Studies on Monomolecular Films. VIII.
Rigidity of the Monolayer of Stearic Acid on the Surface of Salt Solutions

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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 condensing 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.

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(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, 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.(1)

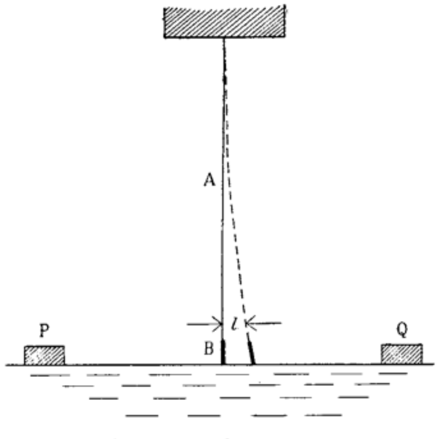

Fig. 1.—Apparatus for measurement of film rigidity.

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.(5) 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, aluminum, 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

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(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. Matuura and I. Hayasi, *Memoirs of the Faculty of Science, Kyûshû University, Ser. C*, Vol. 1, 31 (1948).

(5) V. J. Schaefer, *J. Phys. Chem.*, **42**, 1089 (1938).

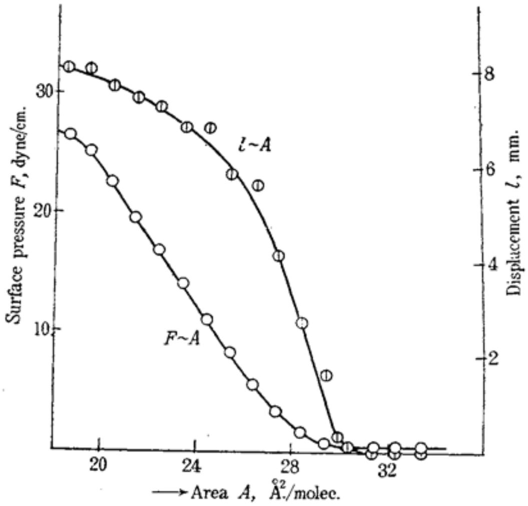

Fig. 2.—Pressure∼area and displacement∼area curves of the monolayer of stearic acid on water containing aluminum ion.

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 *p*H 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 neary the same surface area at which the surface pressuse 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 *p*H value of the substrate. This relation is shown in Fig. 3, where the maximum displacement, *i. e.*, the displacement just before the collapse of the film, at each *p*H of the substrate is plotted. In the same figure the area∼*p*H 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 *p*H 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.

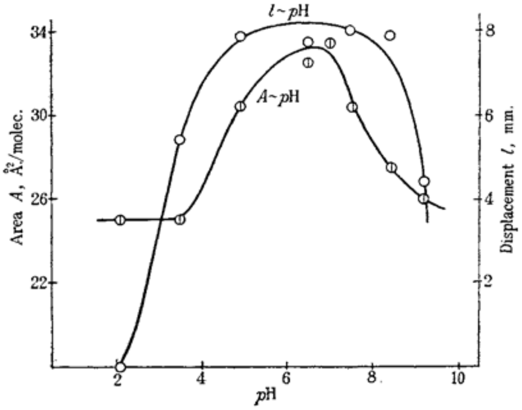

Fig. 3.—Area∼*p*H and Displacement∼*p*H curves of the monolayer of stearic acid on water containing aluminium ion.

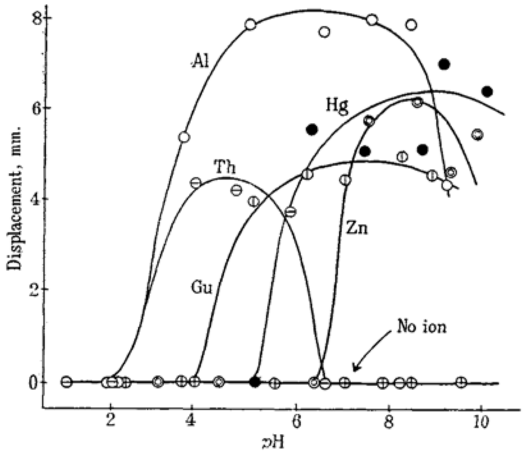

Fig. 4.—Displacement∼*p*H curves of the monolayer of stearic acid on water containing some metallic ions.

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⁾

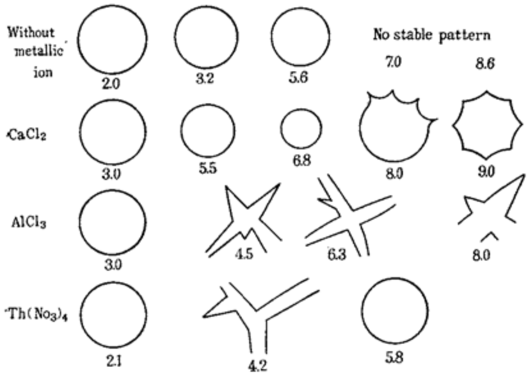

Fig. 5.—Expansion patterns. The numeral for each pattern represents pH of the solution.

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 remakable 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.

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(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.