Physicochemical Properties of the Surface of Aqueous Solutions. V. Mechanical Properties of the Surface of Dye Solution

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Some dyes are known to be remarkably surface active and their surface physicochemical properties have been studied in connection with the adsorption,(1) film strength,(2)(3) foam(4)(5) etc. Especially in our laboratory, the interaction between stearic acid and some dyes was investigated using wetting,(6) monolayer(7) and built-up film techniques.(8) In connection with these experiments, the present author has also studied the mechanical properties of the surface of dye solution.

Experimental

The experiment was carried out by the same concentric ring apparatus as described previously.(9) Dyes used in this experiment were conventionally classified according to their molecular structure into three groups, namely those of cationic, anionic and amphoteric ones. As anionic dyes, phloxine and scarlet red; as cationic dyes, crystal violet and night blue; as amphoteric dyes, methyl orange and congo red were chosen. Of the dyes used, crystal violet, methyl orange and congo red were specially purified by salting out or recrystllization(10) and the mechanical behavior of each was compared with that of crude ones, but they could not be distinguished from each other. So the rest of the dyes were used without special purifications. Each of these dyes was dissolved in water to the concentration of 10^{-2} mol./l. and was aged for about ten days before use. Just before the measurements, the solution was diluted to 10^{-4} mol./l. except for crystal violet, which was made to 10^{-3} mol./l. The hydrogen ion concentration of dye solution was varied from 1 to 13 in *p*H using hydrochloric acid and ammonium hydroxide. Here the use of ordinary buffer salt was avoided because of its disturbing effect upon the properties to be measured. The experiments were carried out at room temperature (10~13°C) and the time of aging prior to the measurement was kept to thirty minutes.

Result

As to the rheological property measured, the surfaces of solutions of scarlet red and methyl orange could not be distinguished from the surface of distilled water throughout the whole range of *p*H and up to the concentration of 0.1 mol./l. in the present experiment, while the formation of a coherent adsorbed layer was perceptible and sometimes remarkable in the solution of the rest of the dyes. The results

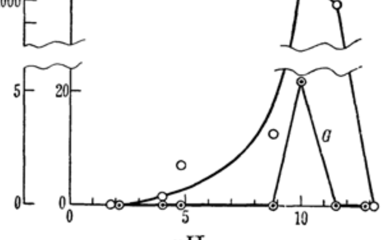

Fig. 1.—Crystal violet solution. 10^{-3}mol./l.

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(8) M. Muramatsu, to be published in a near future.

(9) T. Sasaki and H. Kimizuka, This Bulletin, **25**, 318 (1952).

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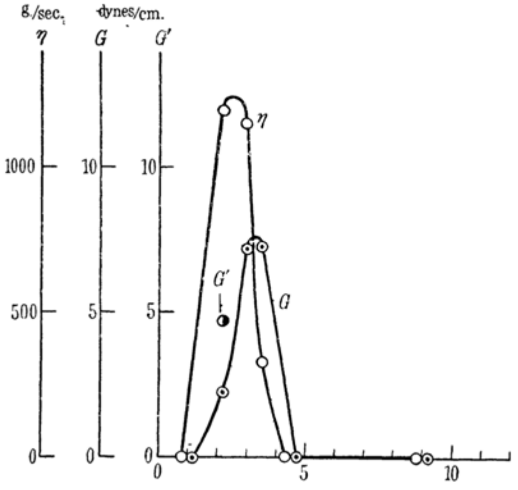

Fig. 2.—Congo red solution. 10^{-4} mol./l.

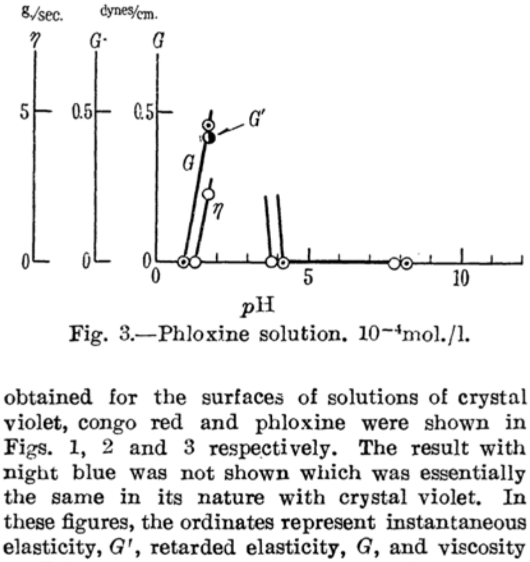

Fig. 3.—Phloxine solution. 10^{-4}mol./l.

obtained for the surfaces of solutions of crystal violet, congo red and phloxine were shown in Figs. 1, 2 and 3 respectively. The result with night blue was not shown which was essentially the same in its nature with crystal violet. In these figures, the ordinates represent instantaneous elasticity, G', retarded elasticity, G, and viscosity coefficient, η, corresponding to those of the three-parameter model,(9) the abscissa, pH. As seen in these figures, the surfaces showed the transformation of a mechanical model as well as sharp maxima in the value of surface rigidity and surface viscosity when pH of the solution was changed, keeping concentration constant.

Discussion

In our laboratory, Matuura(7) observed a remarkable expansion of the monolayer of stearic acid on the aqueous substrate containing dye at certain range of pH, and accounted for its mechanism by the interaction between the dyes and stearic acid. Inaba(6) confirmed this view by the experiment on wettability and Muramatsu,(8) by the study of built-up film. The present experiment also shows that the solution of dyes forms a coherent adsorbed layer in certain range of pH, where a remarkable effect on stearic acid was reported by the above authors. It may be emphasized from the above facts that the formation of a coherent adsorbed layer at surface together with the interaction between dyes and stearic acid result in the characteristic behavior of the monolayer.

Recently, Buzagh(3) made the measurement of strength of an adsorbed layer with respect to a change in pH and pointed out that anionic dyes formed a coherent adsorbed layer in an acid region, cationic, in an alkaline region and amphoteric, in neutral condition; but unfortunately he did not study the mechanical behavior of the film precisely. The result obtained in the present experiment shows that the mode of transformation of mechanical model exhibited by the dye solution belongs to that of micellar solution reported in the preceding paper(11) which again confirms the view presented there that the difference in mechanical behavior is due to a difference in higher order structure rather than a molecular one. Further, Buzagh(3) studied an effect of electrolyte on the surface of dye solution and emphasized that the formation of a coherent film is governed by the same factors determining other aggregation phenomena. This is in agreement with the behavior observed with the solution of congo red, crystal violet and night blue at appropriate range of pH.

In the case of scarlet red and methyl orange, the failure in the formation of a coherent adsorbed layer may be due to the weak attractive force between molecules in the surface layer because of its strongly ionizable $-SO_3Na$ group and therefore strongly hydrophilic character. The formation of a coherent adsorbed layer might be expected here if the solution is rendered much more acidic than in this experiment.

In the preceding paper,(5) the close correlation between surface viscosity and foam stability of solutions were reported, in which the neutral solution of congo red, fuchsine, auramine, crysoidine and malachite green were reported to form no coherent adsorbed layer. In the case of congo red solution, however, a change in pH of solution enables the formation of stable foam(4) as well as the coherent adsorbed layer which was overlooked in the preceding report.

Summary

The rheological property of the surface of dye solution with a change in pH under constant concentration was studied. Solutions of crystal violet, night blue, congo red and phloxine form the coherent adsorbed layer, while those of scarlet red and methyl orange, do not. The differences between them was considered to be due to the difference in the

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(11) H. Kimizuka, This Bulletin, **26**, 30 (1953).

intensity of the interaction between molecules in the adsorbed layer. The surfaces of solutions of crystal violet, night blue, congo red and phloxine show the transformation of a mechanical model as well as sharp maxima in the value of surface rigidity and surface viscosity coefficient with a change in pH.

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