On the Nature of Built-up Film. I. Adsorption of Ion on Built-up Film of Stearic Acid

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Introduction

It has been shown by several investigators that the heavy metallic ions exhibit remarkable effects on the surface properties of monolayer of fatty acid spread on water(1) or multilayer transferred onto a solid surface.(2),(3) That the built-up film of fatty acid on solid shows a high wettability when conditioned with the solution containing polyvalent ion, such as aluminum,(4) thorium,(5) or uranyl ion,(6) and that the protein molecules can be adsorbed on such a conditioned surface also suggest a special action of heavy metallic ion on fatty acid.

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(1) I. Langmuir and V. J Schaefer, *J. Am. Chem. Soc.*, **58**, 284 (1936); **59**, 2400 (1937).

(2) K. B. Blodgett, *J. Phys. Chem.*, **41**, 975 (1937); K. B. Blodgett and I. Langmuir, *Phys. Rev.*, **51**, 964 (1937).

(3) I. Langmuir, "Recent Advances in Surface Chemistry and Chemical Physics", Science Press Printing Co., Lancaster, 1939, p. 1.

(4) I. Langmuir and V. J. Schaefer, *J. Am. Chem. Soc.*, **59**, 1406 (1937).

(5) I. Langmuir and V. J. Schaefer, *J. Am. Chem. Soc.*, **59**, 1762 (1937); **60**, 135 (1938).

(6) G. H. A. Clowes, "Recent Advances in Surface Chemistry and Chemical Physics," Science Press Printing Co., Lancaster, 1939, p. 61.

The experimental data, presented by Clowes(6), which showed that the built-up film adsorbed a maximum amount of protein when it was conditioned with the aqueous uranyl salt solution at pH 6.0~6.5, lead us further to the presumption that the metallic ion requires an optimum pH range for the adsorption. If we adopt the opinion of Kraus and Nelson, (7) insisting rather a complex nature of uranyl ion in aqueous solution, its adsorption may naturally be of a more complex nature than it appears. The present authors have also intended to study the action of polyvalent ion for the built-up film of stearic acid, concerning such a problem.

Experimental

a. Material.—Stearic acid used was Merck's pure chemical reagent. Barium, aluminum, and mercuric chlorides, copper sulfate, and thorium nitrate were recrystallized repeatedly. Substrate water was made pure enough so as no impurity could be detected from the detail of the pressure~area curve obtained for monolayers of fatty acid spread on it.

b. Method.—Most of the experiments were carried out in the temperature range of 23~28°C., in which, however, the monolayer of stearic acid on mere distilled water tends to expand when the pressure of the piston oil is too low, and collapses when it is high(8). Since the collapsing effect readily appears (2 min. after the spreading), the echelon consisting of pure stearic acid could hardly be prepared while the monolayer on water is stable. For this reason, the following procedure was adopted. The highly polished stainless steel slide, on which a mixed multilayer of stearic acid and barium stearate was deposited, was immersed in $N/100$ hydrochloric acid in order to convert barium stearate to free fatty acid(9), and this converted layer was covered with a few layers of stearic acid by means of an ordinary technique. Thus, barium stearate could be converted to free acid in the depth of several layers at temperature above 25°C.

To minimize the accidental experimental error, a half part of the slide (called the treated side hereafter) was dipped in a solution containing metallic ion, and the other half (the control side) in a control solution. An apparent increase in thickness due to the adsorption was then determined by means of the optical interference method(10), assuming that the spacing and refractive index of barium stearate are 24.4 Å. per layer and 1.462 respectively(8). The number of equivalent layers on which the ions were supposed to be compactly adsorbed was determined by the skeletonization with benzene.

The pH of the solution was adjusted simply by redistilled hydrochloric acid and aqueous ammonia solution when required.

Experimental Results and Discussion

a. Effect of Acid and Alkali.—When the echelon was treated with various kinds of acid or alkali solutions, an appreciable change in composition generally occurred, frequently the change reaching several layers in the depth. For instance, when the echelon was treated with solution of $p\text{H}<2$ for 30 sec., the thickness of echelon decreased, indicating presumably the conversion of barium stearate underneath into free acid. A more remarkable decrease appeared in a strong alkaline region. After treating the control side of the echelon with acid solution of $p\text{H}=2$ and the other half with that of varying pH, the difference in thickness between both echelons was measured as shown in Table 1. These changes may be ascribed to the dissolution of stearate ion into the bulk of solution.

Table 1

Change in Thickness of Echelon
Treated by Acid or Alkali

pH	2.0	3.2	3.9	5.0	6.6	
Change in thickness, Å.	control	0.0	−0.1	−0.8	−0.3	
pH	7.3	8.3	8.8	9.0	9.4	9.8
Change in thickness, Å.	+0.4	+0.5	−5.2	−6.8	−34.3	−32.9

b. Adsorption of Various Ions. — The amounts of the adsorption of barium, mercuric, cupric, aluminum, and thorium ions from 10^{-4} mol/l. aqueous solutions of varying pH were determined and shown in Fig. 1, where the abscissa denoted pH and the ordinate, the amount of adsorption expressed by the difference in thickness (in Å.) between the treated and the control sides of a slide. The figure shows that there exists an optimum pH range of adsorption for each metallic ion. The adsorption is usually not remarkable in other region of pH, presumably due to the decrease in the concentration either of metallic ion in the solution or of stearate ion on the surface. It can therefore be expected that the optimum range of pH for the adsorption depends on the nature of metallic ion concerned.

The apparent increment in the ordinate in Fig. 1 at pH exceeding 9 may be accounted

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(7) K. A. Kraus and F. Nelson, *J. Am. Chem. Soc.*, **71**, 2510, 2517 (1949).

(8) K. B. Blodgett, *J. Am. Chem. Soc.*, **57**, 1007 (1935).

(9) A. Rothen, *J. Am. Chem. Soc.*, **70**, 2732 (1948).

(10) T. Tachibana, *Seikagaku* (*Biochemistry*, in Japanese), **20**, 8 (1948).

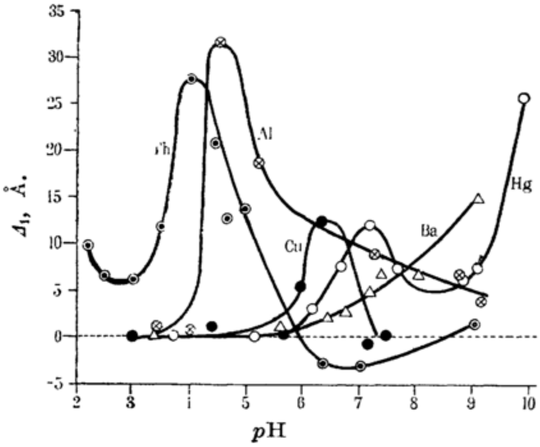

Fig. 1.—Apparent increase (Δ_1) in thickness due to adsorption.

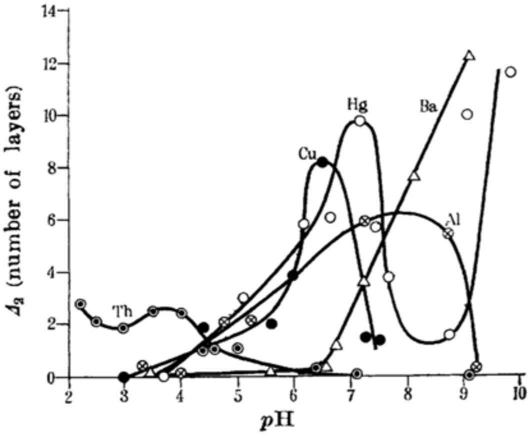

Fig. 2.—Apparent difference (Δ_2) in thickness between treated and control sides of echelon after skeletonization, taking the thickness of barium stearate monolayer as unit.

for by the dissolution of stearate molecules in the multilayers of the control side into the bulk of solution as shown in Table 1, and not by the increase in thickness on the treated side; practically a remarkable decrease was seen on the control side with increasing time of soaking, while only a little increment was observed on the treated side. Barium ion, and perhaps some other ions such as mercuric ion, when they were adsorbed on multilayers, showed a protecting effect against its dissolution into the alkaline medium, just as the effect of these ions on the monolayer spread on water(11).

c. Skeletonization of Adsorbed Layers. —The echelon treated as mentioned above was immersed into benzene for thirty seconds. This procedure brought a very striking difference in thickness between the control and the treated sides. It may be accounted for by the difference in resistance to the dissolution due to the presence of metallic soap on the treated side. Thus the amount of stearic acid which took part in the formation of metallic soap could be estimated by assuming that the metal stearate was practically insoluble in benzene, and that its structure in the multilayer could be preserved after skeletonization. Though it was doubtful whether the experimental conditions were good enough to allow these assumptions, the numbers of stearic acid layers taking part in the adsorption are roughly calculated as shown in Fig. 2. Judging from Figs. 1 and 2, it can be said that the increase in thickness due to the adsorption is rather pronounced in the case of a relatively few position of anchorage for the adsorbing ion. The ratio of the ordinate (Δ_1) of Fig. 1 to that (Δ_2) of Fig. 2 was calculated and illustrated in Fig. 3. This ratio is roughly considered to be the increase in thickness when a stearic acid monolayer is completely changed to metallic soap, and a very specific nature of individual metallic ions can be seen in this figure. Thus, the adsorption of barium ion caused, irrespective of *p*H, the increment of 1.7 Å. in thickness, which was in a good agreement with that expected from the known spacing of stearic acid and barium stearate, whilst cupric and mercuric ions showed a maximum value of thickness in a specific *p*H range. It may be added further that one of the above mentioned assumptions could be valid for these three ions, namely, by contacting with vapor of *n*-octane, the

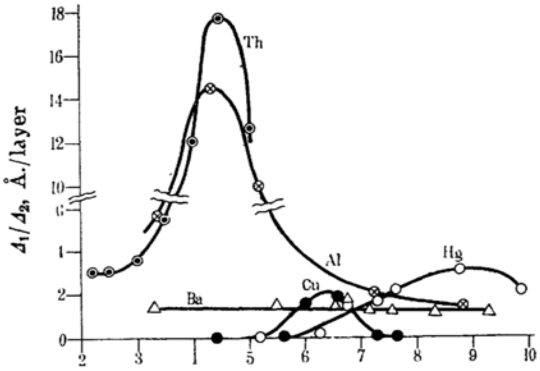

Fig. 3.—Adsorbed amount of ions per layer at various *p*H.

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

skeletonized echelon almost restored the original thickness which it possessed before soaked into benzene.

On the other hand, the values of aluminum and thorium offered a question concerning the limit of the validity of skeletonization. The adsorbed amount per layer shown in Fig. 3 would be too large when compared with the adsorbed amounts of these ions on the multilayers of barium stearate(4),(5) where it could be considered that the adsorption below a layer did not take place.(12) From the experience of the present authors, it seemed impossible to exceed 3 and 5 Å. in any case for alumiuum and thorium respectively. By contacting with *n*-octane vapor, it could be confirmed that the skeleton collapsed after the skeletonization. Furthermore, it has also been pointed out(2) that the meaning of skeletonization is obscure unless the content of metallic soap in the layer is more than 50 per cents. Therefore, we attempted further to determine the reliable value of the number of stearic acid layers taking part in the formation of metallic soap.

If the adsorption takes place in a few outermost layers of the built-up film, there exists a sandwich layer of pure stearic acid between the adsorbed layer and the base multilayer. As a result, when this echelon was skeletonized, the adsorbed layer would be partially detached from echelon into the solution, due to the dissolution of the underlying sandwich layer of stearic acid. Since this effect is considered to be remarkable when only a few surface layers take part in the adsorption, it is evident that the apparent amount of the adsorption per layer is also exaggerated in such a case. These circumstances are still more likely to occur in the case where a large or complex ion may suffer resistance to the penetration of the surface layers for the deeper adsorption.

These presumption could be confirmed from the following experiment. Instead of the multilayers of stearic acid converted from barium salt, definite multilayers of stearic acid were deposited from water the surface of water onto the barium stearate echelon at 8～12°C., at which the monolayers could be transferred repeatedly without collapse, and the experiments of the adsorption of ion and the successive skeletonization were carried out similarly. The experimental results showed that the amounts of the adsorption were nearly the same as in the former case in all *p*H region, while the detachment of stearate during skeletonization seemed to be fairly remarkable. This may be probable, since the stearic acid in this case can be completely removed by skeletonization, while, in the former case, the stearic acid layer contains some barium stearates which resist the detachment effect mentioned above. We could cite further evidence for this argument. From 2 to 10 layers of stearic acid were transferred onto the multilayers of barium stearate. Using these surfaces the similar experiments were repeated. The apparent amounts of the adsorption per layer as a function of the number of layers of stearic acid initially transferred were shown in Table 2. It was about 2 Å. for barium at *p*H 9.0 independent of the number of the layers. This value may be expected from the spacing of the built-up layers of barium stearate (24.4 Å.) and of stearic acid (23.1 Å.).

Table 2

Apparent Amount of Adsorption as a Function of the Number of Layers of Stearic Acid

No. of layers of stearic acid on echelon	Adsorbed amount per layer in Å.		
	Ba at *p*H 7.4	Ba at *p*H 9.0	Al at *p*H 4.3
2	2.6	1.6	5.0
4	3.2	2.1	3.9
6	27	2.5	20.0
8	35	2.1	52.1
10	50	1.9	68

On the other hand, there was a remarkable increase in thickness of the adsorbed film between 4 and 6 stearic acid layers of aluminum at *p*H 4.3 or for barium at *p*H 7.4. These results seem to show that these ions can penetrate only about 4 layers at the corresponding *p*H. This table does not only suggest the existence of the sandwich effect, but also enables us to calculate the adsorbed amount per layer for aluminum, being about 5 Å., which can be expected from the content (usually 60 ～80%) of barium stearate in the ordinary echelon and increment in thickness (～3 Å.), when it was conditioned with aluminum ion. That the aluminum ion could, even at the most favorable *p*H for the adsorption, penetrate only a few layers, suggests its complex nature as compared with barium ion, which has already been pointed out for instance by McGee(13). Recently, Gerovich and Kaptsan(14) pointed out the anomalous surface potential of monolayers of stearic acid spread on water

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(12) I. Langmuir, *Proc. Roy. Soc.*, **A 170**, 1 (1939).

(13) C. G. McGee, *J. Am. Chem. Soc.*, **71**, 278(1949); *etc.*

(14) M. Gerovich and O. Kaptsan, *Zhur. Fiz. Khim.*, **23**, 445 (1949); *C. A.* **43**, 6038 (1949).

containing thorium salt at *p*H 2.5. This also seems to have some relation to our experiment. Furthermore, it was reported by Sasaki and Matuura⁽¹¹⁾ of our laboratory that the monolayers of stearic acid spread on the aqueous solutions containing ions of copper, aluminum, thorium, etc., remarkably expanded at the *p*H ranges corresponding to those of Fig. 3. From the data shown in Figs. 1 to 3, it may also be reasonable to assume more or less large unit of the complicated structure at least in the specific *p*H range for cupric, mercuric, aluminum, and thorium ions in the solution, the degree of complexity being presumably as follows:

thorium ion>aluminum ion>cupric ion.

Summary

The adsorption of barium, mercuric, cupric, aluminum, and thorium ions on the built-up films of stearic acid both transferred from water the surface of water, and converted from barium stearate multilayers, was studied.

The adsorbed amount of barium ion increased with increasing *p*H, but the increase in thickness corresponding to the saturate adsorption for monolayer was constant for all *p*H. On the contrary, other ions studied showed the specific *p*H range for the optimum adsorption. A more or less complicated and large structure for these ions was concluded from the special nature of the adsorption hereby exhibited by these ions. Such a complex nature was most pronounced for aluminum and thorium ions.

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