Studies on the Interaction of Surface Films with Solute in Solution. IV. Effect of Congo Red Dissolved in Aqueous Substrate upon the Monolayers of Octadecylamine, Cetyl Alcohol, Ethyl n-Hexadecyl Ether, Ethyl Stearate and Cholesterol

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(Received August 8, 1958)

In the Part II[1] of this series, the interaction between various dyes in aqueous solutions and stearic acid in the built-up film has been studied. There it was suggested that pH dependence of the amount of dye taken up by the film may be explained by the interaction between dye and stearic acid, involving ionic, dipolar and van der Waals' force. This was generally in agreement with the effect of aqueous dye solution on the monolayer of stearic acid spread on it[2] and has further been supported by the experimental results of a profound effect of aqueous dye on the monolayer of octadecylamine[3]. As has been pointed out in Part II[1], however, there still remained some uncertainty in establishing the mechanism of the interaction between amphoteric dye and the surface film.

Of many amphoteric dyes, Congo red is most familiar to us and the surface-chemical properties of its solution have widely been studied by the measurement of ultrasonic velocity[4], diffusion coefficient[5], viscoelasticity of the adsorbed film[6], and foaming power[7]. Hence Congo red was also adopted in the present work as a representative for the amphoteric dyes and its effect upon the monolayers of several amphipathic compounds has been studied. It may be expected that such a study would also contribute to the understanding of the mechanism of dyeing processes of fibers by so-called direct dyes to which many of the amphoteric dyes belong.

Experimental

Apparatus and procedure were the same as used in the preceding work[3]. The same samples of Congo red[1] and octadecylamine[3] as those which appeared in the preceding reports were used also in of the present experiments. Cetyl alcohol was first grade of Katayama Pure Chemical Co. Ethyl *n*-hexadecyl ether and ethyl stearate were synthesized by the reaction of sodium ethylate with purified hexadecyl bromide and stearyl chloride, respectively. All these amphipathic compounds were purified repeatedly by fractional distillation in vacuo and successive recrystallization from suitable solvents. The highly purified sample of cholesterol was kindly supplied by Dr. E. Kimoto of Kurume Medical College.

Results

Octadecylamine.—It has been suggested[3,8] that the surface pressure, F, of

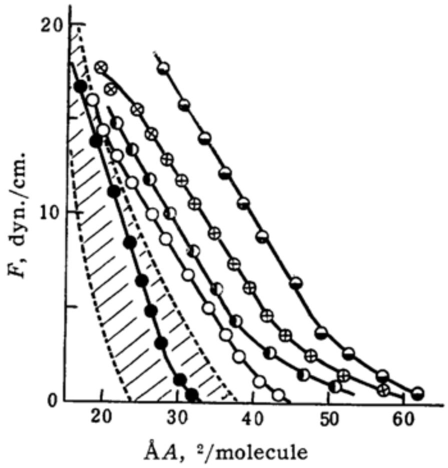

Fig. 1. $F\sim A$ curves for the monolayers of octadecylamine spread on the solutions of Congo red.
Substrate pH; ◐, 1.0; ⊕, 3.6; ◒, 5.5; ○, 7.3; ●, 9.3: $F\sim A$ curve for monolayer spread on water lie always in a range of hatched zone.

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[1] M. Muramatsu, This Bulletin, **31**, 871 (1958).
[2] R. Matuura, ibid., **24**, 282 (1951).
[3] M. Muramatsu, ibid., **31**, 878 (1958).
[4] T. Sasaki and T. Yasunaga, to be published.
[5] M. Nakagaki, This Bulletin, **23**, 104 (1950).
[6] K. S. G. Doss, *Kolloid-Z.*, **84**, 138 (1938); **86**, 205 (1939); **87**, 272 (1939), etc.; H. Kimizuka, This Bulletin, **26**, 33 (1953).
[7] M. Nakagaki, ibid., **23**, 47 (1950); T. Sasaki and H. Kimizuka, ibid., **24**, 230 (1951).
[8] T. Sasaki and M. Muramatsu, ibid., **26**, 96 (1953).

this film fluctuated considerably for a given molecular area, A. This came from the effects of ageing of the film, carbon dioxide in the substrate, velocity of compression, etc. This tendency disappeared when Congo red was added to the substrate phase. The effect of dye upon $F \sim A$ curve of the monolayer of octadecylamine is shown in Fig. 1 in which the hatched zone is quoted from the preceding report[3]. It can be seen in this figure that the addition of dye results in a remarkable expansion of the monolayer when pH of the substrate is around 5.5. In Fig. 2 curve A shows the effect of substrate pH on the area, A_0, of octadecylamine molecule in the monolayer which spread on the solution of dye and is compressed to $F=2$ dyn./cm. In the same figure the hatched zone B expresses the limit of fluctuation of A_0 for a given pH value of the substrate without dye. Maximum expansion of the monolayer was observed at pH 5.5.

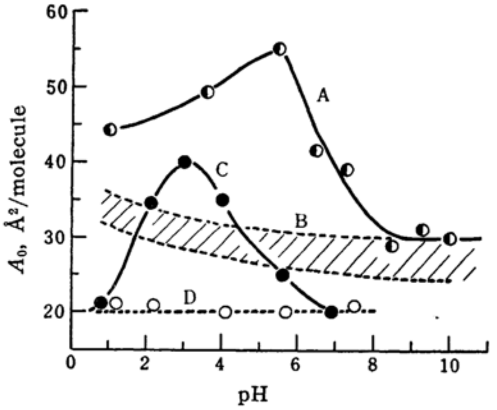

Fig. 2. Effect of Congo red upon A_0 for the monolayer of octadecylamine and cetyl alcohol.
A and B, amine on the substrate with or without dye, respectively; C and D, alcohol on the substrate with or without dye, respectively.

Cetyl Alcohol. — No effect of substrate pH was observed upon A_0 for the monolayer spread on the surface of water. When the dye was dissolved in the substrate of pH 2∼4, the film expanded considerably. Such an effect of dye is shown in Fig. 2, in which the curve C and D express the pH dependence of A_0 for the monolayer spread on aqueous substrate containing or lacking the dye, respectively. Maximum expansion of the monolayer occurred at pH 3 in this case.

Ethyl *n*-Hexadecyl Ether. — Characteristic kinds of behavior in $F \sim A$ relationship were observed for this film. When the monolayer on the surface of water was compressed, we usually observed an instantaneous rise and subsequent lowering of the surface pressure. A typical example is shown in Fig. 3 (a). The behavior could be reproduced fairly well, though F was determined by means of the vertical plate method which proves to be unsuitable when we measure the decreasing surface pressure. A similar curve was obtained for the film spread on the surface of water of any acidity. The pH dependence of the area, A_0, at $F=2$ dyn./cm. is expressed as curve B in Fig. 4.

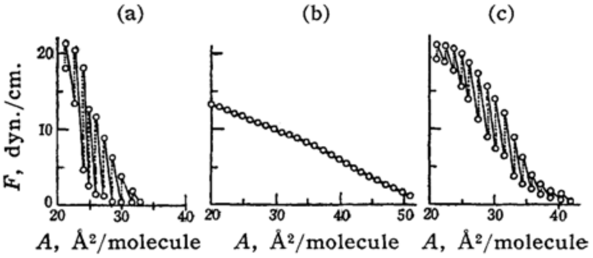

Fig. 3. $F \sim A$ curves for the monolayers of ethyl *n*-hexadecyl ether spread on (a) water of pH 4.0, (b) dye solution of pH 3.8, and (c) dye solution of pH 1.9.

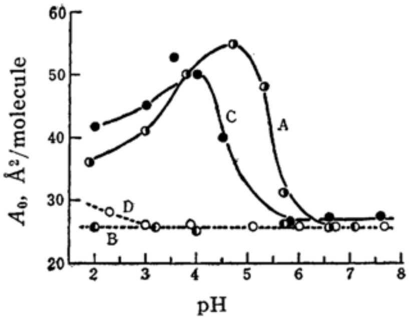

Fig. 4. Effect of Congo red upon A_0 for the monolayer of ethyl *n*-hexadecyl ether and ethyl stearate.
A and B, the ether on the substrate with or without dye, respectively; C and D, the ester on the substrate with or without dye, respectively.

The addition of the dye to the substrate generally resulted in an expansion of the monolayer, as shown in curve A of Fig. 4. The maximum expansion seemed to appear when pH of the dye solution was around 4.4. Precisely speaking, however, there is a difference between the form of $F \sim A$ curve for the region of pH 3.5∼5.5 and that for the rest of pH region. In the former region, as illustrated in Fig. 3 (b) for example, dye not only expanded the monolayer remarkably but also prevented the subsequent lowering of the initial surface pressure. In contrast to this, the effect of surface pressure lowering was evident in the latter region as illustrated in Fig. 3 (c).

Ethyl Stearate.—Effect of substrate pH upon A_0 for the monolayer spread on water is shown by curve D in Fig. 4. Apparently no change in the $F\sim A$ curve was observed throughout pH 3~8. When the monolayer was spread on a substrate water of pH 2.3 and compressed to $F>$ 15 dyn./cm., we usually observed an instantaneous rise and subsequent fall of surface pressure which reached finally an equilibrium value. Such a tendency was most remarkable when the film was compressed fifteen minutes after initial spreading. Any time of elapse longer or shorter than this proved to result in less exaggeration. These phenomena may be due to the hydrolysis of the ester, which was reported for the same film spread on an alkaline substrate[9], and to the change in surface pressure effected by ethanol thereby formed at and ejected from the surface phase. Actually, standing of the monolayer for sixty minutes caused an $F\sim A$ relationship identical with that for stearic acid.

The effect of added dye upon A_0 of the monolayer is shown by curve C in Fig. 4 in which, however, A_0 at pH 1.9 accompanies an inevitable error due to the hydrolysis mentioned above. Even if we took account of this ambiguity, it would be clear that the maximum expansion was observed at pH 3.0.

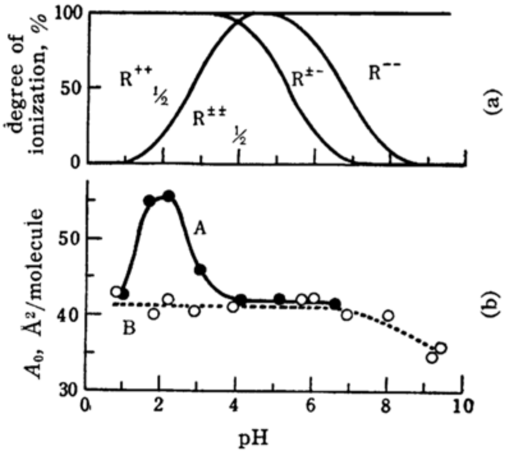

Fig. 5. (a) Effect of pH on the degree of ionization of Congo red. (b) Effect of pH on A_0 for the monolayer of cholesterol spread on the substrate, (A) containing Congo red and (B) lacking it.

Cholesterol.—Curve B in Fig. 5 (b) shows pH dependence of A_0 for the monolayer of cholesterol spread on the surface of water. In conformity with the results appearing in the other reports[10], the monolayer proved to be of low compressibility and of large area when it was spread on distilled water pH of which was less than 7. In more alkaline region, however, A_0 decreased slighty with increasing pH, while the compressibility was scarcely affected at all by the change of the acidity throughout all pH region investigated. This might be ascribed to the dissolution of cholesterol, as predicted by the experimental results on surface evaporation[11].

For the aqueous substrate containing dye, pH dependence of A_0 is shown by the curve A in Fig. 5 (b). Maximum expansion was observed at pH 2 where A_0 was larger by ca. 15 Å^2/molecule than that for the control experiment.

Discussion

In Fig. 5 (a) are shown the ionization curves for each ionizable groups in the molecule of Congo red. They are obtained from respective values of the ionization constants which have been reported in Part I[12] of this series. It should be emphasized that the calculations for the dissociation constants were based on the treatment of the dye as a high-polymer electrolyte. When we compare these curves with $A_0\sim$pH curves shown in Figs. 2 and 4, it can be seen that the interaction of Congo red with various amphipathic compounds is favored in the isoelectric region, irrespective of the types of their polar heads. In Part II[1] of this series, it has been presumed that the conditions for mutual cohesion of dye molecules among themselves would play simultaneously an important rôle in its interation with film materials. Actually the film materials seem to interact with the colloidal aggregates of dye formed in the solution. Remarkable changes both in the ultrasonic velocity in bulk[4] and in the rheological property of the surface[6] of the solution

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9) A. E. Alexander and J. H. Schulman, *Proc. Roy. Soc.*, **A161**, 115 (1937).

10) e. g., J. H. Schulman and E. K. Rideal, *Proc. Roy. Soc.*, **B122**, 29 (1937), etc.

11) E. Sebba and H. V. A. Briscoe, *J. Chem. Soc.*, **1940**, 114.

12) M. Muramatsu, This Bulletin, **31**, 864 (1958).

13) A. Inaba, unpublished.

TABLE I

EFFECT OF CONGO RED UPON A_0 OF VARIOUS MONOLAYERS

Film substance		$\mathrm{pH}_{\max.}$	Area, Å²/molecule			Surface polarity	
Name	Mol. wt.		$(A_0)_{H_2O}$	$(A_0)_{\text{dye}}$	ΔA_0	ΔV, mV	$(A_0)_{H_2O}\cdot\Delta V$ Å²·mV/molecule
Cholesterol	386	2.0	41	56	15	ca. 400[10]	16.1×10^3
Cetyl alcohol	242	3.0	20	40	20	400[14]	8.0×〃
Ethyl stearate	312	4.0	25	50	25	370[9]	9.3×〃
Ethyl *n*-hexadecyl ether	270	4.4	25	55	30	——	——
Octadecylamine	269	5.5	28	55	27	710[15]	19.9×〃

of Congo red being in the same pH range have also been attributed to the formation of colloidal aggregates of dye. Therefore the present results had better be discussed along this line. Additional support for this suggestion was obtained by Matuura[2] who has reported an expanded film of stearic acid spread on a solution of Congo red, pH of which was ca. 3. Inaba[13] has observed that a surface of paraffin was wetted thoroughly by the same solution. All these phenomena emphasize the importance of the rôle of van der Waals' attraction in the interaction. For the other region of pH, ionic repulsion due to the same sign of the charge of dye molecules would suppress the tendency of forming colloidal aggregates in which the molecules of dye interlink each other by the molecular forces other than ionic.

In Table I is summarized the effect of added Congo red on A_0 for various monolayers, spread on the substrates, pH values of which are optimum corresponding to the largest expansion. In this table $(A_0)_{H_2O}$ and $(A_0)_{\text{dye}}$ represent values of A_0 on pure water and dye solution respectively. Further, the data on surface potential, ΔV, of the monolayer on water are quoted from other literatures. As is seen in the table the amount of increase, ΔA_0, in the area due to the addition of dye seems to depend on the quantity, $(A_0)_{H_2O}\cdot\Delta V$, which may be expressed as the surface polarity, rather than the molecular weight of the monolayer substance. Noticeable deviation from this is observed only for cholesterol which differs in its molecular structure from the other substances. This suggests the distinct contribution to $A\Delta_0$ of the dipolar attraction, in addition to van der Waals' force. It was pointed out[16] that dipolar attraction acting between each other of dye molecules of zwitterion type enhanced the possibility of forming colloidal aggregates of the dye in aqueous medium. A similar explanation was also made for the mechanism of dyeing of fibers[17].

Let us draw attention to the conspicuous nature of the monolayer of ethyl *n*-hexadecyl ether spread on distilled water. As far as the author is aware, the nature of this film has not been studied before. In the case of the monolayer of octadecyl methyl ether, some investigators[18] reported an intramolar rotation of $-\mathrm{O}-\mathrm{CH}_3$ bond when the film was compressed to some extent. There the methyl group was considered to orientate itself toward the bulk of substrate, so that the process resulted in a decrease of resultant dipole. It seems to be probable, however, that such a distortion is accompanied by a strong resistance when the end group is ethyl radical as was the case in the present experiment. In Fig. 3 (a) the instantaneous rise and subsequent lowering in surface pressure due to the compression would be an evidence for this effect. In connection with this, it is of interest to note that such an effect disappears whenever Congo red is added to the substrate of pH 3.5∼5.5 where the largest expansion of the film is observed. Intramolecular rotation is evidently hindered by Congo red with which the film substance interacts. It should be further noticed that the molecules of dye are almost in the form of $\mathrm{R}^{\pm\pm}{}_{1/2}$, as seen in Fig. 5 (a). This increases the possibility of the dipolar attraction between dye and ethyl *n*-hexadecyl ether, if we take account of the hindrance toward reorientation of ethyl group accompanying the change of resultant dipole moment. Presumably both van der Waals' and dipolar force are

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

[15] J. Glazer and M. Z. Dogan, ibid., **49**, 448 (1953).

[16] W. Pauli and F. Lang, *Monatsh.* **67**, 159 (1936).

[17] e. g., E. L. Valko, "Colloid Chemistry", edited by J. Alexander, Vol. 6, Reinhold Publ. Corp., New York, 1946, p. 594.

[18] J. H Schulman and A. H. Hughes, *Proc. Roy. Soc.*, **A138**, 430 (1932); A. E. Alexander, *Trans. Faraday Soc.*, **37**, 426 (1941).

chiefly responsible for the expansion of the monolayer.

Similar kinds of attractive force can also be mentioned to explain the mechanism of the interaction of dye with cetyl alcohol or ethyl stearate. Optimum pH values for the maximum expansion of these films lie in a range of 3∼4 where dye molecules are also in the form of zwitterion. On the other hand it is of interest that ΔA_0 for cetyl alcohol is less than that for ethyl *n*-hexadecyl ether. This comes from a decreasing van der Waals' force corresponding to ethyl group. Presumably such a force overwhelms the attraction due to hydrogen bond through the hydroxyl radical of alcohol even if it would be possible. Thus the present result suggests the importance of the rôle of van der Waals' force rather than hydrogen bond in the dyeing process of fibers by the direct dye[17].

Differing from such non-ionic compounds as mentioned above, we may suggest a possibility of ionic interaction in addition to hydrogen bonding, dipole-dipole and van der Waals' force to explain the mechanism of the interaction between Congo red and octadecylamine. The largest expansion of this film is observed when it is spread on the solution of dye of pH 5.5, where a considerable amount of dye molecules are partly ionized, while the molecules of octadecylamine in the film are considered to be perfectly ionized[15]. Therefore we should take account of the additional contribution of ion-ion attraction between dye and octadecylamine to explain the expansion of the monolayer. This is similar to the fact which the present author has pointed out in the case of interaction of basic dye with stearic acid[1] and acid dye with octadecylamine[3]. In connection with this it may be of some values to discuss the effect of dissolved Congo red upon mono- and multilayers of stearic acid and barium stearate. Matuura[2] reported an expansion of the monolayer of stearic acid spread on the dye solution of pH 3. The present author has reported a remarkable increase in thickness of the built-up film of stearic acid and decrease in thickness in the case of barium stearate, when each of them soaks into the dye solution of pH 3.6[1]. In this case both increase have been attributed to the strong interaction. The dye molecules in such a solution are considered to be charged somewhat positively, as shown in Fig. 5 (a). However, no negative charge seems to exist in the molecules of stearic acid in the monolayer spread on pH <6[15,19]. It is probable that the same arguments can also be applied to the case of the multilayers of the same substance. Therefore it would be reasonable to ignore the ion-ion attraction between stearic acid and dye. On the other hand we can not ignore the ion-dipole attraction arising from the positive charge of dye, when dye molecules are allowed to orientate and bind themselves to stearic acid.

Various kinds of behavior of interaction of cholesterol with dye are somewhat erratic. Apparently they are similar to the case of stearic acid rather than cetyl alcohol. This may come from the molecular structure of sterol back-bone being hydrophobic. We can only say at present that the explanation is similar to the case of stearic acid. The detailed discussion may be a future problem.

Summary

Effect of dissolved Congo red upon the monolayers of octadecylamine, cetyl alcohol, ethyl *n*-hexadecyl ether, ethyl stearate and cholesterol spread on the substrate containing the dye has been studied, under varying pH of the solution. It has been observed generally that all monolayers expanded when they were spread on aqueous solution, the pH of which was in such a region that the molecules of dye were almost in zwitterion form. Dipolar and van der Waals' attraction were tentatively postulated to explain the nature of the cohesive force by which the molecules of dye were bond together so that the colloidal aggregates were formed in the solution. The expansion of the monolayer can be accounted for by the binding of the aggregate to film materials. This explanation could successfully be applied to the films of such nonionic substance as cetyl alcohol, ethyl *n*-hexadecyl ether and ethyl stearate.

The largest expansion of the monolayer of octadecylamine was observed when the substrate containing dye showed acidity so that the molecules of dye were partly of negative charge while those of octadecylamine were of positive charge. In this case we had better take account of the possibility of ion-ion attraction between octadecylamine and dye, in addition to the

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[19] E. Havinga and M. der Hertog-Polak, *Rec. trav. chim.*, **71**, 64 (1952); E. Havinga, ibid., **71**, 72 (1952).

forces which appeared in the cases of nonionic substances.

The author wishes to express his hearty thanks to Professor T. Sasaki for his kind guidance and encouragement in this work. He is also indebted to Professor R. Matuura of Kyūshū University for his helpful discussion, to Professor H. Saikachi of the same university for the elemental analysis of the samples, and to Mr. H. Ōshima of Fukuoka Gakugei University for his assistance on the synthesis and purification of amphipathic compounds. The cost of this research has been defrayed from the Scientific Research Expenditure of the Ministry of Education.

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