Physicochemical Studies of Stearic Acid Monolayer-Aluminum Ion Interaction. I. The Surface Pressure

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There exist a number of reports on the interaction of the monolayers of fatty acid with aluminum ion[1-12], but no work has succeeded in establishing a complete picture of the structure and constitution of the monolayers resulting from the interaction. Schulman et al.[5-7], studying the effect of the presence of aluminum ion in underlying solutions on monolayers, suggested that the solidification of monolayers could be brought about by hydrogen bonding between the monolayer soaps produced through the dissociated monolayers-basic aluminum ion interaction. Spink and Sanders[8] could not arrive at any conclusion as to the interaction of the stearic acid monolayer with aluminum ion, reporting that the interaction was obviously complicated and further work was required. It was shown by Ekwall and Bruun[9-12] that the final product of the interaction was dibasic aluminum soaps. On the other hand, Sasaki and Matuura[2,3] ascribed the rigid expanded monolayer resulting from the interaction to a complicated polymeric structure in which the backbone of -Al-O- would lie flat on the surface. We think it reasonable that the interaction should be considered from the standpoint of the adoption of aluminum ion on the monolayer as well as

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

[2] T. Sasaki and R. Matuura, This Bulletin, **24**, 274 (1951).

[3] R. Matuura, ibid., **24**, 278 (1951).

[4] H. Kimizuka, ibid., **29**, 123 (1956).

[5] G. A. Wolstenholme and J. H. Schulman, *Trans. Faraday Soc.*, **46**, 475 (1950).

[6] G. A. Wolstenholme and J. H. Schulman, ibid., **47**, 788 (1951).

[7] J. G. N. Thomas and J. H. Schulman, ibid., **50**, 1131 (1954).

[8] J. A. Spink and J. V. Sanders, ibid., **51**, 1154 (1955).

[9] P. Ekwall and H. Bruun, *Acta Chem. Scand.*, **9**, 412 (1955).

[10] P. Ekwall and H. Bruun, ibid., **9**, 424 (1955).

[11] P. Ekwall and H. Bruun, ibid., **9**, 1057 (1955).

[12] P. Ekwall and H. Bruun, ibid., **9**, 1069 (1955).

of the formation of aluminum soaps in the monolayers.

In the following series of investigations, our object is to determine, with the aid of surface pressure and viscoelasticity measurements, the structure and constitution of the stearic acid monolayers which have interacted with aluminum ion in the underlying solution. For this purpose the monolayers of aluminum distearate on water and aluminum salt solutions have also been investigated. It is also attempted in this paper to report the results of the surface pressure measurement and to find how they can be accounted for.

Experimental

The monolayers of stearic acid and aluminum distearate were prepared from benzene solutions on substrate solutions, and their surface pressures were measured by the modified Wilhelmy type surface balance described elsewhere[13]. The stearic acid was purified by repeated recrystallization from ethanol. The aluminum distearate was prepared by the addition of an excess of aluminum chloride solution to a solution of potassium soap. This was washed with water until the filtrate was free from chloride, thoroughly extracted free or loosely bound stearic acid with dried acetone and dried over phosphorus pentoxide for a few days. It was found by analyzing the aluminum content that the aluminum distearate thus obtained was almost in accord with the theoretical composition.

Redistilled water was used for preparing the substrate solution. The concentration of aluminum chloride was kept at 10^{-4} mol./l. The pH was adjusted with hydrochloric acid or sodium hydroxide over a wide range. The use of buffer salts was avoided so that they might not lead to an anomalous result due to their interaction with the monolayers. As the pH value of the solution, a mean value before and after the experiment was taken, but the deviation did not exceed 0.1 pH unit.

In order to maintain the experimental temperature constant, a constant temperature box was used. All the experiments were carried out in this box, kept at 25 ± 0.5°C.

The monolayers were left to stand for thirty minutes after spreading, and then their compression was started. The monolayers of stearic acid and aluminum distearate on aluminum chloride solutions were almost stable over the whole range of areas studied. On the contrary, the surface pressure of the aluminum distearate monolayer on distilled water varied distinguishably with time. As the surface pressure of this monolayer, therefore, we, for convenience's sake, read the value which the monolayer exhibited when left to stand for one minute.

Results

Stearic Acid Monolayer on Aluminum Chloride Solution.—The variation of surface pressure of the stearic acid monolayer on aluminum chloride solutions with the area occupied by a stearic acid molecule was measured over a range of pH values of the solution. Typical surface pressure-area curves are shown in Fig. 1, in which the numerals represent the pH values. It was found that the folds of the film were visibly detected at smaller areas than the inflection point of the pressure-area curves. It is obvious from this figure that the influence of aluminum ion is extremely characteristic for the pH, which suggests that it depends on the state of aluminum ion in the solution. This may be more clearly elucidated by plotting a limiting area, which we define as the area at which an appreciable rise in surface pressure occurs when the monolayer is compressed, against the pH of the solution. This relation is given by the curve 1 in Fig. 4. It is seen that the curve has two maxima and one minimum. In the previous work[2] only one maximum was found; another maximum and a minimum were overlooked since the intervals of pH were so coarse there. The shape of the curve characterizing the interaction between the stearic acid monolayer and aluminum ion is very similar to that already shown by Spink and Sanders[8], although in the magnitude of limiting areas there is a great difference, which might arise from the use of different aluminum salts or from other artificial causes. There is, however, no obtaining of further information on the reaction in the monolayer with only this finding. To gain a deeper insight into the problem, we investigated the monolayer of aluminum distearate which had been known to have a polymeric structure in the hydrocarbon solution as well as in the solid state.

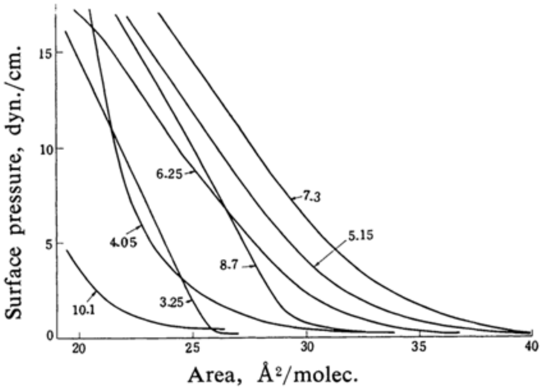

Fig. 1. Effect of pH on the pressure-area curves of stearic acid monolayer spread on 10^{-4} mol./l. aluminum chloride solution at 25°C.

Aluminum Distearate Monolayer on Distilled

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[13] R. Matuura and I. Hayasi, *Memoirs Fac. Sci., Kyushu Univ., Ser. C*, 1, 31 (1948).

Water.—The monolayer of aluminum distearate on distilled water at various pH values was unstable, as has been previously stated, but it was revealed by the talc method that the monolayer was solid expanded at pH values between about 4.5 and 9.0. Figure 2 illustrates some pressure-area curves of the monolayer. These curves are less expanded than that of stearic acid on aluminum chloride solution when the area per chain of aluminum distearate is compared with that occupied by a stearic acid. In the same way as in the case of the stearic acid monolayer, the limiting area-pH curve is depicted in the Fig. 4 curve 2. This curve resembles curve 1 in shape; this might be considered to suggest that the reaction of the stearic acid monolayer with aluminum ion in the underlying solution forms aluminum distearate in the monolayer. However, there are considerable differences in the value of the areas between the two curves. In order to interpret this difference, it seems necessary to study the interaction of the aluminum distearate monolayer with the aluminum ion in the solution.

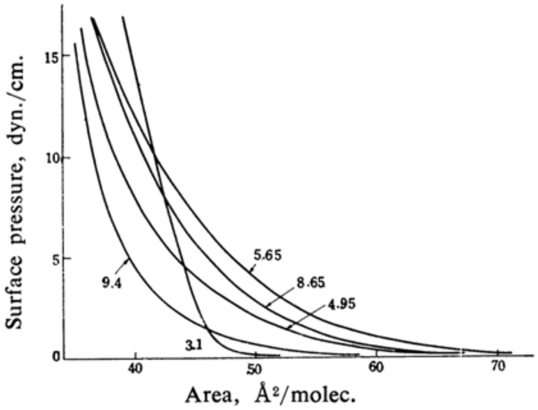


Fig. 2. Effect of pH on the pressure-area curves of aluminum distearate monolayer on distilled water at 25°C.

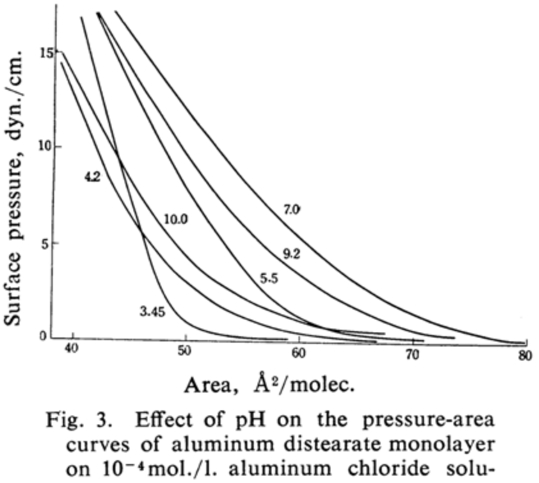


Fig. 3. Effect of pH on the pressure-area curves of aluminum distearate monolayer on 10^{-4} mol./l. aluminum chloride solution at 25°C.

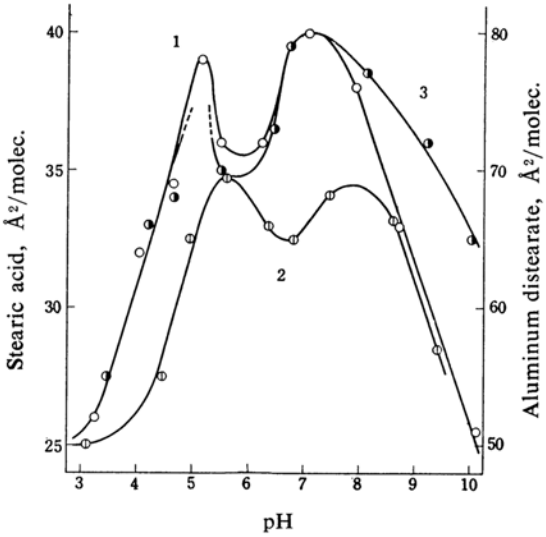


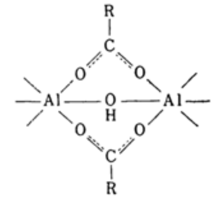
Fig. 4. Comparison among limiting area-pH curves of the monolayers of stearic acid and aluminum distearate on underlying solutions at 25°C: (1) Stearic acid on aluminum ion (○); (2) Aluminum distearate on water (⦶); (3) Aluminum distearate on aluminum ion (◑).

Aluminum Distearate Monolayer on Aluminum Chloride Solution.—The results obtained for the influence of aluminum ion at various pH values on the pressure-area curve of the aluminum distearate monolayer are shown in Fig. 3. The behavior of these pressure-area curves is typically solid-expanded and is extremely similar, not to that of the aluminum distearate monolayer on water, but to that of the stearic acid monolayer on aluminum ion. The limiting area-pH curve produced from Fig. 3 is curve 3 in Fig. 4. This curve is partially a little different from curve 1, but there seems to be essentially no difference between them.

Discussion

The interaction of the monolayers of fatty acids with various metal ions has been discussed from the standpoint of the formation of metallic soaps in the monolayers ever since Langmuir and Schaefer[1], and many investigators have tried to shed light on the compositions of the interacted monolayers from only the results of chemical analysis carried out on the matter collected after the monolayers were compressed to collapse. Through the investigation of tanning by chromium ion of various monolayers, e. g., the myristic acid monolayer, practicing at the same time the chemical analysis of them, Schulman and Dogan[14] thought it likely that the structure of solid monolayers can be brought about by the interlinking between chromium monosoap molecules by hydrogen bonding between two hydroxyl groups attached to the chromium ion or between hydroxyl and carbonyl in the carboxyl group. A similar investigation was made by Ekwall and Bruun[11,12] of the interaction of the myristic acid monolayer with aluminum ion; they concluded that the final product of the interaction seemed to be a dibasic aluminum monomyristate with regard to the composition of the interacted monolayer. The matter used by these authors for the analysis was, however, that which had been removed with a scoop at the very small area where the monolayers might be collapsed and, moreover, perhaps included physically adsorbed metal ions. Therefore, it seems doubtful whether the monolayer compositions thus estimated will express the true ones even if the physically adsorbed metal ions are taken into account experimentally. It is a well-known fact that the reaction of alkali salts of a fatty acid such as stearic acid with aluminum ion in an aqueous medium always results in aluminum disoap. It is conceivable, therefore, that when the stearic acid monolayer is spread on the solution containing aluminum ion at certain pH values, the former will combine with the latter to form aluminum distearate in the monolayer.

With aluminum disoap investigated by many workers from various viewpoints, it has been made clear that the structure of aluminum disoap is polymeric in its hydrocarbon solutions as well as in the solid state. Bauer et al.[15,16] elucidated by means of the technique of the infrared absorption spectra that the polymeric structure of aluminum disoaps is constituted not through hydrogen bonding between hydroxyl groups but through a coordinate bond between aluminum and oxygen in the hydroxyl group. Taking account of experimental results of various kinds, a reliable polymeric structure of aluminum disoap may be that of Leger et al.[17], similar to that of Bauer et al., i. e.,



in which R represents the hydrocarbon part. When aluminum distearate is spread on the substrate from the benzene solution, it is natural that the aluminum distearate will, in the monolayer state, hold the polymeric structure, the backbone chain of which will attach to or be immersed in the underlying solution. It was found that the pressure-area curve of a aluminum distearate monolayer spread on a sodium fluoride solution became less expanded with an increasing sodium fluoride concentration and finally coincided with that of stearic acid on water (i. e., it contained no aluminum ion) at about 10^{-3} mol./l. sodium fluoride solution. This is considered to show that the coordinate bond was cut by the fluorine ion which preferentially coordinates on aluminum ion[18]. Further discussions from the rheological aspect of the aluminum distearate monolayer will appear in part II of this series.

If the two-dimensional polymeric structure of aluminum distearate monolayer on distilled water is valid, its unstable behavior on compression can be ascribed to the fact that the rearrangement of aluminum distearate into the true equilibrium state takes a long time. Therefore, the pressure-area curves in Fig. 2 and the limiting area-pH curve illustrated by curve 2 in Fig. 4 may not be referable to those of the equilibrium, but some properties characteristic of the aluminum distearate monolayer would be disclosed in these curves. In this stage it is not easy to say what monolayer structures are corresponding to these pressure-area curves at respective pH values. However, the depression of the limiting area of the monolayer at the acidic side may be explained by its decomposition into stearic acid and aluminum ion, and at the alkaline side by its dissolution into water as sodium stearate.

Comparing the findings concerning the stearic acid monolayer on aluminum ion with those concerning the aluminum distearate monolayer on distilled water, we find a not negligible difference, even though they resemble each other in shape, as is clearly shown in Fig. 4. If only aluminum distearate was formed in the monolayer of stearic acid on aluminum ion and no other effects were exerted, the film 1 should agree with the film 2. In fact, the film

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

15) F. A. Scott, J. Goldenson, S. E. Wiberley and W. H. Bauer, *J. Phys. Chem.*, **58**, 61 (1954).

16) W. O. Ludke, S. E. Wiberley, J. Goldenson and W. H. Bauer, ibid., **59**, 222 (1955).

17) A. E. Leger, R. L. Haines, C. E. Hubley, J. C. Hyde and H. Sheffer, *Can. J. Chem.*, **35**, 799 (1957).

18) K. Motomura and R. Matuura, to be published soon.

1 is very much analogous to film 3 in various properties. This suggests that the interacted stearic acid monolayer may be that in which aluminum ion is adsorbed on the aluminum distearate monolayer. In the limiting area-pH curves, however, there seems to be a little partial disagreement between curves 1 and 3 in Fig. 4. Perhaps this disagreement may be not essential. It is accordingly conceivable that these two curves would fall into agreement with each other if all the measurements of surface pressure were carried out on the monolayers which attained to a state of complete equilibrium after very long times.

In view of the above discussion, it may be concluded that the interaction of the stearic acid monolayer with aluminum ion in the underlying solution occurs only over a characteristic pH range, below which the acid monolayer does not dissociate enough to interact appreciably and above which the monolayer tends to dissolve in the underlying solution; the solid expanded film brought about through the interaction is quite similar to the polymeric aluminum distearate monolayer adsorbing aluminum ion.

In part II of this series we present a further discussion on the interaction by making use of the results of surface rheological measurements.

Summary

In order to throw light on the interaction of the stearic acid monolayer with aluminum ion in underlying solutions, surface pressure measurements were carried out on (1) the stearic acid monolayer spread on 10^{-4} mol./l. aluminum chloride solution, (2) the aluminum distearate monolayer spread on distilled water, and (3) the aluminum distearate monolayer spread on 10^{-4} mol./l. aluminum chloride. It was found that their pressure-area curves were all solid expanded films over characteristic pH ranges, with the curve of 1 especially analogous to that of 3. In the limiting area-pH curves, there seemed to be a little partial disagreement between them which would not be essential. From these results it was concluded that the monolayer of stearic acid interacting with aluminum ion might be analogous to the two-dimensional polymeric aluminum distearate adsorbing aluminum ion.

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