Studies on the Interaction of Surface Films with Solute in Solution. V
Deposition of Monolayers of Several Amphipathic Compounds from Surfaces of Aqueous Solutions of Congo Red and Crystal Violet

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It has been shown by several investigators that useful knowledge could frequently be obtained for the surface interaction of the insoluble monolayer formed at air-water interface with the other additives, by investigating the nature of the built-up film obtained from the surface of aqueous substrate. Thus, the nature of the mixed monolayer of stearic acid and normal paraffin[1] or cetyl alcohol[2] has been studied by means of this method. In the latter case, formation of a stoichiometric complex of 1:1 ratio was suggested by the measurement of the surface potential, which was in agreement with the experimental result on the mixed monolayer of the same materials spread on the surface of water[3]. Such a method could sometimes be applied to study the interaction between the insoluble monolayer and the aqueous solute in the solution underlying the film. The present author[4] obtained the built-up film of stearic acid of low refractive index by transferring the monolayer from the surface of aqueous solutions containing copper, aluminum and thorium ions and discussed the structure of metal soap formed at the solution-air interface. A similar method could successfully be applied to the case of interaction between dicarboxyacids in aqueous phase and octadecylamine in the monolayer spread on it[5].

In the preceding reports[6,7] it has been shown that the addition of dye to aqueous substrate resulted in a remarkable expansion of the monolayer of amphipathic compound spread on it, when pH of the substrate was in a proper range where the binding of dye to the film material as well as the aggregation of the former

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[1] H. Sobotka and S. Rosenberg, *J. Colloid Sci.*, **5**, 581 (1950).

[2] T. Isemura and R. Nakagawa, *Memoirs Inst. Sci. Ind. Research, Osaka Univ.*, **8**, 140 (1951).

[3] J. Marsden and J. H. Schulman, *Trans. Faraday Soc.*, **34**, 748 (1938).

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

[5] T. Sasaki and M. Muramatsu, ibid., **26**, 96 (1953).

[6] M. Muramatsu, ibid., **31**, 878 (1958).

[7] M. Muramatsu, ibid., **32**, 114 (1959).

was remarkable. This could be ascribed to the interaction between the dye and the amphipathic compound, involving ionic, dipolar and van der Waals' forces. A similar conclusion was obtained by Matuura[8] in the case of the monolayer of stearic acid. To obtain further confirmations for such an interaction, the present author has intended to study the nature of the built-up films of several amphipathic compounds transferred from the surfaces of aqueous solutions of Congo red and Crystal violet.

Experimental

Materials. — Amphipathic compounds and dyes were purified thoroughly by the methods similar to those used in the former experiments[6,7]. Oleic acid and castor oil as piston oils were pure grade commercial products of Kahlbaum and Takeda, respectively, which were used without any further purification. Tri-*p*-cresyl phosphate was synthesized by the reaction of *p*-cresol and phosphorus pentachloride[9] and was distilled three times in vacuo.

Method.—Monolayers were spread from the benzene solutions of amphipathic compounds onto the aqueous substrates, containing or lacking the dyes. They were built up onto the base echelon of successive Y-multilayers of barium stearate deposited on a highly polished slide of stainless steel, by means of Langmuir-Blodgett technique[10] under the spreading pressure, F, of either of tri-*p*-cresyl phosphate ($F=10$ dyn./cm.), castor oil (15 dyn./cm.) or oleic acid (30 dyn./cm.), unless otherwise mentioned. The spacing of the built-up film was determined by means of the simplified optical method[11], assuming the same refractive index of 1.462 for the film as that of the base echelon, spacing of which was reported to be 24.4Å[10].

Concentration of the dye solution was kept to 10^{-4}mol./1. The acidity of the substrate was adjusted simply by twice-distilled hydrochloric acid and ammonia using the Beckman glass electrode. In the case of dye solution, experiments were conducted under the pH of largest expansion of each monolayer[7,8].

Results

Ease of Building-up of the Films.— Successive Y-multilayer of stearic acid could easily be obtained in pH range of 4~7 by transferring the monolayer under the spreading pressure of oleic acid or castor oil from the surface of water containing no dye. When pH of water was less than 4, however, the monolayer adherred neither to the bare surface of the slide nor to the base echelon of barium stearate. These facts are in agreement with what was reported[10]. In contrast with this, the successive Y-multilayer was obtained from the surface of the aqueous solution of Congo red the pH of which was 3.2. Deposition of the monolayer was clearly favored by the addition of the dye at least in the region of low pH, presumably owing to an increased stability of the film. From the surface of the solution of Crystal violet, we could obtain the Y-multilayer only when the monolayer was compressed by oleic acid and the slide was dried thoroughly after each transfer of the film.

Attempts were made to build the multilayers of cholesterol from the substrates of water and solution of Congo red. In the former case the substrate water of pH 5.8 proved to be favorable for obtaining the successive Y-layer for any piston oil used, while deposition of the monolayer was unsuccessful on the substrate of pH 2.0. Here, the addition of Congo red to the substrate resulted in promoting the easiness of building-up of the film even at pH 2.0. In this case the use of oleic acid and castor oil as piston oil effected Y-layer and occasionally X-layer.

The monolayers of cetyl alcohol, ethyl *n*-hexadecyl ether and ethyl stearate adhered neither to the bare surface of the slide nor to the base echelon, irrespective of the addition of Congo red to the substrate. This was indeed the fact under the spreading pressure of any piston oil used. Further efforts were also made to build up the multilayers under the spreading pressure of benzene solutions of film material placed near the slide covered with the base echelon. This method proved to be suitable for the deposition of such monolayers as copper, aluminum and thorium stearate, to which the ordinary technique of Langmuir-Blodgett method failed to apply[4]. However, it was unsuccessful in the present case even with this method.

The monolayer of octadecylamine could be deposited onto the base echelon only when the fiilm was compressed by tri-*p*-cresyl phosphate, under the substrate pH of 5~9. This was in agreement with the results reported in a former paper[5]. When Crystal violet was added to the aqueous substrate, no monolayer could be deposited in many cases onto the solid surface. Even when it could be built up,

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[8] R. Matuura, This Bulletin, **24**, 282 (1951).

[9] W. Autenrieth and A. Geyer, *Ber.*, **41**, 146 (1908).

[10] K. B. Blodgett and I. Langmuir, *Phys. Rev.*, **51**, 964 (1937), etc.

[11] T. Tachibana, *J. Japanese Biochem. Soc.* (*Seikagaku*), **20**, 8 (1948).

TABLE I

BUILT-UP FILMS OF STEARIC ACID, CHOLESTEROL AND OCTADECYLAMINE TRANSFERRED FROM THE SURFACES OF AQUEOUS SUBSTRATES CONTAINING OR LACKING DYE

Film material	Conditions of building-up			Nature of the built-up film			
	Substrate sol.		Piston oil*	Type of the film	Apparent spacing, Å	Wetting toward	
	Dissolved dye	pH				water	benzene
Stearic acid	none	$4\sim7$	C or O	Y	23.1±0.2	hydrophobic	oleophobic
〃	Congo red	3.2	C or O	Y	22.1±0.4	〃	oleophilic
〃	Crystal violet	7.2	O	Y	29.2±2.9	〃	〃
Cholesterol	none	5.8	T, C or O	Y	18.4±0.2	〃	〃
〃	Congo red	2.0	C or O	Y or X	25.8±0.3	〃	〃
Octadecylamine	none	$5\sim9$	T	Y	24.4±0.5	〃	oleophobic
〃	Congo red	5.5	T	Y	22.4±0.4	〃	oleophilic

* C, castor oil; O, oleic acid; T, tri-*p*-cresyl phosphate

we merely obtained optically heterogeneous films, irrespective of the nature of the piston oil and of the substrate pH. In contrast with this, homogeneous Y-multilayer was obtained successively from the surface of the solution of Congo red of pH 5.5, when the monolayer was compressed by tri-*p*-cresyl phosphate and the built-up film was dried after each transfer of the film.

The conditions for the successful deposition of the film were summarized in the columns of Table I from the first to the fourth columns. In this table the fifth column expresses the types of the multilayers thus obtained.

Spacing of the Built-up Films. — In Table I, the sixth column shows the spacing of the built-up films of stearic acid, cholesterol and octadecylamine, transferred from the surfaces of aqueous substrates containing or lacking dye. They are expressed in average values of 5—12 independent experiments. When the monolayer was deposited from the surface of water, the spacing depended only a little on the acidity of substrate throughout the whole region of pH investigated and on the choice of piston oil. The latter condition was valid also in the case of the solution of dye as substrate. This might come from the low compressibility of these films[7].

Wettability of the Films. — As is cited in the seventh column of Table I, all built-up films were of hydrophobic character when they were once dried. Of these films, the film of stearic acid was reported to be wetted profoundly by aqueous solutions of copper, aluminum and thorium ions[4,12]. Such an effect of metal ions was observed in the present experiments for the built-up films of stearic acid transferred from the surfaces of water, solution of Congo red and of Crystal violet. However, there were some differences between the three films in their behaviors towards the subsequent procedure. For the first film, the solid surface remained in its hydrophilic condition for at least two minutes after final rinsing with water. For the second and the third films, the procedure under the same condition resulted in peeling-back of rinsing water. After the films were once dried, the subsequent conditioning by aqueous metal ions gave rise to no wetting of the first film, while it rendered the remaining two films wettable.

The last column of Table I represents the wettability of these films toward a drop of benzene placed on them. Though the test was merely qualitative, the result was sufficient to classify the film into two groups with respect to their wetting characters. Benzene showed a large contact angle toward the films of stearic acid and of octadecylamine both transferred from the surface of water. When the slide was tilted, the drop slid on the film on which less color change was observed at the track. On the contrary, the contact angle was very small for the rest of the films and the sliding of the drop resulted in a remarkable change in color, showing the profound dissolution of film materials into the benzene drop.

Discussion

As mentioned in the preceding section, the monolayers of cetyl alcohol, ethyl *n*-hexadecyl ether and ethyl stearate spread on the surfaces of water adhered neither to the metal surface nor to the base echelon of barium stearate. Isemura

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12) I. Langmuir, *Science*, **87**, 493 (1938); A. Inaba, This Bulletin, **26**, 43 (1953).

and Nakagawa[2] have obtained a similar result for the case of cetyl alcohol. In the case of ethyl stearate it was reported[13] that the monolayer could be deposited successively only under the delicate control of substrate pH, speed of down- and up-trip of the slide. The built-up film thus obtained however seems to consist of large crystals transferred heterogeneously on the slide, as was pointed out by the microscopic observation[14]. All these phenomena, as well as the present results, seem to show the difficulty of building up a non-ionic monolayer spread on water. A similar result was obtained for the monolayers of these compounds spread on aqueous solutions of Congo red. Under the present conditions of pH of substrate, the majority of dye molecules were considered to be in a zwitterion form as pointed out in a preceding report[7]. Therefore, there is no net charge in the molecules either of film materials or of dye.

On the other hand, building-up was successful in the cases of the monolayers of stearic acid, cholesterol and octadecylamine spread on the solutions of Congo red, and of stearic acid on the solution of Crystal violet. Of these films, it is noticeable that the building-up of the monolayers of stearic acid and cholesterol is facilitated by an addition of Congo red to the substrate. Here, because of Congo red being in the region more acidic than the isoelectric point, the molecules of the dye have a positive charge while the monolayers are not in a charged state[7]. In the remaining two cases, dye and film materials are charged oppositely to each other, as pointed out in the preceding reports[7,15]. These facts lead us to a presumption that a suitable attachment of charged dye to the film material does not decrease the easiness of obtaining a built-up film of its own.

As seen in Table I, the apparent spacing of the built-up film of stearic acid or octadecylamine is decreased by an addition of Congo red to the substrate of the monolayer. It has been reported that the monolayers of stearic acid[8] and octadecylamine[7] expanded remarkably when they were spread on aqueous solution of Congo red and were compressed to a surface pressure of piston oil used in the present experiment. This could be explained by an attachment of colloidal aggregates of dye to the monolayer. Therefore the attachment of Congo red to the film may cause an increase in film thickness, while it may result in a decrease in surface density of *n*-hydrocarbon chain of the amphipathic compound and consequently a decrease of refractive index of the film. These two effects contribute oppositely to each other to the apparent spacing which we actually measured assuming the same refractive index of the upper layer as that of the base echelon. In the present case, the effect of the former seems to be overwhelmed by that of the latter. A similar effect of solute was observed in the case of the built-up film of stearic acid obtained from the surface of aqueous solutions of copper, aluminum and thorium ions[4]. In contrast with this, an overwhelming contribution of the former is observed for the film of cholesterol spread on the solution of Congo red and for the film of stearic acid on the solution of Congo red and for the film of stearic acid on the solution of Crystal violet.

It is of interest to show that, though all the films studied exhibit hydrophobic property, they are wettable toward benzene, except for the films of stearic acid and octadecylamine transferred from the surface of water which proved to be oleophobic. Zisman et al.[16] obtained the oleophobic monolayers of methyl-rich surface being non-wettable toward methylene liquid such as *n*-hexadecane, benzene, etc. They explained the phenomenon by a difference between methyl-methyl and methylene-methylene attractions[17]. As was pointed out by several investigators[18], the oleophobic character toward methylene liquid seems to suggest the existence of the methyl-rich surface, in which the molecules are closely packed and orientate towards the contacting phase. In Table I the built-up films of stearic acid and octadecylamine show an oleophobic property while the cholesterol film proves to be oleophilic, when they are transferred from the surface of water. This can be explained by the greater difficulty of packing of methyl head for the case of cholesterol, as would be expected from the special structure of

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[13] E. Stenhagen, *Trans. Faraday Soc.*, **34**, 1328 (1938).
[14] G. Knott, J. H. Schulman and A. F. Wells, *Proc. Roy. Soc.*, **A176**, 534 (1940).
[15] M. Muramatsu, This Bulletin, **31**, 871 (1958).
[16] W. A. Zisman et al., *J. Colloid Sci.*, **1**, 513 (1946); **2**, 563 (1947).
[17] W. A. Zisman et al., ibid., **7**, 109, 166, 428, 465 (1952).
[18] See, *Discussions Faraday Soc.*, **3**, 250 (1948).

cholesterol. Similarly, the oleophilic nature of the films taking up the dye can reasonably be explained by the structure of built-up film consisting of widely spaced *n*-hydrocarbon chain. We can find that this is also in a conformity with the effect of added dyes upon the limiting area of the monolayers of stearic acid, cholesterol and octadecylamine[7,8].

Summary

Attempts were made to obtain the built-up films of stearic acid, cholesterol, cetyl alcohol, ethyl *n*-hexadecyl ether, ethyl stearate and octadecylamine, by transferring each monolayer from the surfaces of water and aqueous solutions of Congo red and Crystal violet. Deposition of the monolayers of cetyl alcohol, ethyl *n*-hexadecyl ether and ethyl stearate was unsuccessful, irrespective of whether the substrate contained dye or not. On the other hand, the monolayers of the remaining compounds could easily be deposited onto the solid phase from the surfaces of water and dye solution.

The effect of added dye upon the apparent spacing of the film thus obtained seems to show an attachment of dye to the film substance, though the spacing varied from one case to another. This variation could be explained taking account of the balance of two contributing factors mutually opposite to the apparent spacing: one, increase of the film thickness due to the attachment of dye, and the other, decrease of the refractive index of the film due to the wide separation of *n*-hydrocarbon chain. Such a consideration was supported by the data on the wettability toward benzene. All these phenomena are in agreement with the data on the effect of dissolved dye upon the limiting area of the monolayer spread on it.

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