On the Nature of Built-up Film. II. Deposition of Monolayer of Stearic Acid from Surface of Water Containing Copper, Aluminum, and Thorium Ions

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Introduction

The built-up film of stearate can readily be prepared when the substrate water from which it is built up contains barium or calcium ion. If, however, it contains a trace of heavy metallic ion, the nature of this film is profoundly altered.(1) As pointed out by Blodgett,(2) this effect seems to be very remarkable in case of copper ion which hinders the deposition of monolayer on a metallic slide, even if the other conditions are favorable for the successive deposition. She also reported(3) that the monolayer spread on water containing aluminum chloride could not be deposited onto the slide. In the preceding report,(4) the authors were inclined to the opinion that some metallic ions, *e. g.*, cupric, mercuric, aluminum, and thorium ions, somewhat differ in the manner of adsorption from alkali earth ions. They seem to behave rather as a large unit of the complicated structure in a specific *p*H range, at which the adsorption is remarkable. This conclusion has also been supported by the experimental results on monolayer spread on water, carried out by Sasaki and Matuura of our laboratory.(5) In the present report, it was attempted to build up stearic acid monolayers by transferring from the surface of aqueous solutions containing cupric, aluminum, and thorium ions, and the properties of these films were studied.

Experimental

Materials used were purified similarly as describ-

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

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

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

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

ed in the preceding report.(4) Stearic acid was spread as benzene solution on the surface of aqueous solutions of copper sulfate (*p*H 6.5), aluminum chloride (*p*H 6.3), and thorium nitrate (*p*H 4.0), *p*H of which was properly adjusted using ammonia and hydrochloric acid. Concentration of salts was 10^{-4} mol/l. The method of deposition will be described in the following section. The spacing of film, transferred onto the echelon of barium stearate, was determined by means of the optical method as in the preceding report.(4) The contact angle was measured by an image method.(6) Thereby we ignored the disturbance due to the evaporation of water, but the results were quite satisfactory for the present purpose.

Results

a. Deposition of Monolayers onto the Slide.—It was confirmed by the preliminary experiments, that the difficulty of transference onto the slide of monolayers of stearic acid spread on aqueous solution containing copper, aluminum, and thorium ions, chiefly comes from their mechanical properties. High rigidity and brittleness spoil the fluidity and flexibility of monolayer which are necessary for building up monolayers. Actually, the piston oil could not exert a uniform pressure on a film. It must be noted further that, in this case, films are so sensitive even for a slight mechanical agitation accompanying dipping and withdrawing of the slide,(1) that the piston oil of high spreading pressure usually employed for this purpose can not be used. Moreover the heavy metal ions in a substrate water seem to influence the nature of an ordinary piston oil, such as castor oil, as it does for stearic acid. Taking into account of these circumstances, the following procedure was adopted to prepare a built-up film. Successive *Y*-multilayers of barium stearate, deposited onto the metal slide, were conditioned with aluminum chloride solution of *p*H 4.3 or with thorium nitrate of *p*H 4.0, and immersed in water containing ion under the investigation. Benzene solution of stearic acid was then applied to that surface of water by a micro-pipette, until only a small drop of benzene remained. The additional drops were put on several positions about 4 cm. apart from the place where the slide was withdrawn. As the slide was withdrawn and monolayer was transferred, drops of benzene spread with the irregular shape, as if they wedge into cracks formed in a rigid surface layer of stearic acid. Here drops behave as a piston oil of the spreading pressure of about 10 dynes per cm. presumably unaffected by a substrate ion. The spreading of drops was the indication of transference of monolayer. It must be noted that, although the first layer of copper, aluminum, and thorium stearates could be built up relatively easily, successive deposition of these films, especially of thorium stearate, occurred in an irregular manner, *i. e.*, we often encountered the folding or the defection of monolayers during its transference from the surface of water.

The first layers of built-up films thus obtained were wettable, to some extent, soon after withdrawal, but became very hydrophobic once they were dried. The contact angle in such a state towards water are shown in Table 1. Here, an *X*-film of barium stearate was built from substrate water of *p*H 9, and the contact angle value was the mean of four to eight experiments.

Table 1

Contact Angles of Built-up Films towards Water

Lower layer	45*Y* Ba-st.		47*Y* Ba-st.		
Upper layer	2*Y* Ba-st.	3*X* Ba-st.	1*B* Cu-st.	1*B* Al-st.	1*B* Th-st.
Contact angle, degree	99±12	102±10	104±11	106±10	110±6

Further the calculation was made for the apparent spacing of monolayers of these built-up films, using the value of 24.4 Å. for the spacing of barium stearate monolayer and refractive index of 1.462 which was assumed to be equal to that of base echelon. The result was shown in Table 2. The value of spacing was obtained from the results of five to seven experiments.

Table 2

Apparent Spacing of Copper, Aluminum, and Thorium Stearates

Film	Apparent spacing, Å.
Barium stearate	24.4
Copper stearate	23.0 ± 4.1
Aluminum stearate	17.8 ± 4.7
Thorium stearate	20.5 ± 3.6

b. Property of Conditioned Built-up Film.—As reported in the preceding paper, copper, aluminum, and thorium ions behave in the case of adsorption on stearic acid multilayers as a fairly large unit. They also render the treated surface highly wettable as

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(6) E. Kueen and W. W. Benton, *J. Phys. Chem.*, **41**, 1195 (1937).

was already reported by Inaba of our laboratory,(7) but this effect was known to be more remarkable in the case of barium stearate multilayers than in the case of stearic acid.(8) We can also observe a characteristic behavior for wetting, when we examine the built-up layers of stearate of some other heavy metal, as are summarized in Table 3.

Table 3

Wettability of Variously Conditioned Built-up Film

Conditioning		Built-up Film			
Reagent	*p*H	Barium stearate (*Y*-layer)	Copper stearate (*B*-layer)	Aluminum stearate (*B*-layer)	Thorium stearate (*B*-layer)
Barium chloride	6.5	—	—	—	—
Copper sulfate	6.5	+++	++	—	—
Aluminum chloride	6.3	++++	+++	+	—
Thorium nitrate	4.0	++++	++++	++	—

—, Non-wettable after soaking for 1 hr.; ++++, perfectly wettable after soaking within 30 sec.; +, ++, and +++, more than a half of total area of a slide being wettable after soaking for 20 min., 5 min., and 30 sec., respectively, but water peeling back by the subsequent washing.

Discussion

In the data shown in Table 1, it will be noticed that the films of stearate of heavy metal are very hydrophobic, despite the difficulty of their deposition. Bikerman(9) reported that the monolayer is deposited as *Y*- or *X*-layer according to whether the contact angle being variable on both sides of 90° or variable only on the larger side of 90°. According to this view, *X*-layer should be transferred during down-trip which could be the case for copper stearate if it was built up with thorough precaution. However it was unsuccessful with aluminum and thorium stearates. This may perhaps come from their speciality in the mechanical behaviors. On the other hand, it will be noticed that the apparent spacings of all these films are smaller than that of barium stearate. Since the actual length of stearyl radical can not be considered to be affected by the presence of heavy metal, the results seem to indicate a smaller refractive index for stearate of copper, aluminum, and thorium than that of barium. The smaller refractive index in turn predicts that the stearyl radicals of these stearates exist uniformly separated in the built-up film, provided that the defection or the folding of monolayer mentioned above are absent in this case. This, together with the fact that the monolayer could hardly be transferred onto a slide on account of its mechanical resistance, leads us to the conclusion that these stearyl radicals are rigidly bound together by a somewhat long chain consisting of, say, aluminum and oxygen. Such a conclusion has been obtained also by Sasaki and Matuura(5) of our laboratory. In this connection we should refer to the macromolecular structure of aluminum soap which is recently proposed by many authors(10) to explain its peculiar and complex nature. Perhaps, we should not use the term aluminum stearate, as it was reported that we could merely find the adsorption complex consisting of hydrated alumina and stearic acid rather than the stearate.(11) But it is not a matter of fundamental importance for the present argument how they are combined together. Experimental result in Table 2 shows in agreement with these authors, that the substance thereby formed is of a complex nature.

Now, let us pay attension to the fact that the built-up films of barium, copper, aluminum, and thorium stearates exhibit nearly the same wettability towards water as shown in Table 1, which is due, of course, to the fact that a hydrocarbon part of the stearate constitutes an outermost layer in all cases. But precisely looking, we can arrange these ions in series of barium, copper, aluminum, and thorium according to the decreasing order of the wettability of their stearate, though it is not so distinct. This series is, of course, in contradiction to what would be expected from apparent spacing of stearate shown in Table 2, and can therefore be ignored as an experimental error, but we should like rather to take it for the slight indication of overturning effect allowed for molecules,(12) with the easiness decreasing in the order shown in the above series. Precisely speaking, it can reasonably be assumed that the stearate molecule is allowed to overturn itself in the surface layer, with the degree of difficulty proportional to the complexity of its structure.

A more clear evidence of this view can be

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(7) A. Inaba, This Bulletin, **23**, 146 (1950).

(8) I. Langmuir and V. J. Schaefer, *J. Am. Chem. Soc.*, **59**, 1762 (1937).

(9) J. J. Bikerman, *Trans. Faraday Soc.*, **36**, 412(1940).

(10) V. R. Gray and A. E. Alexander, *J. Phys. Colloid Chem.*, **53**, 9, 23 (1949); C. G. McGee, *J. Am. Chem. Soc.*, **71**, 278 (1949); *etc.*

(11) L. J. Edwards, Thesis for Fellowship, Royal Institute of Chemistry (1946): Unfortunately the authors have not yet seen the original report.

(12) I. Langmuir, *Science*, **87**, 493 (1938).

found in Table 3. Here again it is confirmed that above ions hinder the overturning of stearic acid molecule and re-overturning of once overturned molecule, with the intensity increasing in the order mentioned above. The easiness of overturning was here corelated with the degree of wettability semiquantitatively expressed in this table. This order is also in agreement with that of the preceding report. (4) Thus we are inclined to the opinion that the metallic stearate increases the complexity of its structure in the order of barium, copper, aluminum, and thorium, among which aluminum and thorium stearates are complex enough to be called macromolecule or micelle, as was proposed by McGee *et al.*,(10) while barium stearate forms merely a simple stoichiometric compound as is usually considered. It is interesting in these relation to point out that although the film of free stearic acid or barium stearate can readily be conditioned (rendered wettable) by treating with aluminum or thorium salt solution, thorium stearate film itself is not wettable, and moreover can not be conditioned similarly, and further that stearic acid conditioned by aluminum salt proves to be fairly wettable, while aluminum stearate is well known as one of the efficient water-repellant. All these apparent contradictions can be explained reasonably. Special nature of water-repellent ferric stearate frequently employed for the coating of a trough for the surface film experiment(13) can also be understood from such a point of view.

Summary.

Monolayer of stearic acid spread on water containing copper, aluminum, and thorium ions, has been transferred onto solid surface, and the apparent thickness of monolayer as well as its wettability towards water after the treatment with or without aqueous solution of salts were measured. Tentative explanations for these phenomena are given, taking into account of a macromolecular structure of aluminum soap.

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(13) I. Langmuir, *Cold Spring Harbor Symposia Quant. Biol.* **6**, 171 (1938).