Studies on the Interaction of Surface Films with Solute in Solution. III. Effect of Dissolved Dyes upon the Monolayer of Octadecylamine

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(Received June 24, 1958)

In a preceding paper[1] the action of dissolved dye on the built-up film of stearic acid and barium stearate was reported. There it has been shown that the maximum amount of solute taken up by the film was observed for dye solution in a specific pH range where the remarkable change of dissolved state in bulk[2], as well as the change of rheological properties in surface[3], was observed for dye solution. Various kinds of behavior in such a type of interaction could be explained chiefly by the balance of the attractive and repulsive forces acting between film materials and dyes, when we take account of their ionized as well as dissolved state. This was in general accord with the experimental results on the effect of the aqueous dye solutions not only upon the nature of the monolayer of stearic acid[4] but also upon the wettability of its solid surface[5].

In order to check the validity of such reasoning it has been attempted in the present work to investigate the interaction between several dyes in aqueous solution and octadecylamine monolayer spread on it.

Experimental

Of the samples of dyes used in the preceding work[1], chrysoidine, crystal violet, scarlet red, phloxine (C. I. No. 778*), trypan red (C. I. No. 438), and benzoazurin G (C. I. No. 502) were chosen also for the present experiment, because of the typical behavior of each in the interaction with stearic acid. Each of these dyes was dissolved in water and a stock solution of 10^{-2}mol./l. was made, which was diluted to 10^{-4}mol./l. prior to use as a substrate solution of the monolayer. To minimize the disturbing effects of coexisting ions for dye, pH of the solution was controlled simply by the solutions of hydrochloric acid and ammonia, both of which are twice distilled in an all-ground glass apparatus. The hydrogen ion concentration of this solution was determined using Beckman's glass electrode.

The octadecylamine was the same as that used in a former experiment[6]. It was spread from benzene solution onto the aqueous solution of dye. As we actually used bicarbonate of amine, calculation of the cross-sectional area, A, per molecule was based on the nitrogen content of material which was determined for original samples by micro Dumas method. Surface pressure, F, was measured by means of the modified hanging-plate method[7].

All experiments were carried out at room temperature.

Results

Effect of pH of Substrate Water upon the Monolayer of Amine Spread on It.— It was pointed out by the present author[6] that poor reproducibility was observed for the $F\sim A$ curves of the monolayers of octadecylamine when they were spread on the surface of distilled water. This could be ascribed chiefly, in agreement with the opinion of the other investigators[8,9], to differences in the content of carbon dioxide in water, aging of the film, the velocity of compression, etc. Such an effect was observed also in the present experiment in which pH of substrate water was widely changed over the range of 1 to 10. But $F\sim A$ curve of the monolayer fluctuated only within the hatched zone shown in Fig. 1, though the solution was rendered sufficiently acidic.

In Fig. 2 open circles represent the area, A_0, of octadecylamine molecule at $F=2$ dyn./cm. for varying substrate pH. If we take account of the ambiguity mentioned above, we could not express the $A_0\sim$pH relationship more precisely than as a hatched zone shown in the figure. In

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[1] M. Muramatsu, This Bulletin, **31**, 871 (1958).
[2] T. Sasaki and T. Yasunaga, to be published.
[3] H. Kimizuka, This Bulletin, **26**, 33 (1953).
[4] R. Matuura, ibid., **24**, 282 (1951).
[5] A. Inaba, unpublished work.
* Abbreviation according to "Color Index" edited by F. M. Rowe, First edition, (1924).

[6] T. Sasaki and M. Muramatsu, This Bulletin, **26**, 96 (1953).
[7] T. Sasaki, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **62**, 796 (1941).
[8] J. Marsden and J. H. Schulman, *Trans. Faraday Soc.*, **34**, 748 (1938).
[9] W. C. Bigelow, E. Glass and W. A. Zisman, *J. Colloid Sci.*, **2**, 563 (1947); E. J. Hoffman, G. E. Boyd and A. W. Ralston, *J. Am. Chem. Soc.*, **64**, 498 (1942).

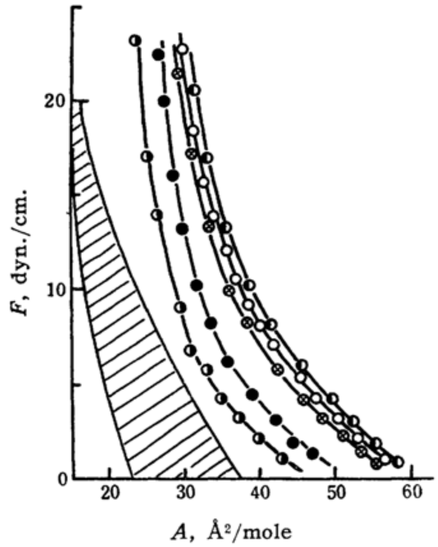

Fig. 1. $F \sim A$ curves for monolayers of octadecylamine spread on aqueous solution of crystal violet under varying substrate pH: hatched zone expresses the limit of fluctuation of $F \sim A$ curves in the control (without dye) experiments for varying substrate pH.

◑ pH 2.9
● 5.5
⊗ 6.1
◐ 7.1
○ 9.8

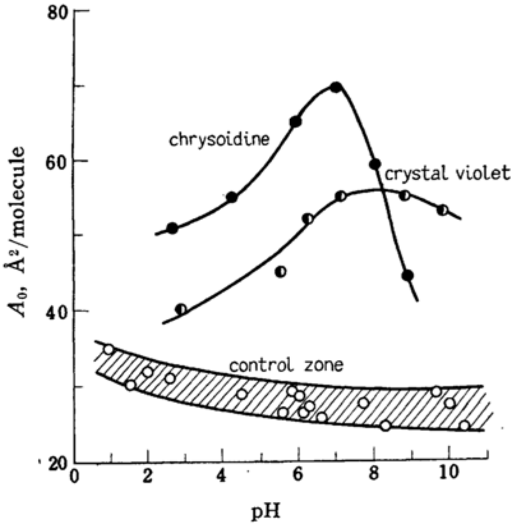

Fig. 2. Effect of substrate pH upon A_0 of octadecylamine spread on aqueous solution of basic dye and on distilled water (control experiment).

general the monolayer showed a tendency of expansion on an acidic substrate. This made a contrast with the case of stearic acid spread on an alkaline substrate[10] and, as assumed by the other authors[8,10], might be attributed to the ionic repulsion due to the ionization of the monolayer.

Monolayer of Amine on the Solution of Basic Dye.—In Fig. 1 are shown the $F \sim A$ curves for the monolayers of octadecylamine spread on the solutions of crystal violet of varying acidity. It is seen in the figure that the $F \sim A$ curve shifts gradually towards right, showing the increasing expansion of the monolayer with increasing pH of substrate. Such an effect of pH upon the nature of the monolayer is reproduced in Fig. 2, in which pH dependence of A_0 of octadecylamine is shown for the cases of crystal violet and chrysoidine. For both dyes we observed characteristic pH ranges for maximum expansion of the monolayer.

Monolayer of Amine on the Solution of Acid Dye.—In the presence of phloxine in the substrate, we observed a marked effect of pH upon $F—A$ curve for the monolayer of octadecylamine, as illustrated in Fig. 3. It can be seen in the figure that the remarkable expansion and increase in compressibility of the film were observed when pH of the substrate was

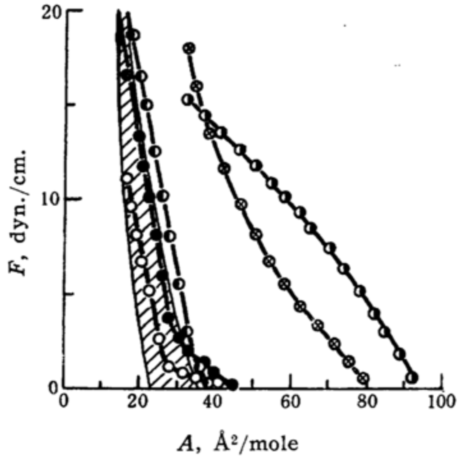

Fig. 3. $F \sim A$ curves for monolayers of octadecylamine spread on aqueous solutions of phloxine, under varying pH: hatched zone expresses the limit of fluctuation of $F \sim A$ curves for the control experiments.

◐ pH 1.7
◑ 2.9
⊗ 3.5
● 4.1
○ 7.9

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[10] N. K. Adam, "The Physics and Chemistry of Surfaces", Oxford University Press, London, (1937), p. 71.

around 3~3.5. In the case of scarlet red, however, little change was observed in the cross-sectional area of amine even if pH of the substrate solution was small. The compressibility of the monolayer of amine was not affected by the presence of this dye. Fig. 4 shows the A_0~pH relation for these dyes, together with for trypan red which made the monolayer expand at pH less than 4 but did not affect its compressibility throughout the whole pH range investigated. It has been pointed out in a preceding paper[1] that trypan red, in spite of its molecule containing five sulfonic and two amino groups, should be regarded rather as an acid dye from the viewpoint of pH dependence of the dye solution.

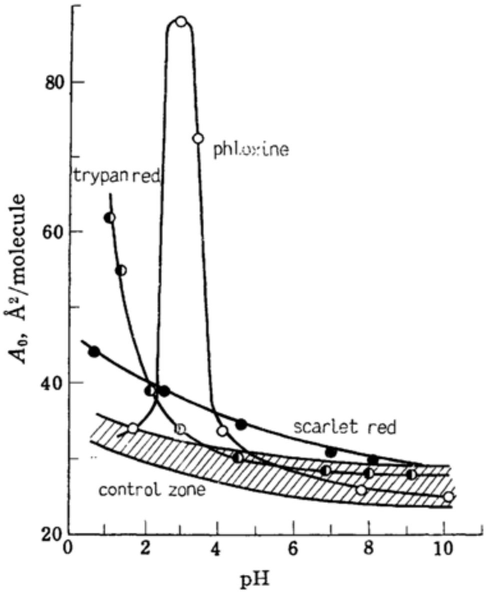

Fig. 4. Effect of substrate pH upon A_0 of octadecylamine on aqueous solution of acid dye.

A somewhat different feature was observed in the case of benzoazurin G. When a fresh surface of a solution of pH 1.7 was compressed by barriers, we recorded a remarkable increase in surface pressure, F, owing to its adsorption to the surface of its own. Though the value of F fluctuated considerably for a given area, σ, of the surface bounded by two barriers, $F\sim\sigma$ curve lies always in the zone A in Fig. 5. A more exaggerated feature of $F\sim\sigma$ relationship was observed for the monolayer of octadecylamine spread on this solution. In Fig. 5, the hatched zone B and C express the limit of fluctuation in $F\sim\sigma$ relationship for the monolayer of 1.29×10^{16} molecules of octadecylamine spread on a substrate of the same pH, containing or lacking benzoazurin G. As is seen in the figure, behavior in the low pressure region exhibited a typical example of the profound effect of benzoazurin G upon the monolayer of amine spread on it. Now, let us compare the surface area, σ_0, at $F=2$ dyn./cm. for

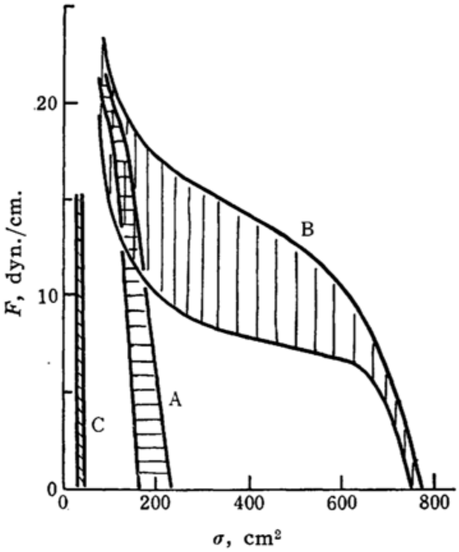

Fig. 5. Limit of fluctuation of $F\sim\sigma$ curves: (A) for the surface of solution of benzoazurin G, (B) for the monolayer of 1.29×10^{16} molecules of octadecylamine spread on the substrate containing and (C) lacking the dye. Substrate pH 1.7.

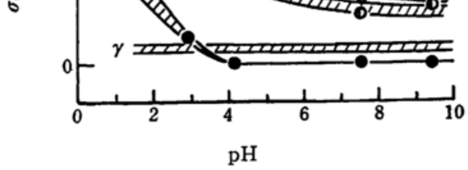

Fig. 6. pH dependence of σ_0 and of $\Delta\sigma_0$ at $F=2$ dyn./cm.: zone α, pH dependence of σ_0 for adsorbed dye film of its own; β and γ, for the monolayer of 1.29×10^{16} molecules of octadecylamine spread on the substrate containing or lacking, respectively, this dye.

zone B with those for A and C. A similar procedure was applied also for the experiment, varying pH of substrate. The results are illustrated in Fig. 6 in which the velues of σ_0's are plotted against pH. It can be seen that the amounts of σ_0 for zone β (amine+dye) are generally far greater than the sum of those for zone α (amine alone) and γ (dye alone). Such behavior is favorably expessed in terms of the deviation, $\Delta\sigma_0$, from the additivity in σ_0 of the monolayers of amine and the adsorbed dye film of its own and it is plotted against substrate pH in the same figure. It is surprising that the amount of $\Delta\sigma_0$ for around pH 1.7 was evaluated to be 500 cm.^{2}, the figure corresponding to 380 Å^2/molecule of amine. Again, we can see a similar effect as observed in the case of scarlet red or trypan red.

Discussion

It would be reasonable to assume that in the present results an expansion of the monolayer of octadecylamine spread on an aqueous solution of dye comes from an interaction between the monolayer and the dye. Then, the more profoundly the interaction arises between octadecylamine and a certain dye, the more remarkably the monolayer would be expected to expand, apart from the quantitative discussion on the amount of expansion.

Adam$^{11)}$ observed an expansion of the monolayer of octadecylamine spread on a solution of simple organic acid and explained the phenomenon by ion—ion attraction between the amine and the acid. Such a consideration was verified by means of the mono- and multilayer techniques applied for the interaction between octadecylamine in film state and such simple acids as oxalic, malonic, succinic and adipic acid in an aqueous solution$^{6)}$. It has been shown$^{12)}$, however, that we should also take account of an additional contribution of van der Waals' attraction to the expansion of monolayer of amine, which interacts with organic compound of large molecular weight such as thapsic acid or *pp'*-dihydroxydibenzyl in an aqueous substrate. Because of the dye molecule being larger than these compounds, the present results can hardly be explained at all unless we take account of various forces of interaction. Actually, the behavior of basic dye in alkaline region, as shown in Fig. 2, can not be explained by ion—ion attraction. In this case, ionic repulsions between dye molecules themselves and between the molecules of amine and the dye are considered to decrease with increasing pH of the substrate. Therefore increase of substrate pH may cause an increasing tendency of dye to be bound to the monolayer of amine by the attraction different from ion—ion interaction. This would be valid for the region of pH not large enough to form an aggregate of dye, due to the perfect disappearance of the repulsion. Such a consideration has also been made to explain the action of dissolved acid dye upon the mono-$^{4)}$ or multilayer$^{1)}$ of stearic acid.

It has been pointed out in a preceding paper$^{1)}$ that the conditions favorable for the formation of aggregate of dye are generally in accord with those for the enhancement of the surface interaction. Chrysoidine makes the monolayer of amine expand most remarkably, when it was dissolved in the substrate of pH 7 in which the molecules of dye have little ionic charge, as expected from its pK values, i. e., $pK_1=3.32$ and $pK_2=5.21^{13)}$. In contrast with this, the maximum amount of aluminon, one of the acid dyes, sorbed on the built-up film of stearic acid was observed when pH of the dye solution was around 2~3 where we can expect the effect of ionic repulsion due to the remaining charge$^{1)}$. The difference in the molecular weight between chrysoidine (M. W. =250) and aluminon (M. W.=480) may be responsible for the difference in the contribution of van der Waals' attraction to the interaction between dye molecules themselves by which the difference in easiness of aggregation can also be accounted for. However, it should be noticed that the molecules of amine in the monolayer were considered to be in perfectly ionized state as presumed from the experimental data of surface potential$^{14)}$. In this case, therefore, we can expect the possibility of an additional contribution of ion—dipole attraction to the expansion of the monolayer.

A similar explanation can also be made for the effect of acid dye upon A_0 or alternatively $\Delta\sigma_0$ of octadecylamine which is shown in Fig. 4 or 6, respectively; namely, decreasing charge of dye with

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11) N. K. Adam, *Proc. Roy. Soc.*, **A126**, 526 (1930).

12) E. G. Cockbain and J. H. Schulman, *Trans. Faraday Soc.*, **35**, 716 (1939).

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

14) J. Glazer and M. Z. Dogan, *Trans. Faraday Soc.*, **49**, 448 (1953).

decreasing pH of the substrate will cause the formation of aggregate of dye with which octadecylamine interacts. If we confine ourselves to this point of view, the expansion of a monolayer may be accounted for by such attractions as dipolar and van der Waals' forces. However, it has been pointed out by means of mono-[4] and multilayer[1] technique, that the effect of basic dye dissolved in alkaline medium upon the surface film of stearic acid was due to the strong interaction being of complex nature, involving not only dipolar and van der Waals' force but also ionic attraction. For the present results, therefore, we had better take into consideration ionic attraction in addition to dipolar or van der Waals' force. At least we can find no objection to such a reasoning for the expansion of octadecylamine monolayer by scarlet red, trypan red and benzoazurin G. Since small pK values are expected for sulfonic groups in the molecules of these dyes[15], an electrostatic attraction may contribute throughout a wide range of substrate pH to the expansion of the monolayer of octadecylamine, the pK of which is reported to be 8.5[14].

It has been shown[2,3] that acid dye formed colloidal aggregates when it was dissolved in aqueous solution of pH being slightly larger than that for distinct precipitation. A typical example was observed in the case of phloxine dissolved in aqueous medium. Actually we observed faint turbidity in this solution when pH was less than 3. Thus the remarkable expansion of the monolayer on substrate of pH 3 can be accounted for by the interaction between the molecules of octadecylamine and the colloidal aggregates of dye. In connection with this, it is interesting to note that the more the monolayer of octadecylamine expands, the more it becomes compressible. This behavior is shown in Fig. 3. The same type of $F \sim A$ curve was observed also for the interaction between stearic acid in the monolayer and cobalt ion in the substrate[16]. This has been explained by the ionized monolayer of stearic acid with which the colloidal aggregate of cobalt ion interacts. Studies on the dissolved state of cobalt ion[17] seemed to support this explanation.

Summary

The interaction between octadecylamine in monolayer and various dyes in aqueous substrate under varying pH was studied. Such a basic dye as chrysodine or crystal violet remarkably expanded the monolayer when pH of the solution was in a certain range on alkaline side. This has been attributed to the interactions between the molecules of dye themselves and that between dye and octadecylamine. Thus, it is mainly dipolar and van der Waals' attraction, which was considered to be overshadowed by ionic repulsion when substrate pH was in the other region. Additional possibility of ion-dipole attraction due to the remaining charge of the monolayer was discussed in connection with the ionizations of octadecylamine and basic dyes.

In contrast with this, the monolayer expanded remarkably when it was spread on an acidic solution of acid dye. The behavior could be accounted for by the sum of ionic, dipolar and van der Waals' attraction. The possibility of the formation of colloidal aggregate of dye with which octadecylamine interacts has been discussed, in connection with the effect of metal ion in the substrate upon the monolayer of stearic acid.

The author wishes to express his hearty thanks to Professor T. Sasaki for his kind guidance and encouragement throughout this research. His thanks are also due to the Ministry of Education for the Scientific Research Expenditure.

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[15] N. Andō, "Senryō Kōshitsugaku (Chemistry of Dye Stuffs in Japanese)," Shōkabō, Tokyo, (1948), p. 44.

[16] T. Sasaki and M. Muramatsu, This Bulletin, **29**, 35 (1956).

[17] R. Matuura and H. Kimizuka, This Bulletin, **28**, 668 (1955); T. Sasaki and K. Izawa, unpublished work.