The State of Metal Ion in Aqueous Solutions and its Surface Chemical Effects. III. Rheological Study for the Effect of Metal Ions on the Monolayer of Stearic Acid

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So far a number of investigations have been carried out on the metal ion-monolayer interaction. The remarkable effects of polyvalent or transition metal ions on the fatty acids were shown by the studies of the monolayers[1,2], built-up film[3] and wetting[4]. Although the effects are characterized by the formation of rigid film over a pH range characteristic of each ion[1,2], the quantitative measurement of viscoelasticity has not yet been carried out on the system, so the application of the rheological technique to the system may be expected to give more detailed information concerning the interaction. The present paper describes the result obtained by this technique and gives an explanation for it.

Experimental

The monolayer of stearic acid was prepared by spreading it from a benzene solution on the substrates containing 10^{-4} mol./l. salts of various kinds. The salts were used as chloride, nitrate and sulfate, which were purified by recrystallization. Of these salts, the effect of anion on the monolayer of stearic acid was found negligible[1].

The surface pressure was measured by the method already described elsewhere[5].

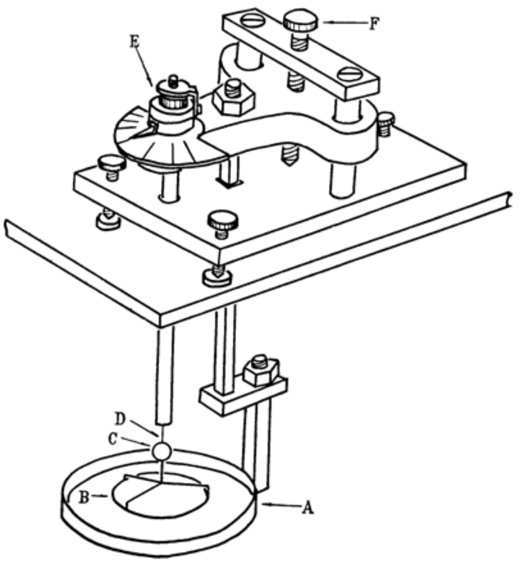

Fig. 1. Rheometer.

In Fig. 1 the rheometer is shown, in which A is a brass ring, 6 cm. in diameter, coated with paraffin, B, the platinum ring, 4 cm. in diameter C, the mirror, D, the suspension wire of phosphor bronze, $40\,\mu$ in diameter and 30 cm. in length, the torsion constant of which being 0.328 dyn. cm., and E, the torsion head. In this figure A and B are allowed to move vertically by means of a screw F and are made to touch the surface of solution, B can rotate around the wire axis while A is fixed. With this apparatus the rheological behavior of the surface film was measured as described in the preceding paper[6]. The time scale taken for rheological measurement was five minutes. The experiments were carried out at room temperature and pH was controlled using hydrochloric acid and sodium hydroxide.

Result

When the suspension wire having the torsion constant of 1.24×10^{-2} dyn.cm. was used, the monolayer of stearic acid giving the area of 20.5 Å^2/molecule on distilled water showed the rheological behavior of Voigt model at 20°C, viscosity coefficient being 0.13 g./sec. and modulus of rigidity, 8.4×10^{-3} dyn./cm., with the elastic limit (yield value) of 9.0×10^{-4} dyn./cm. This suspension wire has, however, too small torsion constant to measure the mechanical behavior of an extremely rigid film formed by the interaction with metallic ion, so the other experiments were carried out with a different suspension wire already mentioned, towards which the monolayer of stearic acid, spread on the substrates containing no metal ion, behaved as the fluid film for all the region of applied pH. The rigid film thus formed could hardly be rendered fluid when the solution of ethylene diamine tetraacetic acid (EDTA) was injected, while the formation of rigid film could not be observed when EDTA was added to the substrate containing metallic ion before stearic acid

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1) R. Matsuura, This Bulletin, **24**, 274, 278 (1951).

2) G.A. Wolstenholme and J.H. Schulman, *Trans. Faraday Soc.*, **46**, 475 (1950); **47**, 787 (1951), etc.

3) M. Muramatsu and T. Sasaki, This Bulletin, **25**, 21, 25 (1952).

4) A. Inaba, Ibid., **25**, 175 (1952); **26**, 43 (1953).

5) T. Sasaki, ibid., **14**, 796 (1941); R. Matsuura and I. Hayashi, *Memoirs of the Faculty of Science, Kyusyu University*, Ser. C, **1**, 31 (1948).

6) T. Sasaki and H. Kimizuka, This Bulletin, **25**, 318 (1952); H. Kimizuka, ibid., **26**, 449 (1953).

was spread on it. This is a similar phenomenon to that reported in a preceding paper⁷⁾ and may be ascribed to be the prevention of the formation of metal stearate due to the EDTA-complex formation. Consequently the developments of visco-elastic property may be considered due to the formation of network structure of insoluble metal stearate films.

Some of the results for the interacted film are shown in Figs. 2a and 2b, in which the surface pressure, F, and the yield value, Y, of the film are plotted against the area per stearyl group, A.

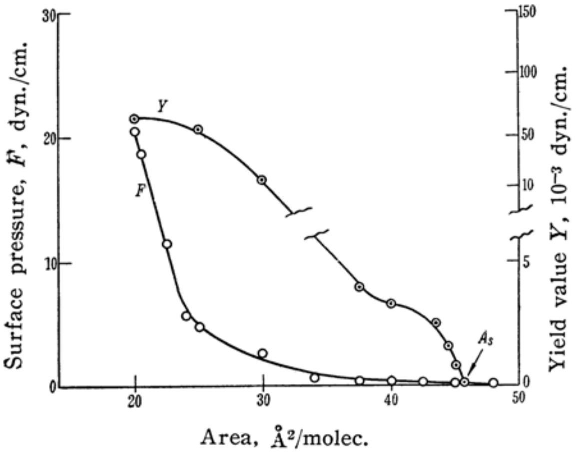

Fig. 2a. Pressure-area and yield value-area curves of the monolayer of stearic acid on substrate containing aluminium ion at pH 5.2.

In this figure the area of the solidification of surface film, A_S, is indicated by that of the sudden development of the yield value. In Fig. 3 A_S–pH diagrams are shown for the various metallic ions.

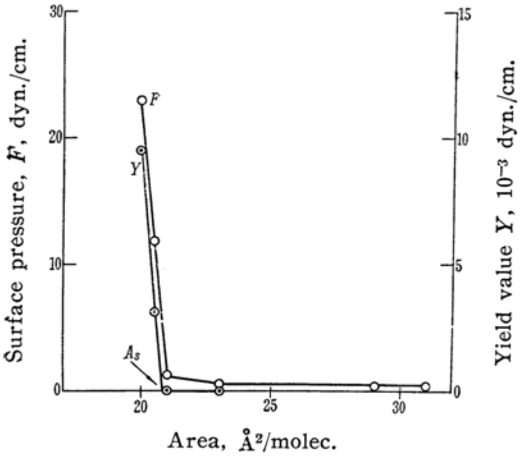

Fig. 2b. Pressure-area and yield value-area curves of the monolayer of stearic acid on substrate containing calcium ion at pH 10.6.

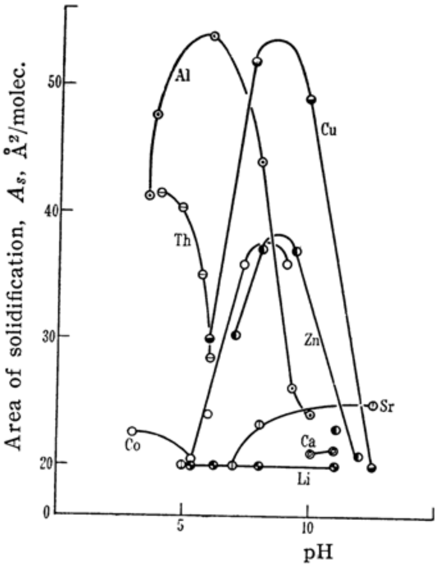

Fig. 3. Area of solidification-pH curves of the monolayer of stearic acid on substrates containing various metallic ions.

The metallic ions forming the solid film are classified into two groups based upon the mechanical behaviors of the films as in a former report⁸⁾, namely, one exhibiting Voigt model and the other, Maxwell model; they are summarized

TABLE I

MECHANICAL BEHAVIOR OF STEARATE FILM

Ions	Change of mechanical model with decreasing area
Group 1; Li, Ca, Sr and Ba	Viscous flow → Voigt model
Group 2; Th, Al, Fe, Co, Cu and Zn	Viscous flow → Maxwell model → three parameter model⁸⁾ → elastic behavior

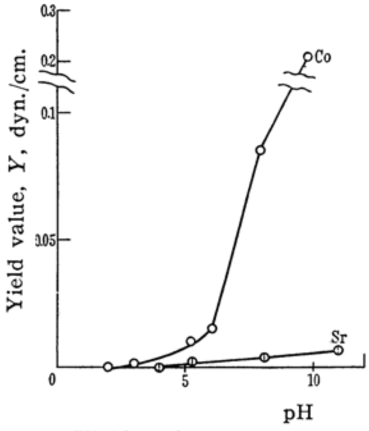

Fig. 4. Yield value-pH curves of the monolayer of stearic acid on substrates containing cobalt and strontium ion.

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[7] R. Matsuura and H. Kimizuka, ibid., 28, 668 (1955).

[8] H. Kimizuka, This Bulletin, 26, 30 (1953).

in Table I. The presence of the ions, Na, K, Rb and NH_4, in the substrates yields no perceptible solid film in the present experiment.

The strength of the interacted film varies, in general, with pH. Thus, in Fig. 4 the yield values of the films at 20 Å/stearyl group on the substrates containing Sr or Co ions are plotted against pH.

The effect of colloid in the substrate was also investigated. A solution of ferric chloride was introduced into boiled water to prepare the colloidal solution of ferric hydroxide, and then the colloidal solution was dialysed with distilled water till the dialysate was no longer colored red with potassium rhodanide. Fig. 5 shows the $F-A$ and $Y-A$ diagrams for the effect of colloid and the freshly prepared solution of ferric chloride at pH 6, the former contains 5×10^{-5} mol./l. of Fe_2O_3 and the latter, 10^{-4} mol./l. of $FeCl_3$.

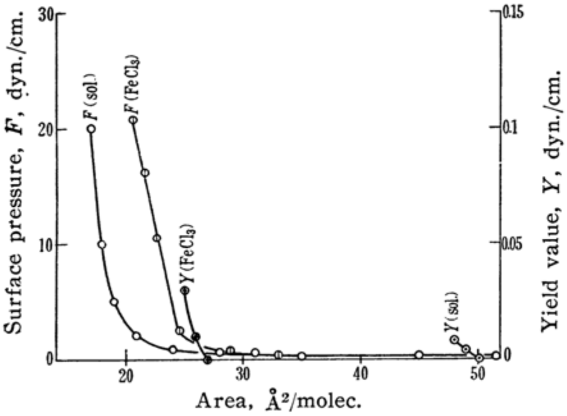

Fig. 5. Surface pressure-area and yield value-area curves of the monolayer of stearic acid on substrate containing ferric ion and ferric hydroxide sol at pH 6.

Discussion

The previous works on the effect of metallic ions on stearic acid suggested the classification of them into three groups. In conformity with this the same conclusion was also accepted in the present experiment. The results obtained are summarized in Table II together with those of the other experiments·

Here, the characteristic region of pH exhibited by a metal ion of group 2 agrees with those found in the other phenomena listed in this table. All these facts can reasonably be explained as due to the interaction between the monolayer and metallic ion in the substrate. It is interesting to note here that the mechanical behavior of the interacted monolayers with 1st and 2nd groups correspond to those of the adsorbed layer of the solutions of the micellar and the high-polymeric materials[8] respectively.

Of the group 1, the formation of simple stoichiometric compound was suggested[9,10], which may also explain our result of the formation of condensed solid film. Recently it has been shown in the preceding paper[10] and also in other report[11] that the film-bound Ca and Sr increase with pH. Fig. 4 shows the increase in the strength of strontium stearate film with the increase in pH,in which the pH of solid film formation coincides with that of appreciable amount of film-bound ion[10]. A similar correlation is recognized in this figure for the film of cobalt stearate. This fact may indicate that the rheological technique is another useful means for the study of surface film interaction. Ellis and Pankhurst[12] studied the interaction between the colllagen monolayer and tanning materials by means of the surface viscosity measurement and showed that the interaction results in a change in surface viscosity. This technique, however, would be rather inadequate to obtain the information about the structure of film, because the surface viscosity measurement may be carried out on the film which has been destroyed.

TABLE II

EFFECT OF METAL IONS ON STEARIC ACID

Groups	1	2	3
Ions	Li, Ca, Sr, Ba	Th, Fe, Al, Co, Cu	Na, K, Rb, NH_4
Region of pH	Alkaline gegion	Characteristic region of each ion	Alkaline region
Rheological behavior of stearate film	Condenced soid flim	Expanded soid filim	Fluid film
$F-A$ behavior of stearate film[1]	Insoluble condensed film	Extended film	Soluble film
Wettability of solid surface of steari cacid[4]	Non-wettable	Wettable	Wettable
Adsorption of ion on the built-up film[3]	Low constant adsorption independent of pH	Profound rdsorption	Dissolution of built-up film

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[9] W.D. Harkins and E. Boyed, *J. Phys. Chem.*, **45**, 20 (1941).

[10] T. Sasaki and M. Muramatsu, This Bulletin, in the press.

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

[12] S.C. Ellis and K.G.A. Pankhurst, *Diss. Faraday Soc.*, No. **16**, 170, (1954).

Of the second group, the rheological property of interacted film was already investigated by a somewhat different means[1]. As seen in Fig. 2a, A_S may be accounted for as the area of completion of network structure of the metal stearate and the solid film thus formed is strengthened with the successive compression of the film as shown by the increase in the yield value. Further, it may be pointed out that A_S is a characteristic point other than A_f, the limiting area estimated from the F-A diagram, since the value of A_f is frequently different from that of A_S. Further, A_S is defined more clearly than A_f as seen in Fig. 2a. Similar results were observed for the monolayer of high polymeric materials[13].

As shown in Fig. 5, the values of A_f are not so different from each other (about 25 Å²/mol.) on the both substrates, the solution of ferric chloride and the ferric hydroxide sol, while the values of A_S are widely different namely 27 Å²/mol. for the former and 50 Å²/mol. for the latter. This probably means that the presence of a larger aggregate capable of interaction with the monolayer is responsible for the larger area of solidification which is also our common view as reported in the former papers[1,3,4]. In the characteristic region of pH, in which the rigid film of metal stearate are produced by the ions of 2nd group, the ions may be hydrolysed in various grade[7,14], i. e. may exist as the various forms of dispersion from the simple ion through the basic metal ion finally to the colloidal aggregate[15]. So these various forms of solute seem to have much to do with the formation of complex metal soap. Further investigations will, however, be required to obtain more detailed information on the mechanism of interaction.

Summary

The effect of metallic ions on the monolayer of stearic acid was studied by the rheological method.

(1) It was shown that the development of visco-elastic property of the film is closely correlated with the formation of metal soap. Result obtained by the rheological measurement enables us to classify the metal ions into three groups; Li, Ca, Sr and Ba belong to the 1st, showing the formation of the condensed solid film and the rheological behavior of Voigt model; Th, Fe, Al, Co, Cu and Zn, the 2nd, exhibiting the formation of the expanded solid film and the rheological behavior of Maxwell model; Na, K, Rb and NH_4, the 3rd, forming no solid film. These results were discussed in relation to the phenomena observed in the studies of the metal ion monolayer interaction, the adsorption of ion on the built-up film and the effect of ion on the wettability of a solid surface. These phenomena could be correlated with the formation of simple soap or complex metal ion-monolayer aggregate, the 1st and 3rd resulting in the former and the 2nd, in the latter.

(2) It was frequently observed for the interacted film with the ions of the 2nd group that the area of solidification is larger than the limiting area estimated from the surface pressure-area curve, while in the case of the film with the ions of 1st group the values of both area coincide with each other.

(3) It was shown that the monolayer of stearic acid, spread on the substrate containing ferric hydroxide sol, formed an expanded solid film.

(4) It was shown for Co and Sr ions that the strength of interacted film is a measure of film-bound ion.

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[13] T. Tachibana and K. Inokuchi, *J. Colloid Sci.*, 8, 341 (1953).

[14] N. Bjerrum, *Z. Phys. Chem.*, A **110**, 656 (1924); R.E. Connick and W.H. McVey, *J. Am. Chem. Soc.*, **71**, 3182 (1949); B.O.A. Hedström, *Arkiv. för kemi.* **6**, 1 (1952); R.M. Milburn and W.C. Vosburgh, *J. Am. Chem. Soc.*. 77, 1352 (1955), etc.

[15] H. B. Weiser, "*Inorganic Colloid Chemistry*" N. Y. (1935), Vol. II; J. D. Kurbatov and M. L. Pool, *Phys. Rev.* 65, 61 (1944); M. H. Kurbatov, H. B Webster nd J. D. Kurbatov, *J. Phys, & Colloid Chem.*, **54**, 1239 (1950), etc.