The State of Metal Ion in Aqueous Solutions and its Surface Chemical Effect. II. Uptake of Metal Ions from Aqueous Solutions by Stearic Acid Monolayer*

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Introduction

It has been pointed out previously[1] that the metallic ions are classified into two groups from their effects upon monolayers of fatty acid. One includes such metal ions as Co, Cu, Al and Th which make the monolayer expand and remarkably rigid, and the other includes mainly alkaline earth metals which condense it. A built-up film of stearic acid takes up many of the former ions from[2] and is wetted by[3] their solutions, while it does not show such effects with the latter ions. All these phenomena could be explained by the difference in types of the structure of metallic soap formed by the interaction between fatty acid in the film and metal ions in the solution[1-3].

In the case of the former ions, the metallic soaps seem to consist of molecules of stearic

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* Part I of this series has been published recently by R. Matuura and H. Kimizuka[9].

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1) T. Sasaki and R. Matuura, This Bulletin, **24**, 274 (1951); R. Matuura, ibid., **24**, 278 (1951).

2) M. Muramatsu and T. Sasaki, ibid, **25**, 21, (1952).

3) M. Muramatsu and T. Sasaki, ibid., **25**, 25 (1952); A. Inaba, ibid., **26**, 43 (1953).

acid and polymeric and complicated aggregates of metal ions in solution, the acidity of which is adjusted to be in the region of pH where the metal hydroxide begins to precipitate[1-3]. Schulman et al.[4,5], using myristic acid monolayer, reached the similar conclusion and postulated that the polymeric nature of metallic soap is attributed to hydrogen bonding between mono- and dihydroxyl metal ions combined stoichiometrically with each acid molecule. In connection with this, it may be noteworthy that the mode of interaction between aqueous sodium alginate and octadecylamine monolayer spread on it resembles closely that between such metal ions and stearic acid monolayer[6].

In contrast with this, the latter alkaline earth ions are considered to be bound to stearate ions with simple stoichiometric relation and the metallic soaps thus formed are also considered to have no lateral binding as was postulated in the former case[1-3].

In order to obtain further knowledge about the difference between two types of metallic soap as mentioned above, it was attempted to determine the binding ratio of strontium and cobalt atoms to the acid molecules in the surface film formed by the interaction between a solution of strontium and cobaltous chlorides and monolayers of stearic acid spread on them.

Experimental

Radioactive strontium chloride was chloride of an isotopic mixture of ^{90}Sr (half-life 53 days) and ^{90}Sr (25 years) and therefore contained ^{90}Y (61 hr.) as a radioactive daughter. It was diluted isotopically to 10 mC/g. with recrystallized strontium chloride and was brought to a desired concentration and acidity with distilled water and redistilled ammonia solution. From six to twenty layers of the surface film spread on such a solution were transferred onto a metal slide coated with five layers of barium stearate under the piston pressure (30 dyn./cm.) of oleic acid. The radioactivity of this multilayer was measured with and without an aluminum disc (15 mm. diameter and 1.5 mm. thickness) placed on the center of the slide and exactly beneath the window of the GM tube. The difference between these counts was taken as the radioactivity of the part of multilayer covered by the disc, and was compared with radioactivity of the standard $SrCl_2$ mounted on cigarette papers (15 mm. diameter)[7] which were fixed on the metal slides of the same magnitude as that coated by multilayer. Identical conditions were maintained for both the disc and the papers. Number, x, of bound Sr atoms per cm^2 of monolayer was calculated from the radioactivity at transient equilibrium between ^{90}Sr and ^{90}Y which was attained after at least fifty days.

Owing to a difficulty in building up the monolayer spread on the solution of cobaltous chloride, the amount of bound cobalt atoms was determined as follows. The monolayer was collected to one side of the trough by moving the barrier and collapsed film was scooped up with a strip of filter paper. The water content of the paper was first measured by drying, from which the amount of Co atom carried merely with the solution was determined. It was then burned in a crucible and the remaining ash was treated repeatedly with 6 N hydrochloric acid. The resulting solution was transferred onto a cigarette paper, evaporated to dryness, and its radioactivity was measured by means of GM counter. The amount of Co atom bound to monolayer could be calculated from the radioactivity of this sample, taking account of the amount of cobalt mentioned above.

The surface pressure of the film was determined by the same method as used in a former report[6]. The acidity of substrate solution was adjusted by redistilled hydrochloric acid and redistilled ammonia unless otherwise mentioned.

All monolayers were kept on substrates of room temperature for from three to eight minutes after spreading, before the experiments were carried out.

Results

Interaction between Sr Ion and Monolayer.—In Table I are shown the effects of pH of substrate solution and of the number of layers in the built-up film upon x, where the concentration of strontium chloride in the substrate is maintained at 10^{-4} mol./l. According to Bikerman[8] the deposition ratio of monolayer of stearate of alkaline earth metal is always unity when it is transferred onto a solid surface. Therefore, if we assume that the cross-sectional area of stearic acid in multilayer is 20 Å^2, number, R, of Sr atoms bound to one molecule of stearic acid is calculated and listed in the last column. It is seen in this table that R increases with increasing pH and has little dependence upon the number of layers at each pH.

When substrate pH was greater than 9.6, the monolayers were unsuccessfully built up onto the slide. Actually it was observed that the silk thread separating the monolayer from piston oil did not move in accord with the up and down trip of the slide, and that the wettign condition as well as interference color of the surface was uneven and irregular.

Effect of concentration, c, of strontium chloride solution upon x was examined at the constant

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[4] J.H. Schulman, et al., *Trans. Faraday Soc.*, **46**, 475 (1950); **47**, 788 (1951); **50**, 1139 (1954).

[5] J.H. Schulman and M.Z. Dogan, *Discussion, Faraday Soc.*, **16**, 158 (1954).

[6] T. Sasaki and M. Muramatsu, This Bulletin, **26**, 96 (1953).

[7] G. Friedlander and J.W. Kennedy, "Introduction to Radiochemistry", John Wiley and Sons, Inc., New York, N.Y. (1949), p. 231.

[8] J.J. Bikerman, *Proc. Roy. Soc. London*, **A170**, 130 (1939).

pH value of 5.7, the result being shown in Table II.

TABLE I

EFFECT OF SUBSTRATE pH UPON NUMBER OF Sr ATOMS BOUND TO ONE MOLECULE OF STEARIC ACID; $SrCl_2$ 10^{-4} mol./l.

Sub-strate pH	No. of Built-up layers, n	Number of bound Sr atoms/cm² of mono-layer, x	Number of bound Sr atoms/ molecule of stearic acid, R	Mean
4.0	8	0.70×10^{13}	0.014	0.016
〃	10	0.85× 〃	0.017	
5.0	10	6.65× 〃	0.137	0.132
〃	20	6.30× 〃	0.126	
6.1	10	10.63× 〃	0.213	0.209
〃	14	10.56× 〃	0.211	
〃	20	10.22× 〃	0.204	
7.5	6	12.11× 〃	0.242	90.24
〃	10	13.06× 〃	0.261	
〃	14	12.14× 〃	0.243	
〃	20	12.43× 〃	0.249	
9.2	6	26.33× 〃	0.527	0.437
〃	10	21.17× 〃	0.423	
〃	14	24.05× 〃	0.481	
〃	20	23.12× 〃	0.462	
9.3	10	26.68× 〃	0.534	0.517
〃	20	25.02× 〃	0.500	

TABLE II

EFFECT OF CONCENTRATION OF $SrCl_2$ UPON NUMBER OF BOUND Sr ATOMS per cm² OF MONOLAYER; SUBSTRATE pH 5.7

$SrCl_2$ concentration, c, mol./l.	Number of bound Sr atoms/cm² of mono-layer, x
1.0×10^{-3}	1.35×10^{14}
7.0×10^{-4}	1.06 × 〃
4.0 × 〃	0.83 × 〃
2.0 × 〃	0.78 × 〃
1.0 × 〃	0.72 × 〃
7.0×10^{-5}	0.49 × 〃
4.0 × 〃	0.31 × 〃
1.0 × 〃	0.28 × 〃
5.0×10^{-6}	0.19 × 〃
1.0 × 〃	0.22 × 〃

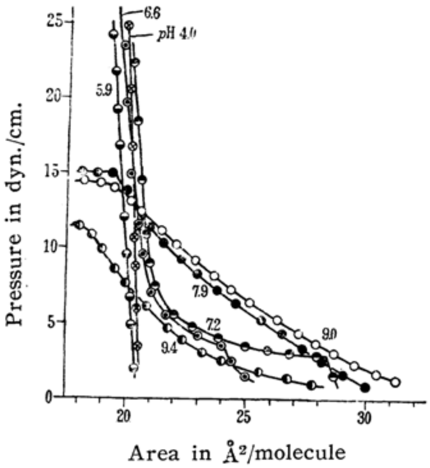

Fig. 1. Pressure—area curve of monolayer of stearic acid spread on 10^{-4} mol./l. $CoCl_2$.

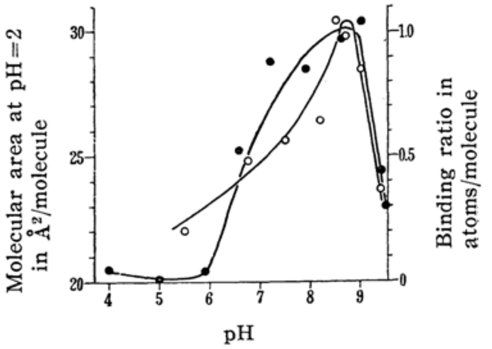

Fig. 2. Effect of pH upon molecular area at pH=2, ●, and binding ratio, R, ○, of Co atom in the film.

Interaction between Co Ion and Monolayer.—Fig. 1 shows the effect of substrate pH upon the pressure—area curve of stearic acid spread on 10^{-4} mol./l. solution of cobaltous chloride. Generally speaking, it was seen that the monolayer condensed up to pH of about 6, while remarkable expansion and increase in compressibility of the film were observed at pH 8–9. This is similar to the result in the case of 10^{-3} mol./l. solution of the same substance, which was reported in a preceding paper[9]. pH dependence of the area per molecule at F=2 dyn./cm. is shown in Fig. 2, together with that of number, R, of bound Co atoms per one molecule of stearic acid. It is interesting that both curves changed with pH similarly, and that the maximum value of R being unity was obtained at pH 8–9, where the area reached the maximum value of 30 Å²/molecule or larger.

When sodium or potassium hydroxide was used as pH-adjusting agent instead of ammonia, we observed the less exaggerated effects of Co ion upon both area at pH=2 and compressibility, while the same result was obtained for R—pH relationship. This is represented in Table III in which the effects of pH-adjusting agent upon the nature of the film are listed.

TABLE III

EFFECT OF pH-ADJUSTING AGENT UPON MOLECULAR AREA AT pH=2, R, AND COMPRESSIBILITY OF FILM; SUBSTRATE pH 8.9

pH-adjusting agent	NH_4OH	NaOH	KOH
Molecular Area, Å²/molecule	30.5	25.7	24.8
R, atoms/molecule	1.01	0.97	0.93
Compressibility, Å²·cm./molec.·dyn.	0.76	0.49	0.43

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[9] R. Matuura and H. Kimizuka, This Bulletin, 28, 668 (1955).

In a region more alkaline than about pH 9.5–10, the measurement could not be performed without large accidental error, presumably due to the dissolution of monolayer or precipitation of cobalt hydroxide.

Discussion

It has been shown that[1,10] alkaline earth metals in aqueous solution exert their effects upon either pressure or mechanical properties of monolayer of fatty acid spread on it, when pH of the solution is larger than 5–6. In order to explain the phenomena, electrostatic binding was presumed between monolayer and metal ions. Experimental result in Table I supports this presumption. Since the dissolving state of Sr ion is not considered to be greatly affected by the acidity of the medium when pH$<$9, pH dependence of R comes mainly from an increasing ionization of stearic acid with decreasing acidity of the substrate. This consideration is also supported by a decreasing surface potential of the monolayer of stearic acid when pH of the substrate solution increases in the range of pH 3–12[11].

Such a type of binding in terms of ion—ion attraction results in formation of metal stearate in the film, the composition of which should be discussed. That R attains a maximum value of 0.5 when substrate pH is adjusted to 9.3 may favorably be explained by assuming interaction between one Sr ion and two stearate ions. Therefore it is probable that the monolayer on aqueous $SrCl_2$ of pH$<$9.3 consists of stearate ions, molecules of stearic acid and of Sr stearate which is formed as a result of the following reaction.

$$\underset{\text{(bulk)}}{Sr^{++}}+\underset{\text{(surface)}}{2C_{17}H_{35}COO^-}=\underset{\text{(surface)}}{(C_{17}H_{35}COO)_2Sr}$$

Ignoring the decrease of substrate concentration, c, and the surface contraction of stearate ion due to interaction, the following equation holds as far as strontium hydroxide does not precipitate,

$$\frac{K_2{}^2c}{K_3x}\left\{\frac{a-2x}{[H^+]+K_2}\right\}^2=\frac{K_0{}^2}{K_1[H^+]^2}, \qquad (1)$$

where K_0, K_1, K_2 and K_3 are dissociation constant of water, strontium hydroxide, stearic acid and strontium stearate (at the air-water interface), respectively, a the surface concentration of stearyl radical and x the surface concentration of strontium stearate. It is easy to understand the increase of x at constant c with decreasing $[H^+]$, provided that $K_0{}^2/K_1$ is much less than $[H^+]^2$.

At constant acidity, Eq. (1) can be transformed into the following relation,

$$a/2-x=k\sqrt{x/c} \qquad (2)$$

where constant k denotes $\{[H^+]+K_2\}K_3/2K_2$. Fig. 3, in which $\sqrt{x/c}$ is calculated using the data in Table II and is plotted against x, seems to show a partial validity of Equation (2). In the range of substrate concentration of $10^{-5}-10^{-3}$ mol./l., x decreases linearly with increasing $\sqrt{x/c}$ and this linear portion cuts the ordinate at $x=19.5\times10^{13}$ atoms/cm.^{2} of monolayer, when it is extrapolated. Thus $10^{16}/(2\times19.5\times10^{13})=26$ Å^2/molecule is obtained for the cross-sectional area of stearate ion or molecule of stearic acid in the film. This value is in fair agreement with that obtained from extrapolation of $F-A$ curves or from X-ray data. The deviation from the linearity at low concentration of solute may be due to the invalidity of the assumption that c does not change with reaction.

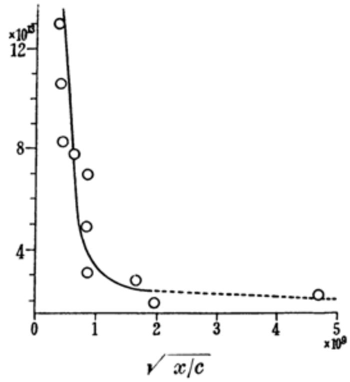

Fig. 3. Relationship between x and $\sqrt{x/c}$.

In the case of aqueous Co ion of pH less than 6.5, the structure of metallic soap formed in the film is considered to be the same as in the case of strontium stearate. In this pH region, the monolayers took up cobalt ions giving R less than 0.5 and did not show a remarkable expansion but rather a small condensation as pH decreased. Cobalt ions in solution are considered to be in the simple form of Co^{++} when pH of solution is maintained below 7, as seen from the measurement of self-diffusion[9]. On the other hand, decreasing surface potential[11] of stearic acid monolayer with increasing substrate pH can be accounted for by the increasing surface ionization of stearic acid. Taking account of these circumstances change of R at pH$<$6.5 can be explained by the change in binding ratio of one Co^{++} ion with at most two stearate ions.

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[10] I. Langmuir and V. J. Schaefer, *J. Am. Chem. Soc.*, **59**, 2400 (1937).

[11] J. Glazer and M. Z. Dogan, *Trans. Faraday Soc.*, **49**, 448 (1953).

Now we should draw attention to the remarkable expansion of monolayer at pH 7–9, where R is always greater than 0.5. This fact, together with that $R_{\max.}=1$, seems to be explained rather by assuming interaction betweeen one stearate ion and one monobasic cobalt ion. However, this cannot explain the extraordinarily large expansion quantitatively, so we take account of the dissolved state of monobasic cobalt ions in this pH range, which may be different from that at pH$<$7. Possibility of polymer formation of basic metal ions has been shown in the case of, for instance, uranyl[12] or ferric ion[13] and also in our cases[1–3]. Remarkable decrease of self-diffusion coefficient[9] of aqueous cobalt ion, when pH of it is beyond 7, is presumably due to the formation of aggregates. Actually it was observed that the colorless solution (10^{-4} mol./l.) of cobalt chloride was changed to pale blue when pH of it was increased to above 7, and that it was further changed to pale yellow after standing for 7–10 days, concentrations of Co atom in supernatant solutions being 69×10^{16} and 36×10^{16} atoms/cc. for pale blue and pale yellow solutions, respectively. These facts lead us to the conception of colloidal aggregates formed in the solution, which may consist of basic metal ions, water molecules and ammonia molecules, the latter if it is used.

The monolayer of stearic acid when spread on such a solution gives a film consisitng of widely spaced molecules, showing the large cross-sectional area as shown in Fig. 2. Low surface density of hydrocarbon chain in such a film can also be expected from the low refractive index of built-up films of Cu, Al and Th stearates[3], the behaviors of which at air-water interface are similar to those of cobalt stearate at pH 8–9. Similarly, unsuccessful building up of this film is presumably due to high compressibility and low collapsing pressure (see Fig, 1), as discussed in the case of Cu, Al or Th stearate[3]. The high compressibility of the film suggests that the interlinks between cobalt atoms in these aggregates are so loose that some cobalt atoms in them may be ejected partly from air-water interface when monolayer was compressed. There are cobalt atoms which are considered to be bound so firmly to stearate that the linkage is not destroyed by compression of monolayer, even when the other elementary ions or molecules in the aggregate are ejected from the surface. This consideration is supported by the fact that the higher compressibility was seen in the more expanded and the more brittle film. However, since we actually measured the binding ratio, R, after collapsing the film, the observed value indicates the Co atoms attached directly to stearate ions and the result of experiments is not adequate to confirm the loose structure giving rise to the anomalous expansion of the film.

This is also the reason why area—pH relation depends upon the choice of pH-adjusting agent, whilst $R-$pH relation does not. It is probale that the co-ordination of ammonia molecules towards Co atom has some contributions to size, shape and other nature of the aggregate, by which the cross-sectional area and compressibility of film molecules are largely affected. As is seen in Table III, this results in the increase of film expansion and compressibility. On the other hand, R is not affected by the presence of ammonia, showing that the co-ordination has no effect for direct and firm binding between the cobalt atom and stearic acid.

Many attempts[5,14,15] were made to determine the amount of metal ion bound to monolayer of fatty acid spread on it, where the ordinary microanalytical methods were used for this purpose. In our experience, however, it seems to be inevitable that these methods include an accidental error, presumably due to the long time required for collecting a few decades (or more) of monolayers. It has been pointed out in the preceding report[9] that the nature of surface film of stearic acid is changed by ageing of aqueous cobalt ion. The present radio-tracer method offers the advantage that only few times of the collection of monolayer are sufficient for the measurement and consequently it enables us to determine the binding ratio with slight accidental error.

Summary

It has been attempted to determine the binding ratio of strontium and cobalt atoms in the monolayer of stearic acid spread on aqueous strontium and cobalt solutions, respectively, containing radioactive cations.

The number of strontium atoms bound to one molecule of stearic acid increased with increasing pH of substrate solution as well as concentration of strontium ion in it. Tentative explanation was made by assuming interaction between strontium and stearate ions. A theoretical formula based on ionizations of stearic acid, strontium hydroxide,

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[12] K. A. Kraus and F. Nelson, *J. Am. Chem. Soc.*, **71**, 2510, 2517 (1947).

[13] B. O. A. Hedström, *Arkiv för Kemi*, **6**, 1 (1952).

[14] I. Langmuir and V. J. Schaefer, *J. Am. Chem. Soc.*, **58**, 284 (1936)

[15] E. Havinga, *Rec. trav. chim.*, **71**, 72 (1952).

and strontium stearate proved to support the validity of this presumption.

A similar explanation was also made for interaction between monolayer of stearic acid and substrate solution containing cobaltous chloride of pH less than 6.5, where the monolayer showed no expansion but rather a small condensation, while the number of bound Co atoms per one molecule of stearic acid increased with increasing pH up to 0.5. At pH 7–9, remarkably expanded and compressible films were obtained and the binding ratio reached a maximum value of unity. Films thus formed were considered to consist of stearate ions and polymer ions of cobalt which may exist as aggregates in the solution.

Co-existing ammonia used as a pH-adjusting agent of the solution of cobaltous chloride resulted in exaggeration of these effects. It might be attributed to co-ordination of ammonia molecules towards Co atoms.

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