Studies on the Interaction of Surface Films with Solute in Solution. II. Sorption of Dye on the Built-up Film of Stearic Acid and Barium Stearate

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Knowledge of the surface interaction between amphipathic compounds in the film state and dyes in aqueous solutions contributes considerably not only to the understanding of the mechanism of the dying processes of fiber, the solubilization of dye, the physiological action of bile and other living dye, etc., but also to the knowledge of the substance in its two-dimensional state. From this standpoint the effect of aqueous dye solution on the monolayer of stearic acid(1), cetyl acetate, synthetic fibers, and other polar-nonpolar compounds(2) were studied. Sobotka(3), studying the adsorption of physiologically active substance including porphyrin derivatives upon the built-up film of stearic acid and protein, pointed out an important role of molecular structure of adsorbate in increasing the film thickness and affecting the wettability. It should be further noticed in the case of dye substance that such a type of interaction may be affected

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1) R. Matuura, This Bulletin, **24**, 282 (1951).

2) M. M. Allingham, C. H. Giles and E. L. Neustädter, *Discussion Faraday Soc.*, No. **16**, 92 (194).

3) Sobotka, "Recent Advances in Surface Chemistry and Chemical Physics", Science Press Printing Co., Lancaster, (1939), p. 54.

considerably by the nature of dye ions, especially by the balance of anionic and cationic charges, as was pointed out for the interaction of a number of dyes and anionic and cationic detergents in an aqueous medium[4].

In connection with these, the present author intends to study the action of dye ion upon the built-up film of stearic acid and related substances, under varying pH of aqueous dye solution. It may be expected furthermore that such a study may contribute to the knowledge of surface interaction between metal ion and fatty acid, which was reported by Sasaki and Matuura[5], Schulman et al.[6], and Sasaki and the present author[7,8].

Experimental

Reagent.—The stearic acid was the same as that used in a preceding experiment[7]. The dyes were all Takeda's or Merck's reagent grade, except for benzoazurin G (C. I. No. 502)* and benzopurpurin 4B which were kindly supplied by Mr. M. Fujimoto of Mitsubishi Kasei Co. Of the dyes used Congo red, methyl orange and crystal violet were thoroughly purified by repeated recrystallization[9]. Other dyes were used without any special purification, since it was confirmed in the preliminary experiments that the successive purification of Congo red and crystal violet resulted in little change in the sorbed amounts of dyes.

Method.—Monolayer of stearic acid spread on a substrate of pH 4 was successively transferred by means of Langmuir-Blodgett technique[10] onto a highly polished slide of stainless steel, so as to obtain a base echelon. Then a half part of it was immersed for thirty seconds into an aqueous solution of the dye 10^{-4} mol./l. varying in its pH, while the other half was immersed into a control solution of the same pH without dye. The surface of dye or control solution was swept by two barriers prior to immersion. After washing the film with distilled water the changes in thickness of both parts of the echelon were measured by means of the simplified optical method[11], assuming the refractive index of dye to be the same as that of the base material. Calculation was based on the fact that spacing and refractive index of stearic acid in the multilayer were 22.9 Å and 1.482, respectively[10]. The difference, Δ, in changes of thickness thus calculated between two halves of the slide was taken for the sorbed amount. In the case of the solution of crystal violet, night blue (C. I. No. 731), benzoazurin G, or phloxine (C. I. No. 778), each of them forming an elastic film, the down- and up-trip of slide sometimes resulted in the building-up of an adsorbed layer at the air-solution interface. For such a dye, therefore, all experiments were carried out for different times of immersion during thirty seconds, against which the amount of Δ was plotted. A typical example is shown in Fig. 1. True values of the sorbed amount were assumed to be obtained by extrapolation of the curves to zero time of immersion.

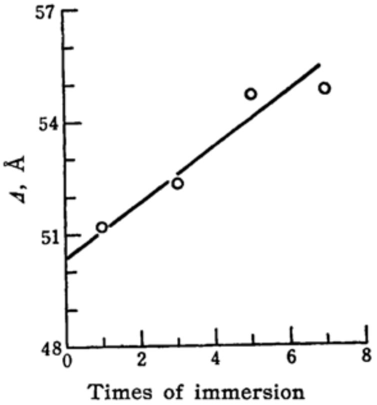

Fig. 1. Effect of immersion upon the apparent amount, Δ, of sorption of crystal violet: pH 6.5.

Experiments were also carried out using the echelon of barium stearate, instead of stearic acid, for the interaction with Congo red and crystal violet. In this case the built-up film was obtained by transferring the monolayer of stearic acid spread on an aqueous substrate containing barium chloride onto the slide. Spacing and refractive index were assumed to be 24.4 Å and 1.462[10], respectively, for this case. All experiments were carried out for 10^{-4} mol./l. of dye solutions, pH of which was varied merely using redistilled hydrochloric acid and aqueous ammonia solution and its value was determined using Beckman's glass electrode.

Results

Acid Dyes.—Fig. 2 shows the effects of pH of dye solution on the amount of aluminon (triammonium aurintricarboxylate) sorbed on the built-up film of stearic acid and on the degree of ionization of three carboxyl groups in the dye molecule. The latter values were calculated using $pK_1 \leq 2$, $pK_2 = 4.80$ and $pK_3 = 7.22$ for each

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4) G. S. Hartley, *Trans. Faraday Soc.*, **30**, 444 (1934).

5) T. Sasaki and R. Matuura, This Bulletin, **24**, 274 (1951); R. Matuura, ibid., **24**, 277 (1951).

6) J. H. Schulman et al., *Trans. Faraday Soc.*, **46**, 475 (1950); **50**, 1128, 1131, 1139 (1954); *Discussion Faraday Soc.*, No. **16**, 158 (1954).

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

8) T. Sasaki and M. Muramatsu, ibid., **29**, 35 (1956).

9) C. Robinson and H. A. T. Mills, *Proc. Roy Soc.*, **A131**, 576 (1931).

* Abbreviation according to "Color Index", edited by F. M. Rowe, Society of Dyers and Colourisis, Bradford, First edition, (1924).

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

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

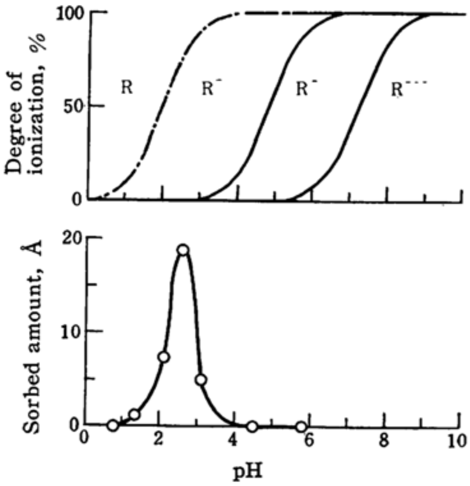

Fig. 2. Effect of pH on the degree of ionization of aluminon and on its amount sorbed on the built-up film of stearic acid.

Semi-dotted curve represents the lower limit of degree of ionization for a given pH, with regard to the reaction, $R \rightleftarrows R^- + H^+$.

groups[12]. They decreased with decreasing pH of the solution, while a maximum sorption was observed at pH from 2 to 3, where the majority of dye molecules were of singly ionized carboxylic acid.

The pH dependence of the amount of phloxine, scarlet red and benzoazurin G sorbed is shown in Fig. 3. All these dyes showed a large amount of sorption in an acidic medium, though there exist some differences in details. Phloxine, one of the triphenylmethane dyes having one carboxyl and one phenolic group, showed a maximum amount of sorption in the range of pH from 3 to 4, where we usually observed a faint turbidity in the bulk and a remarkable rigidity in the surface of the dye solution. Precipitation of dye was evident when pH decreased beyond this range. In the case of benzoazurin G, neither the maximum point of sorption nor the precipitation of dye was observed throughout pH range investigated. The amount sorbed on the film proved to increase with decreasing pH for benzoazurin G. Scarlet red, having both one phenolic and one sulfonic group in the molecule corresponding to a split-in-half structure of benzoazurin G, showed a small amount of sorption at pH less than 3.

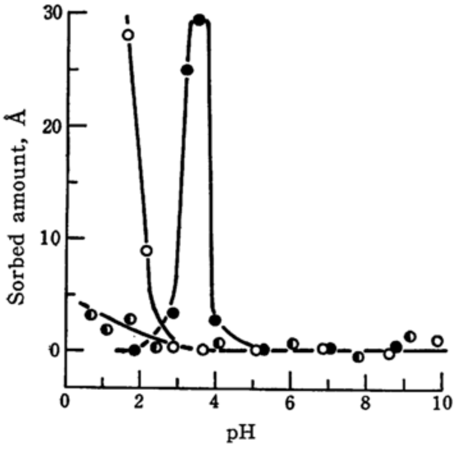

Fig. 3. pH vs. sorbed amount of phloxine (●), scarlet red (◐) and benzoazurin G (○).

Basic Dyes.—In Fig. 4 full curves represent the pH dependence of the amount of crystal violet and night blue sorbed on the built-up film of stearic acid. Maximum sorption was observed in the range of pH from 6 to 8 for both dyes where we often experienced a remarkable wetting of a paraffined wall of the tray by a heavily foaming solution of dye. In the same figure the dotted curve shows the effect of pH upon the amount of crystal violet sorbed on the built-up film of barium stearate. When we compare this curve with the corresponding full curve, it is evident that the use of barium stearate instead of stearic acid resulted in a remarkable diminution of interaction with dye.

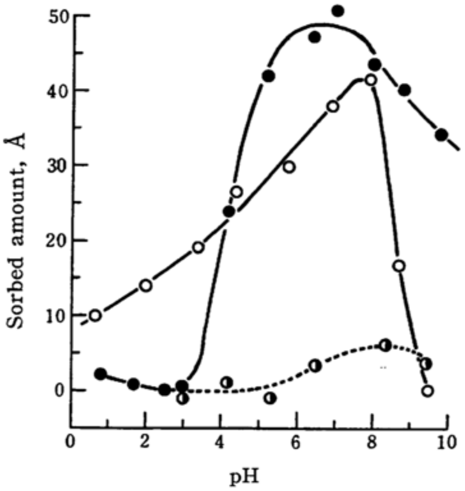

Fig. 4. Effect of pH upon the amount of dye sorbed on the built-up film: ○, night blue on stearic acid; ● crystal violet on stearic acid; ◑, crystal violet on barium stearate.

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

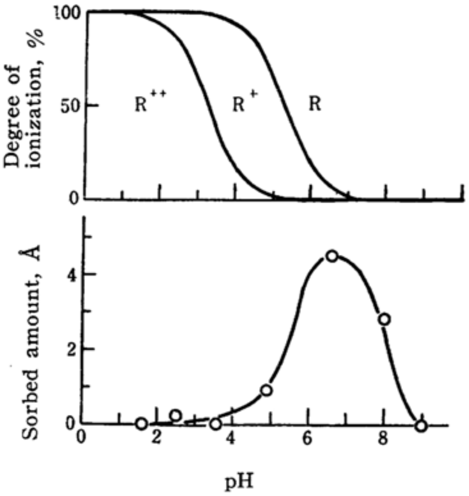

Fig. 5. pH dependence of degree of ionization and of amount of chrysoidine sorbed on the built-up film of stearic acid.

Curves for ionization and sorption of chrysoidine are shown in Fig. 5. The former curves were obtained assuming $pK_1=3.32$ and $pK_2=5.21$[12]. It can be seen in the figure that the maximum of sorption lies in the range of pH from 6 to 7 where one of the amino groups is ionized to the extent of less than 20% while the other is in an entirely non-ionized state.

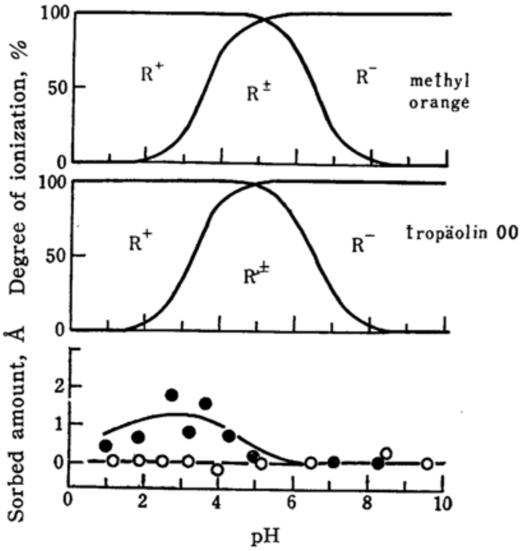

Fig. 6. pH dependence of degree of ionization and of sorbed amount of tropäolin OO (●) and methyl orange (○).

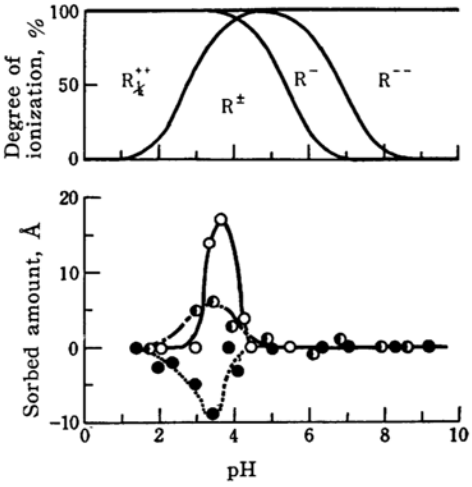

Fig. 7. pH dependence of degree of ionization and of amount of Congo red sorbed on the built-up film of stearic acid (○) and of barium stearate, with (◐) or without (●) the conditioning by the solution of aluminum chloride.

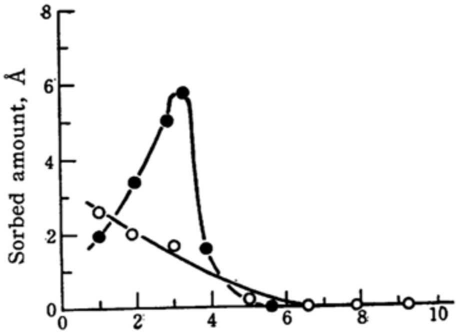

Fig. 8. pH vs. sorbed amount of benzopurpurin 4B (●) and trypan red (○).

Amphoteric Dyes.—In Figs. 6 to 8 are shown the results for the dyes possessing both the acidic and the basic groups. Ionization curves for acid and basic groups in methyl orange, tropäolin OO (C. I. No. 143) and Congo red are calculated from all pK values which have been reported in the preceding paper[12].

Of the dyes investigated, tropäolin OO, Congo red and benzopurpurin 4B showed a maximum of sorption on the film of stearic acid in pH range characteristic of each substance, while no measurable sorption was observed for methyl orange in the pH range from 1 to 10. It can be seen furthermore in Figs. 6 and 7 that pH ranges for maximum sorption of tropäolin OO and Congo red were roughly in agreement with the isoelectric region where the majority of dye molecules were in zwitterion form.

Striking results were obtained for the interaction of Congo red with barium stearate in the film. When the echelon was immersed in an aqueous solution of dye, the pH of which was in the range of 2 to 4, we recorded the decrease in thickness of the echelon, which is shown as a dotted curve in Fig. 7. This might be ascribed to the dissolution of molecules of barium stearate into the solution of dye, which could be seen as the indication of the interaction between the dye and stearate. Similar phenomena have been reported in the case of interaction between serum protein and built-up film of stearic acid[13] or barium stearate[14]. In the other pH range, however, no change was observed in the thickness of the echelon. On the other hand, whenever the film was once conditioned with an aqueous solution of aluminum chloride, the subsequent immersion in the dye solution of pH 2 to 4 always resulted in an increase in the thickness of the film, as is shown by a brokenline in the same figure.

It is seen in Fig. 8 that benzopurpurin 4B has a maximum in pH range for sorption on the built-up film of stearic acid. In contrast with this, trypan red (C. I. No. 438) seemed to be increasingly sorbed with decreasing pH of the solution, this behavior being observed in the case of an acid dye such as benzoazurin G or scarlet red.

Discussion

In our former reports[7], the sorption of metal ion on the built-up film of stearic acid could be explained by the ionic interaction. This has been confirmed[8] by the experiments using radioactive $^{89(90)}$Sr and ^{60}Co. It was pointed out, however, in the case of the monolayer of octadecylamine[15] that the behavior of the surface film depended markedly upon the molecular structure of the solute in aqueous subphase, so that we should take account not only of the ion-ion interaction but also such an interacting force as ion-dipole, dipole-dipole, hydrogen-bonding and/or van der Waals' attraction when the molecule of solute was complicated in structure. From such a point of view, Matuura[1] explained the expansion of the monolayer of stearic acid spread on aqueous solution of dye by an attraction between the dye and the stearic acid, involving ionic and van der Waals' forces.

In the present experiment the action of acid dyes on the built-up film seems to show that van der Waals' attraction plays an important role in the marked adsorption. It would be likely that the decreasing negative charges of both acid dye and stearic acid with decreasing pH of the medium may weaken the repulsive force acting between the dye molecules themselves as well as between the molecules of dyes and stearic acid. On the other hand dipole-dipole and van der Waals' attraction are considered to be largely independent of the pH of the medium. Thus the decreasing repulsion may cause the increasing sorption of dyes on the built-up film. These are the cases with benzoazurin G and scarlet red. The fact that the sorbed amount of the former is much greater than that of the latter, as shown in Fig. 3, may suggest a large contribution of van der Waals' attraction to the amount of sorption, since the latter is of the split-in-half structure compared with the former.

If, however, ionic repulsion is reduced too much, we can expect such a large aggregates that they are removed from the region of the interfacial film. It is therefore probable that the maximum amount of sorption is observed, if the molecular weight of dye is sufficiently great and the pH of the medium is in a range where the molecules of dye retain an appropriate amount of charge. Fig. 2 offers a typical example for such an effect of ionization upon the sorbed amount of aluminon, the molecular weight of which has the order of magnitude of 800. Dye is presumably in a colloidal state when the pH of the solution is in the range of optimum sorption. Such an explanation would also be made for the case of phloxine, the molecular weight of which is of the same order of magnitude as that of aluminon. From the studies on the velocity of ultrasonic wave in the bulk solution[16] and on the rheological properties of the surface[17] of aqueous solution of phloxine, it has been pointed out that dye molecules are presumably in a state of colloidal aggregate at the pH regions beyond which they precipitate. It may be reasonable therefore to ascribe the appearance of maximum

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[13] I. H. Sher and H. Sobotka, *J. Colloid Sci.*, **10**, 125 (1955).

[14] T. Tachibana, K. Fukuda and K. Hamaguchi, This Bulletin, **24**, 155 (1951).

[15] E. G. Cockbain and J. H. Schuman, *Trans. Faraday Soc.*, **35**, 716 (1939); T. Sasaki and M. Muramatsu, This Bulletin **26**, 96 (1953).

[16] T. Yasunaga and T. Sasaki, To be published in future.

[17] H. Kimizuka, This Bulletin, **26**, 33 (1953).

sorption to the formation of colloidal aggregates resulting from the balance between attractive force and ionic repulsion.

A similar explanation can be made for the interaction of basic dyes with stearic acid in the film, results of which are shown in Figs. 4 and 5. A large contribution of van der Waals' force to the interaction may be suggested when we consider the pH dependence of the degree of ionization together with that of the amount of chrysoidine sorbed on the film. It should be noticed, however, that chrysoidine retains still a small amount of positive charge even at pH 6.5 where the maximum interaction is observed, while stearic acid is considered to have a slight negative charge when it is in the state of monolayer spread on distilled water of the same acidity[18]. Therefore the ionic attraction between dye and stearic acid which may exaggerate the sorption should not be neglected. A similar explanation was made for the interaction between stearic acid in the built-up film and metal ion in aqueous solution[7]. Remarkable solidification of the surface film of fatty acid spread on an aqueous crystal violet[1,19] could also be explained from this point of view. This idea is further supported by the fact that the built-up film of barium stearate takes up a smaller amount of crystal violet than that of stearic acid does.

Somewhat complicated results are obtained in the case of amphoteric dyes, which are shown in Figs. 6 to 8. It can be seen in general that the maximum sorption is observed near the isoelectric region of dye. This is indeed the case for tropäolin OO and Congo red. The isoelectric region of benzopurpurin 4B may presumably be around pH 3, where the built-up film of stearic acid takes up the maximum amount of dye from the solution. The exceptional behavior of trypan red would be caused by its negative charge due to five sulfonic groups overwhelming the positive charge due to two amino groups. It might be expected therefore that the maximum sorption could be attained if the solution was rendered much more acidic than in the present experiment.

The majority of molecules of amphoteric dye are considered to be in zwitterion form in the isoelectric region, so that they might exist as colloidal aggregates or micelles differing in size and shape, according to their physico-chemical properties[20]. The molecules in the aggregates would be bound to each other by dipolar attraction, hydrogen-bonding and/or van der Waals' force. In the other pH region the ionic repulsion due to the same sign of charge would suppress the association of dye molecules. Such a presumption may be valid from the results of rheological study on the surface of aqueous dye solution[12], in which it was seen that a film was most coherent for an amphoteric dye when a solution is in an isoelectric region. Such a mechanism for the interaction between dye molecules themselves may also serve to explain the attraction between the built-up film and the aggregate of dye. This presumption is supported by a greater amount of sorption in a respective isoelectric pH range for a larger molecule of dye. Non-sorption of methyl orange may be explained by the smallest molecular weight. An exception is observed however in the relation between Congo red and benzopurpurin 4B. As would be seen in Figs. 7 and 8, the built-up film of stearic acid takes up less benzopurpurin 4B than Congo red, in spite of the molecule being larger by two methoxy groups in the case of the former dye. This may come from the less favorable conditions of forming the aggregate for the latter, presumably owing to the steric hindrance by methoxy groups facing each other in the diphenyl group in the molecule. From the measurement of diffusion velocity of dye, it has been reported[21] that the former dye showed a degree of association of about 9 in 0.01 M sodium chloride solution while the latter had a degree of association of only 6 in the same medium.

It is well known[7,10] that the nonpolar surface of built-up film of barium stearate is rendered polar when it is conditioned by the solution of such cations as copper, aluminum and thorium. This has been explained by the overturning of the molecules in the outermost layer of the film. In connection with this, it is of interest that Congo red interacts with the built-up film of either stearic acid or barium stearate, irrespective of the pre-treatment by the solution of aluminum chloride.

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

[19] E. Heymann and A. Yoffe, ibid., **38**, 408 (1942).

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

[21] E. L. Valko, "Colloid Chemistry", edited by J. Alexander, Vol. 6, Reinhold Publ. Corp., New York, (1946), p. 601.

Similar results were obtained for the wettability of the surfaces of various substances including pure paraffin when they were immersed into the solution of Congo red[22]. Again, van der Waals' attraction plays an important role in such a type of interaction. Precisely speaking, however, the possibility of dipolar attraction interacting between dye and film molecules seems to be open to discussion. This is supposed from the fact that the optimum pH range shifts to a more acid position than the pH region where the molecules of dye are almost in zwitterion form, as shown in Fig. 7. At any rate, it would be reasonably deduced that the same attractive force by which the dye molecules are bound to each other is also mainly responsible for the interaction between dye and built-up film molecules, and thus for the change in thickness of the film.

Summary

The amounts of dyes sorbed on the built-up films of stearic acid and of barium stearate were measured, under varying pH of the dye solutions into which the films were immersed. It has been observed in general that the amount of sorption was greater when the molecular weight of dye became greater. Nonionic attraction such as van der Waals' force, which is considered to be a cause of interaction between dye molecules themselves, and aggregate formation among them may also be responsible for the interaction between dye and built-up film. Such an interaction may be favored by the decreasing ionic charges of the same sign existing on dye molecule and film.

Acid dyes proved to be increasingly sorbed with decreasing pH until the aggregates of dye grew so large that they fell from the interface as a precipitate. The difference in detailed behaviors for sorption of several acid dyes could be explained by the difference in the strength of repulsive force of dye ions, suppressing the attraction, as well as of van der Waals' force which was considered to be largely affected by molecular weight.

In the case of basic dyes, ionic attraction is additionally taken into account to explain their sorption on the film of stearic acid. This has been suggested by the correlation between the degree of ionization and sorbed amount of chrysoidine, and supported by the fact that the built-up film of barium stearate took up less crystal violet than that of stearic acid did.

In the case of the sorption of amphoteric dyes, a maximum was observed in general in a pH range which is roughly in agreement with an isoelectric region of dye. Tentative explanations have been made for this phenomenon, taking account of a change in the dissolved state of dyes.

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[22] A. Inaba, unpublished work.