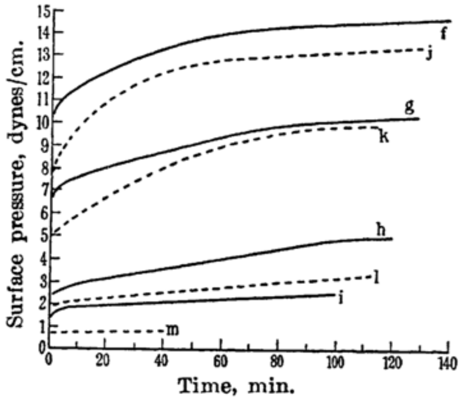

Fig. 3.—The change of surface pressure of sebacic acid solutions with time.—

(I) Solutions in 0.015N HCl (full line): curve f, 1.62×10^{-3} mol/l. (saturated), 22°C.; curve g, 8.1×10^{-4} mol/l., 22°C.; curve h, 4×10^{-4} mol/l., 22°C.; curve i, 2×10^{-4} mol/l., 23°C.

(II) Solutions in water (dotted line): curve j, 1.55×10^{-3} mol/l., 22°C.; curve k, 7.7×10^{-4} mol/l., 23°C.; curve l, 3.75×10^{-4} mol/l., 23 °C.; curve m, 1.87×10^{-4} mol/l., 22.5°C.

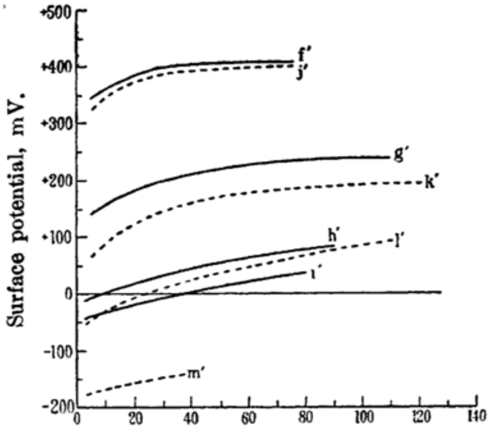

Fig. 4.—The change of surface potential of the sebacic acid solutions with time. Each curve corresponds to that with the same letter without prime in Fig. 3.

a fixed level by the aid of a telescope. Moreover, in the initial stage (5-10 seconds) the disturbance of the surface caused by dipping of the plate and the sweeping could not be avoided. However, the rate of surface tension lowering could be determined very accurately. On the other hand, the rate of change of surface potential was also determined quite correctly since we take care of equilibration, sufficiently for this purpose.

In comparison with our previous results,(1) the results on adipic and γ,γ-dibutyl sulphonic acid were in good agreement with previous ones. The results on other acids showed slight discrepancies. These slight discrepancies may be caused by some fluctuation of the standard potential and by the adsorption of the solute on the electrode dipped in the solution. The electrode in the present experiment was used after equilibration between the solution and the electrode, while the electrode in the previous experiments was used without any such precaution.

ω,ω'-hexadecadicarboxylic acid was examined on 0.1 N HCl solution. It gave the film of gaseous type, however considerably deviated from the ideal law. The surface moment of hexadecadicarboxylic acid was determined from surface potential-area relation and was found 0.41 D at the molecular area of 100 Å.², 0.35D at 200 Å.² and 0.32 D at 300 Å.². 0.35 D was used in the later calculation.

Discussion

The mechanism of the change of surface tension with time was recently studied by several investigators. Some of them(2,3,4) considered that the diffusion of the solute was one of the most important factors. In the case of the fast adsorption such as that studied by Addison,(5) the inference might be correct; however, in the case of slow adsorption such as in our present experiments, this is not

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(2) A. F. H. Ward and L. Tordai, *J. Chem. Phys.* **14**, 453 (1946).

(3) S. Ross, *J. Am. Chem. Soc.*, **67**, 990 (1945).

(4) C. M. Blair, *J. Chem. Phys.*, **16**, 113 (1948).

(5) C. C. Addison, *J. Chem. Soc.*, **1943**, 535; **1944**, 252; **1945**, 98.

applicable.(6,7) In the latter case the rate of adsorption must be much slower than that of diffusion. The inference was examined quantitatively in the following manner. According to Ward and Tordai,(2) the rate of diffusion will be given by

$$\frac{\partial M}{\partial t}=D\frac{n_0}{\sqrt{\pi Dt}} \qquad (1)$$

where D is the diffusion constant, M the number of solute molecules per cm², n_0 the bulk concentration in molecules per cc., t the time in sec. If we assume values approximately as follows,

$$D=10^{-6},\quad n_0=10^{17}\quad t=10^3$$

in relation to our present experiment, it will be obtained from (1)

$$\frac{\partial M}{\partial t}=10^{13}\quad \text{(molecules per cm.}^2\text{ per sec).}$$

On the other hand we shall estimate the actual rate of adsorption to be 10^9 molecules per cm² per sec. from the present experimental results. The reasons for the estimation will be given in a later part of this report. Now we assume the final state of adsorption was reached by passing over an energy barrier which serves as the rate-determining factor. The adsorption was probably pursued through two stages. The first is the fast adsorption which is mainly concerned with diffusion, and the second is the slow adsorption with energy barriers, which are caused probably from dehydration, electrostatic repulsion, reorientation and so on. In our present experiment, only the second stage of adsorption was investigated, since our method did not fit the investigation of such a fast change occurring in the surface as that of the first stage,

In order to study this problem the cage model of a liquid by Fowler and Slater(8) was adopted as the ground. If we consider a sublayer under the adsorbed monolayer in the surface, the concentration in the sub-layer may be equal to that of the bulk since the diffusion is enough to made up for the loss by adsorption quantitatively. Therefore, if the number of solute molecules in a unit area of a sublayer is n_{sub},

$$n_{sub}=\frac{2Nc\delta}{10^3}$$

where N is the Avogadro's number, c the bulk concentration in mol/l., 2δ the thickness of sub-layer in cm. The total number of collisions per unit time of a given molecule with the cage wall by the thermal agitation can be expressed by

$$\nu=\frac{3}{2\delta}\sqrt{\frac{2RT}{\pi M}}$$

according to them,(8) where M is the molecular weight. Now, if we assume that one-sixth of the total collision is effective to adsorption, the total number of the effective collisions, Z against unit area per unit time, is written by

$$Z=\frac{1}{6}n_{sub}\nu=\frac{Nc}{10^3}\sqrt{\frac{RT}{2\pi M}}. \qquad (2)$$

This result is formally analogous to the formula(9) previously proposed. Therefore, the number of the actually adsorbed molecules, n_{ads}, per unit area per unit time is given by

$$n_{ads}=\frac{Nc}{10^3}\sqrt{\frac{RT}{2\pi M}}e^{-\Delta F^*/RT} \qquad (3)$$

where ΔF^* is the free energy of activation for adsorption. According to the cage theory, of course, the size of the cage of the solute molecule is equal to that of the solvent molecule, and all molecules in a cage have a similar energy distribution with a perfect gas. We assume this first approximation is the case in our present experiment.

On the other hand we can estimate the actual rate of adsorption from the rate of the surface potential change as follows. It is generally accepted that the relation between the surface potential ΔV and the contribution of each adsorbed molecule to it, namely, the effective moment μ of each molecule is expressed by

$$\Delta V=4\pi N_{ads}\mu \qquad (4)$$

where N_{ads} is the number of the adsorbed molecules in a unit area of the surface. Hence

$$\frac{d\Delta V}{dt}=4\pi\left(\mu\frac{dN_{ads}}{dt}+N_{ads}\frac{d\mu}{dl}\right) \qquad (5)$$

If it is assumed as a first approximation that,

$$\frac{d\mu}{dt}=0, \qquad (6)$$

that is the orientation of the molecule of ω, ω'-dicarboxylic acid is not changed by

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(6) K. S. G. Doss, *Kolloid-Z.*, **86**, 205 (1939).
(7) A. E. Alexander, *Trans. Faraday Soc.*, **37**. 15 (1941).
(8) Fowler and Slater, *Trans. Faraday Soc.*, **34**, 81 (1938).
(9) Adam, "The Physics and Chemistry of Surfaces", Oxford, 1938, p. 6.

further adsorption, it is obtained from (5)

$$\varDelta(\varDelta V)=4\pi\mu\varDelta N_{ads}=4\pi\mu n_{ads} \qquad (7)$$

where the symbol $\varDelta$ means the change for a unit time. Therefore, if the magnitude of μ of the suitable standard substance is known, the rate of adsorption can be calculated from (7). There exists some doubt in respect to the validity of the equation (4). However, this may be cancelled by applying the same equation to a standard substance. In the present case, ω, ω'-hexadecadicarboxylic acid was used as the standard substance, which has *ca.* 0.35 Debye unit of μ in monolayer as mentioned above. Although this value may be somewhat smaller than that expected from the data of monocarboxylic acid[10] and μ should be dependent upon the state of the surface, the above value was adopted for the present calculation, and n_{ads} obtained was shown in the Table 1. With this value $\varDelta F^*$, the activation free energy of adsorption, can be estimated with (3), which is also listed in the Table 1.

This value of n_{ads} seems to be too large, because the surface energy per molecule is smaller than kT in the lower pressure region from our present result. This contradiction may, probably, be due to the unsuitable estimation of μ. On the other hand, we can at least point out the propriety of the assumptions that (I) all the adsorbed molecules are undissociated in the acidulated solution; and that (II) equation (6) is valid, that is, the contribution of the change of μ of the already adsorbed molecules to $\varDelta(\varDelta V)$ can be neglected. However these assumptions effect the estimation of $\varDelta F^*$ by 0.5 Kcal./mol increase even at the highest, but considerable to that of surface energy per molecule. Neverthless n_{ads} should be smaller, consequently $\varDelta F^*$ larger.

As already pointed out, in the case of the saturated sebacic acid solution (see curves f and f′ in Fig. 3 and 4), the surface potential attained to the stationary state, while the surface pressure was still increasing. This means that in the fairly close-packed film a small increase of packing would produce a marked increase in surface pressure but scarcely any effect on surface potential as interpreted by Alexander.[7]

Also in Fig. 3 and 4 the effect of the hydrochloric acid was examined in comparison with the aqueous solution. It may be noticed that, in the concentrated solution, the equilibrium values of both acidulated and aqueous solution scarcely suffered any effect in spite of the considerable difference in the initial stage, while, in the dilute solution, the considerable difference on the equilibrium value was found. The surface potential of the aqueous solutions was far more negative than of the acidulated solution. This fact can be explained on the

Table 1

Rate and Activation Free Energy of Adsorption

Solute	Curve in figure	Total effective collison number per second	n_{ads} and $\varDelta F^*$	Time, min. 10 ~20	20 ~30	30 ~40	40 ~50	50 ~60	60 ~70	70 ~80	80 ~90	90 ~100	100 ~110	110 ~120
Suberic Acid	a	2.6×10^{22}	n_{ads} (10^9/cm^2/sec)	5.7	—	—	4.3		—	—	—	—	—	—
			$\varDelta F^*$ (kcal./mol)	17.5	—	—	17.8		—	—	—	—	—	—
	b	1.3×10^{22}	n_{ads}	1.7	—	—	—	—	—	—	—	—	—	—
			$\varDelta F^*$	17.9	—	—	—	—	—	—	—	—	—	—
Azeraic Acid	c	1.5×10^{22}	n_{ads}	1.6					0.5				—	—
			$\varDelta F^*$	18.0					18.5				—	—
	d	7.5×10^{21}	n_{ads}	0.7									—	—
			$\varDelta F^*$	18.1									—	—
Sebacic Acid	f	3.9×10^{21}	n_{ads}	25	13	9.5	4.3	1.9	0	—	—	—	—	—
			$\varDelta F^*$	15.4	15.7	16.0	16.4	17.0	∞	—	—	—	—	—
	g	2.05×10^{21}	n_{ads}	30	—	15	—	11	—	—	—	2.5	—	2.2
			$\varDelta F^*$	15.0	—	15.4	—	15.6	—	—	—	16.5	—	16.6
	h	10^{21}	n_{ads}	11									—	—
			$\varDelta F^*$	14.1									—	—
	i	5×10^{20}	n_{ads}	11									—	—
			$\varDelta F^*$	13.8									—	—

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(10) J. H. Schulman and E. K. Rideal, *Proc. Roy. Soc. (London)*, A **130**, 270 (1930).

ground that, the dissociation degree at the surface is somewhat larger on the aqueous solution than on the acidulated solution, if the surface concentration is low, while, the difference of dissociation between both solutions disappears, if the surface concentration is high. The effect of acidulation is not so considerable as in the case of soap.(11) This difference is because of the small dissociation constant of the free acid compared with that of soap. This will be further investigated in future for more evidences.

Summary

The surface aging of the solutions of some ω, ω'-dicarboxylic acids was investigated by measuring the surface tension and surface potential, in a function of time. Only the slow adsorption process was studied in the present experiment.

Adipic, suberic, and azelaic acid reached readily an equilibrium. Sebacic acid showed considerable surface aging. The mechanism of adsorption was assumed in the light of kinetic molecular theory, and the free energy of activation for adsorption was calculated. We obtained the free activation energy, 17.5-17.9 Kcal. for suberic acid, 18.0-18.5 Kcal. for azelaic acid and 13.8 Kcal. or more than this for sebacic acid. Free energy of activation for adsorption was increased to some extent with the surface concentration of already adsorbed solute molecules and consequently, for a certain solution, with the surface age.

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(11) G. C. Nutting and F. A. Long, *J. Am. Chem. Soc.*, **63**, 84 (1941).