The State of Metal Ion in Aqueous Solutions and Its Surface Chemical Effects. I. Cobalt Ion-Stearic Acid Monolayer Interaction

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It has been shown recently by Sasaki and Matuura[1,2] and by Schulman et al.[3,4,5] that certain metal ions interact with fatty acid monolayers specifically over a pH range characteristic of each ion. In the case of the monolayer of stearic acid this specific interaction has been observed through increase in the area per molecule of the acid, in compressibility and in rigidity of the monolayer. Metal ions which have been proved to give rise to such a remarkable change in the properties of the stearic acid monolayer are either ions of the transition elements or polyvalent ions, such as Co, Ni, Cu, Zn, Hg, Al, Fe, Ce or Th ions. The nature of the interaction between these metal ions and fatty acid monolayers has not yet been definitely postulated. Sasaki and Matuura proposed that metal soap of highly polymeric structure is produced in the monolayer by the interaction between fatty acid molecules and metal ions over a pH range characteristic of each ion. Schulman et al. presented the idea that the basic metal ions interact with the fatty acid monolayer at the pH of maximum interaction, and cross-linking results between neighboring molecules in the monolayer by hydrogen bonding. It is probable that the metal ion-monolayer interac-

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

2) R. Matuura, ibid., **24**, 278 (1951).

3) G.A. Wolstenholme and J.H. Schulman, *Trans. Faraday Soc.*, **46**, 475 (1950); **47**, 788 (1951).

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

5) J.G.N. Thomas and J.H. Schulman, *Trans. Faraday Soc.*, **50**, 1139 (1954).

tion has much to do with the state of the metal ion in aqueous solutions. It is known that certain metal ions of the transition elements or polyvalent ions exist in aqueous solutions as polynuclear cations in some cases, and sometimes the solution reveals rather colloidal behaviors around pH of hydroxide precipitation. In this respect information would be given from the studies of the radiocolloids of these elements which have been shown to be formed in dilute solutions under suitable conditions.[6,7] Although the mechanism of radiocolloid formation has not yet been established, it is interesting to note that in some metal ions (e.g., Th[8] or Ce[9] ions) the pH range of the specific interaction with fatty acid monolayers corresponds to that of colloid formation. It may be suggested also that in other metal ions in question their state in aqueous solutions would be much complicated in some cases and this complicated state would have a close connection with the specific interaction with the fatty acid monolayer. It is therefore necessary to study the metal ion-monolayer interaction with special reference to the state of the metal ion in aqueous solutions. In the present work the interaction between stearic acid monolayer and cobalt ion was investigated under various conditions along this line.

Experimental

The surface pressure of the monolayer was measured by the modified Wilhelmy type surface balance described elsewhere[10]. The method of measurement of surface viscosity and rigidity was the same as that in the earlier work[11]. Except for the study of the effect of aging of the solution, the monolayer was formed on a freshly prepared 10^{-3} mol./l. solution of $CoCl_2$, which was purified by recrystallization. Unless otherwise stated, the compression of the monolayer was started ten minutes after spreading. The pH of the solution was adjusted by HCl and NaOH, changing from 2 to 10.

The effect of the aging of the solution on the cobalt ion-stearic acid monolayer interaction was studied by measuring surface pressures of the monolayer spread on the solution stored for periods of time in a large glass-stoppered bottle at room temperature. The pressure-area relations were determined for each aging time of the solution.

In order to know the effect of other electrolytes on the cobalt ion-monolayer interaction, sodium chloride, ammonium oxalate and sodium citrate were added before, or injected after spreading stearic acid, to the substrate solution at the pH of maximum interaction. All these salts were analytical reagents.

All the film experiments described above were carried out at room temperatures.

In relation to the film experiments, in order to obtain information as to the state of cobalt ion in aqueous solutions the self-diffusion coefficient of cobalt ion was measured in $CoCl_2$ solutions of 10^{-3} mol./l. and of varying pH values, using Co^{60} as a radio-tracer. The capillary method[12] was used as shown in Fig. 1. The capillary used was 0.061 cm. in diameter and 1.8 to 2.5 cm. in length. Four capillaries of different lengths were used for each pH value, and the average of the diffusion coefficient was calculated from four values obtained for four different capillaries. The diffusion time was forty to fifty hours and the diffusion temperature was 35.0°C. The difiusion coefficient D was calculated by the equation[13]

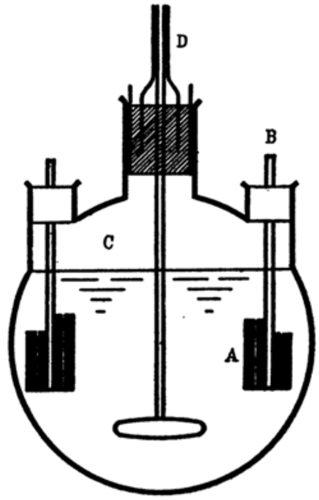

Fig. 1. Diffusion apparatus. A, diffusion cell; B, cell holder; C, three-neck flask (volume 1 liter); D, mercury-sealed stirrer (stirring rate 100rpm).

$$2.303 \log \frac{\pi^2}{8}\left(\frac{C}{C_0}\right) = -\frac{\pi^2 Dt}{4l^2},$$

where, C is the average concentration of radioactive cobalt in a capillary after time t, C_0 is its initial concentration and l is the length of the capillary.

Results

(1) Stearic Acid Monolayer on 10^{-3} mol./l. $CoCl_2$ Solution.—Pressure-area curves of the monolayer of stearic acid on the surface of

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[6] A. C. Wahl and N. A. Bonner (editors), "Radioactivity Applied to Chemistry", John Wiley and Sons, Inc., New York, N.Y. (1951), p. 142.

[7] G.K. Schweitzer and M. Jackson, *J. Chem. Education*, **29**, 513 (1952).

[8] M.H. Kurbatov, H.B. Webster and J.D. Kurbatov, *J. Phys. & Colloid Chem.*, **54**, 1239 (1950).

[9] J.D. Kurbatov and M.L. Pool, *Phys. Rev.*, **65**, 61 (1944).

[10] R. Matuura and I. Hayasi, *Memoirs of the Faculty of Science, Kyushu University, Ser. C*, **1**, 31 (1948).

[11] T. Sasaki and H. Kimizuka, This Bulletin, **25**, 318 (1952).

[12] J.S. Anderson and K. Saddington, *J. Chem. Soc.*, **1949**, S.381.

[13] A.C. Wahl and N.A. Bonner (editors), "Radioactivity Applied to Chemistry", John Wiley and Sons, Inc., New York, N.Y. (1951), p. 77.

10^{-3} mol./l. $CoCl_2$ solution of varying pH values are shown in Fig. 2. From pH 2 to 4 the monolayer showed stable surface pressures and gave pressure-area curves similar to those without cobalt ion, the limiting area being about 25 Å² per molecule. The monolayer did not show appreciable rigidity over this pH range. When the pH of the solution becomes larger than 4, the monolayer begins to show a little condensation until at pH 6.3 the limiting area reaches about 21 Å² per molecule. This condensation of the monolayer occurs at lower pH values than those in the case without cobalt ion, as shown in Fig. 3. It was observed that around pH 6 the monolayer did not show stable surface pressures soon after compression but the pressure dropped considerably when the monolayer was allowed to stand at a definite area after compression. At lower surface pressures the pressure dropped largely during the first minute and attained the constant value several minutes after compression, while at higher pressures the change of surface pressure with time was small. The condensed monolayer around pH 6 was observed to have some rigidity. When the pH of the solution exceeds 6.3, the monolayer begins to expand again, but this time it showed high rigidity. Maximum expansion and rigidity were reached at pH 8.3, where the limiting area attained as large as 50 Å² per molecule. The monolayer was very stable over this pH region of high expansion and rigidity and no such phenomenon of pressure dropping as was found around pH 6 was observed.

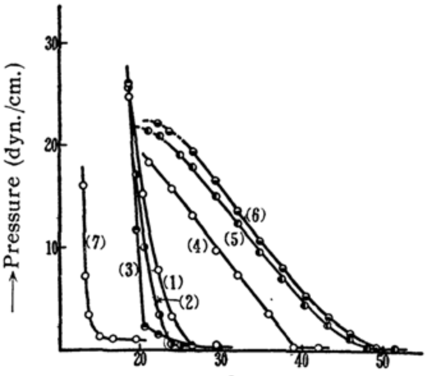

Fig. 2. Pressure-area relations of stearic acid monolayer on 10^{-3} mol./l. $CoCl_2$ solution. pH is (1) 2.0; (2) 5.2; (3) 6.3; (4) 7.6; (5) 8.0; (6) 8.3; (7) 9.6. Temperature 25–26°C.

In Fig. 3 the limiting areas obtained by pressure-area relations are plotted against the pH of the substrate solution. In the same figure the areas which make viscosity (at pH's smaller than 4) and rigidity (at pH's larger than 4) of the monolayer suddenly large on compression are also shown as a function of the pH of the solution. It is observed that the limiting area obtained from the pressure-area relations is almost the same as that obtained from the rheological data at each pH value. The color of 10^{-3} mol./l. $CoCl_2$ solution of varying pH values is recorded in the upper part of Fig. 3. In the alkaline solution the color changed from blue to bluish green, then to yellow with the aging of the solution, and finally after some periods of time the precipitate of hydroxide settled out. Around pH 8.5 the precipitation was observed without aging.

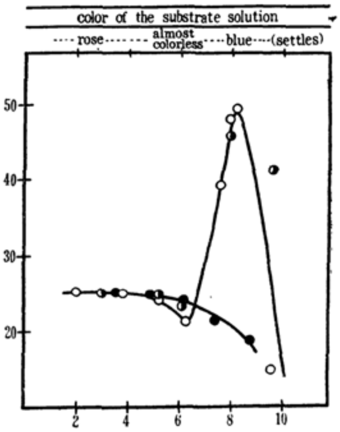

Fig. 3. Limiting area vs. pH of the monolayer of stearic acid on 10^{-3} mol./l. $CoCl_2$ solution. Temperature 25–26°C. ○ with cobalt ion (from surface pressure data); ◑ with cobalt ion (from rheological data); ● without cobalt ion (from surface pressure data).

(2) Effect of Aging of 10^{-3} mol./l. $CoCl_2$ Solution.—Fig. 4 shows pressure-area relations of the monolayer of stearic acid on the *surface of 10^{-3} mol./l. $CoCl_2$ soluion which* has been aged for the periods of time indicated in the figure. The initial pH of the solution was 8.3, but it decreased with time as shown in Table I, in which the change in appearance of the solution was also recorded. It was observed that the monolayer showed a little condensation on the solution in the earlier stage of aging, but it recovered or slightly exceeded the initial expansion by further aging of the solution. The monolayer maintained its high rigidity on the aged solution. No precipitation was observable in the $CoCl_2$ solution before 300 hours of aging;

TABLE I
AGING OF 10^{-3} MOL./L. $CoCl_2$ SOLUTION

Aging time (hr.)	0	0.5	3.5	24	72	144	336
pH	8.3	8.0	7.9	7.8	7.5	7.5	7.5
Appearance	blue	greenish blue	yellowish blue	greenish yellow	yellow	yellow	brownish yellow
	clear solution			slightly turbid solution			precipitated

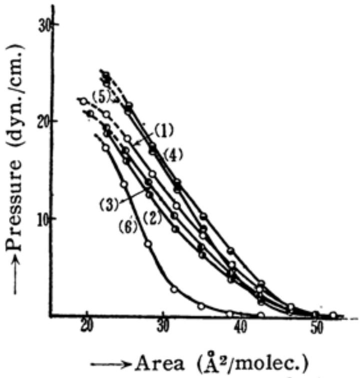

Fig. 4. Effect of aging of 10^{-3} mol./l. $CoCl_2$ solution of pH 8.3 on stearic acid monolayer on it. Aging time is (1) 0; (2) 0.5; (3) 3.5; (4) 24; (5) 72; (6) 336 hours. Temp. 22–27°C.

after that the area of the monolayer showed considerable decrease.

(3) **Effect of Other Electrolytes.**—sodium chloride, ammonium oxalate or sodium citrate was added to 10^{-3} mol./l. $CoCl_2$ solution and the pH of the solution was adjusted to 8.3. The concentration of each added electrolyte was 5×10^{-3} mol./l. The pressure-area curves of stearic acid monolayer formed on these mixed solutions are shown in Fig. 5. It is seen that ammonium oxalate and sodium citrate make the expanded monolayer completely or almost completely condensed, while sodium chloride has no effect. On the other hand, when these electrolytes were injected into the substrate $CoCl_2$ solution after the monolayer had been formed on it, the condensing effect of ammonium oxalate and sodium citrate was small in the uncompressed state (0.1 dyn./cm.)and not observable in the compressed state (about 10 dyn./cm.) of the monolayer.

(4) **Self-diffusion of Cobalt Ion.**—In Table II self-diffusion coefficients of cobalt ion in 10^{-3} mol./l. $CoCl_2$ solution are recorded as a function of initial pH of the solution. In the acid and neutral solutions the diffusion coefficients obtained from four capillaries at the same pH coincided with one another within ±3 per cent. On the other hand in the alkaline solutions the fluctuation of maximum ±16 per cent was observed. Notwithstanding this large fluctuation, it is seen that the diffusion coefficient apparently decreases as the pH of the solution becomes larger than 7. When the Einstein-Stokes equation is assumed to hold, the radius of diffusing species regarded as spherical particles can be calculated from the observed values of the diffusion coefficient, as shown in the last column of Table II.

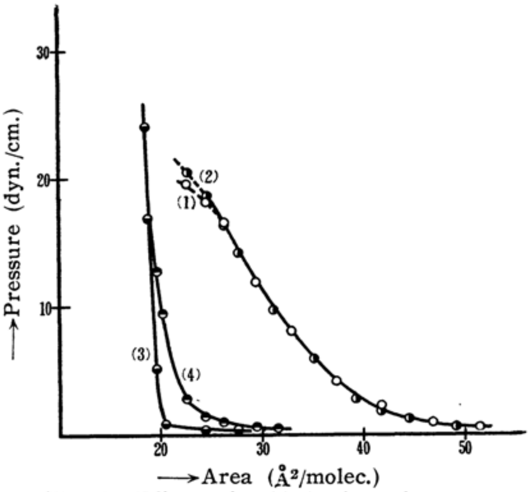

Fig. 5. Effect of added electrolytes on pressure-area relations of stearic acid monolayer on 10^{-3} mole./l. $CoCl_2$ solution at pH 8.3. (1) no salt; (2) sodium chloride; (3) ammonium oxalate; (4) sodium citrate. Temperature 26°C.

TABLE II
SELF-DIFFUSION COEFFICIENT AND RADIUS OF DIFFUSING SPECIES OF COBALT ION AT 35°C

pH	$D\times10^6$ (cm²/sec.)	radius (Å)
2.0	9.4±0.1	3.3
5.2	9.6±0.3	3.3
6.5	9.2±0.1	3.4
7.0	9.5±0.3	3.3
7.2	8.8±0.8	3.6
7.8	7.8±0.8	4.0
8.0	5.0±0.8	6.3
8.8 (precipitated)	—	—

Discussion

In the acid solution cabolt ion exists in the state of hydrated divalent ion which has rose color. When aqueous sodium hydroxide is added to this solution dropwise, the rose color fades gradually away to almost colorless around pH 6.3 in the case of 10^{-3} mol./l. $CoCl_2$ solution, then, by further addition of alkali, the solution turns to blue. It is probable that the change in color of the cobalt solution by addition of alkali corresponds to the change in the state of cobalt ion in the solution. By the addition of alkali to the neutral solution of $CoCl_2$ the first process which is assumed to take place will be that one of the hydrated water molecules is substituted by a hydroxyl group to form basic cobalt salt, which is considered to be blue in color[14]. The colorless solution around pH 6.3 may correspond to the region of transition from hydrated divalent ion to basic salt. The blue solution is not stable enough, because the color changes gradually to yellow by aging of the solution and precipitation takes place after some periods of time. This aging of the alkaline solution, which is accompanied by decrease in pH of the solution as shown in Table I, may be due essentially to transition from basic salt to hydroxide by further combination with hydroxyl group, accompanied by its oxidation to trivalent cobalt. It is to be noted that the solution in this state, before precipitation takes place, reveals colloidal nature. It is shown in Table II that the size of diffusing species at pH 8.0 is almost twice as large as that in the acid and neutral solutions. It is reasonable to assume that cobalt ion forms larger aggregates in the alkaline solution of $CoCl_2$. The large fluctuation of diffusion data in the alkaline solution of the same pH value suggests that the process of aggregation to larger particles depends sensibly upon conditions, the fact being usually the case with colloidal solutions.

The interaction between stearic acid monolayer and cobalt ion in alkaline solutions is closely related to the aggregated state of the ion in the solutions. When stearic acid is spread on the alkaline solution of $CoCl_2$, stearate ions in the monolayer, formed by the dissociation of the acid, will hold cobalt ion aggregates and produce a two-dimensional network structure, which causes large expansion and high rigidity of the monolayer. In the fresh solution the aggregates are considered to be composed mainly of basic ions interlinked by hydrogen bonding, but with aging of the solution the basic ion aggregates will decrease, due to the formation of hydroxide. Still the aged solution shows similar or sometimes greater, interaction with the stearic acid monolayer, as shown in Fig. 4. This seems to suggest that some aggregates are adsorbed physically to the monolayer so that they may offer some contribution to the expansion of the monolayer. On compression those physically adsorbed aggregates will be squeezed out of the monolayer and in the highly compressed state only strongly bound cobalt will remain in the film. It is difficult to explain such large expansion of the stearic acid monolayer as found in the present work only by the interaction with simple basic ion, without taking the aggregated state of ion into consideration.

The effect of complex-forming agents, such as ammonium oxalate and sodium citrate, on the cobalt ion-stearic acid monolayer interaction is remarkable, as shown in Fig. 5. Probably these agents form complex anions with cobalt in the alkaline solution, so that both large expansion and high rigidity of the stearic acid monolayer disappear. However, when these agents are injected into the substrate solution after the monolayer has been formed on it, they are not capable of taking cobalt from the compressed monolayer, because the cobalt atom is attached to the monolayer strongly. Small condensation by ammonium oxalate of the monolayer without compression may be due to extraction of physically adsorbed aggregates. It is interesting to note that these complex-forming agents hinder the formation of radiocolloids of lanthanum[15] and yttrium[16].

Around pH 6.3 the dissociation of stearic acid is not complete and also the formation of basic ion, accordingly, of aggregated state is not enough. The result would be that the monolayer is composed of free stearic acid, normal cobalt stearate and polymeric compound. In such a mixed monolayer the network structure as assumed in alkaline region would not be developed enough, because low-molecular cobalt stearate and stearic acid dispersed in the monolayer would hinder its development. On compression of the monolayer the partly developed network structure will be broken to some extent. This would be a cause of rapid dropping of surface pressure with time over this pH range. Finally the limiting area of 21 Å^2

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[14] J. W. Mellor, "A Comprehensive Treatise of Inorganic and Theoretical Chemistry", Longmans, Green and Co., London (1935), Vol. XIV, p. 628.

[15] G.K. Schweitzer and W.M. Jackson, *J. Am. Chem. Soc.*, **74**, 4178 (1952).

[16] G.K. Schweitzer, B.R. Stein and W.M. Jackson, ibid., **75**, 793 (1953).

per molecule is attained, and this is practically due to the condensing effect of divalent cobalt ion, just as that of calcium ion in the alkaline region[1].

Kurbatov et al.[17] showed in the experiment of adsorption of cobalt ion on hydrous ferric oxide that the number of the equivalent of hydrogen ion displaced by 1 gram-atom of cobalt on the adsorbent was 1.2. This seems to suggest that the complicated state of cobalt as considered in the present work also takes part in the adsorption on the solid surfaces. It is probable that other metal ions of the transition elements or polyvalent ions form the state of aggregates around pH of hydroxide precipitation, just as is the case with cobalt ion, and this state is responsible for the specific effect of these metal ions on various surface chemical phenomena. The behavior of these metal ions found in the adsorption on built-up film of stearic acid[18] and in wettability of solid stearic acid surfaces[19] are also accounted for by this fact. It is to be noted that in these experiments, including the present one, the extent of interaction, the pH range of specifc interaction, and other data are not necessarily reproducible. This indicates that the formation of aggregates is affected by a number of factors such as aging, method of preparation of the solution, purity of water, property of the glass vessel, and others, which are difficult to be put under perfect control.

Summary

The presence of aggregates of cobalt ion in the alkaline solution of 10^{-3} mol./l. $CoCl_2$ was shown by the measurement of self-diffusion coefficients. Large expansion and high rigidity of the stearic acid monolayer caused by cobalt ion in the alkaline solution were accounted for by the interaction of stearate ion in the monolayer with the aggregates of cobalt ion in the solution, resulting in the formation of two-dimensional network structure in the film. This idea was confirmed by the effect of aging of the substrate solution and also by the action of complex-forming agents such as ammonium oxalate and sodium citrate on the monolayer-ion interaction.

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[18] M. Muramatsu, and T. Sasaki, This Bulletin, 25, 21, 25 (1952).

[19] A. Inaba, ibid., 25, 174 (1952); 26, 43 (1953).