Studies on Foams. V. The Effect of Electrolytes on Triphenyl Methane Dye Solutions

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It is usually considered that a solution of alkaline nature, in general, produces much foams when it is shaken, while the acidic one does not foam. This is supposed to be due to the action of the minute quantity of soap produced by the saponification of acidic matters in dirts. For example, Goette ⁽¹⁾ described that some oily dirts contains 31.4% of fatty acids, the mean number of carbon atoms of which being 38. It may be considered that the solution containing organic amines will produce more stable foam in acidic solution than in alkaline one. From this standpoint, the effects of electrolytes on the foam formation of triphenyl methane dye solutions were studied. In the present experiments, the effects of sodium chloride, hydrochloric acid and sodium hydroxide on the foaming ability of

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(1) E. K. Goette, *J. Colloid Sci.*, 4, 459 (1949).

brilliant green and crystal violet solutions have been determined.

One gram of the each dye (Merck's sample) was dissolved in one litre of water, respectively. After keeping it on standing for one week, the electrolytes were added and the concentration of dye was adjusted to 0.8 g. per litre. The method of experiment has been described in the preceding report.⁽²⁾ Twenty cc. of solution was taken in a test tube of 40 cc. capacity, and shaken up and down for 300 seconds. The height of maximum foam zone, A_m, and the reciprocal of the mean velocity of foam collapse in the initial 30 seconds, τ, were determined. The foaming ability, F, of the solution is defined as the products of A_m and τ. Surface tension was measured by du Nouy's tensiometer and recorded as the specific surface tension relative to the solution containing the same concentration of electrolyte: γ/γ_s. Measurements were undertaken at the room temperature (27°). The results obtained for crystal violet are depicted in Fig. 1. An analogous curve is obtained for brilliant green.

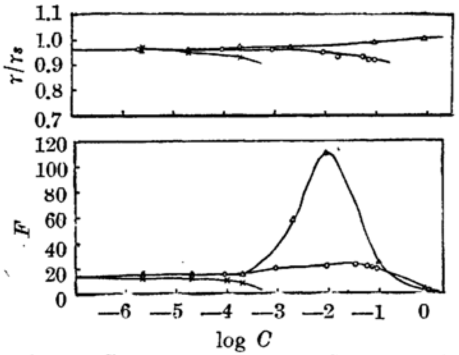

Fig. 1.—Crystal violet, ○, NaCl; △, HCl; ×, NaOH

The surface tensions of the solutions of both dyes decrease by the addition of sodium chloride, while the foaming ability shows a maximum point at the concentration of 0.0356 N sodium chloride. In the cases of hydrochloric acid and sodium hydroxide, the surface tensions increase with the decrease of pH value, and the foaming abilities become maximum at 0.0917 N hydrochloric acid. The foam of the electrolyte solution is by far the less stable than that of the solution containing dye.

The dye, in general, is a colloidal electrolyte and forms micelles in its solution. This was suggested, for instance, by Pauli and Lang⁽³⁾ from the results of measurements of electrical conductivity. The dye micelles are considered to exist in an equilibrium with the single ions of dye in the solution. It has been reported in the foregoing paper,⁽⁴⁾ that the foam formation of the solution is closely connected to the molecular structure of the dye molecules and its surface activity, and the foam formation is mainly influenced by the portion dispersed as single ion. This conclusion was obtained by the comparison of foam formation of dyes having various molecular structures. In order to explain, however, the variation of foam formation of one dye in detail, the displacement of equilibrium, (micelle) $\rightleftarrows$ (ion) should also be taken into consideration.

The variations of foam formation and surface tension by electrolytes are accounted by the displacement of equilibrium and by the change of surface activity, as described in the preceding paper.⁽²⁾ The displacement of equilibrium by neutral electrolytes is understood as a preceding phenomenon of coagulation. These dyes precipitate at about 0.9 N of sodium chloride.

In order to account for the effects of acids and alkalis, both of the change of pH of solution and the structural change following to it should be taken into consideration. For example, the color change of congo red by the variation of pH was attributed by Wo. Ostwald⁽⁵⁾ to the change of particle size. Later, A. Hantzsch⁽⁶⁾ accounted it with the structural change of dye ion. The latter conception has been widely accepted. The change of structure, therefore, should be taken into account, when dye changes its color with the variation of pH. Such a structural change will affect the equilibrium between micelle and ion, and the foam formation will accordingly change.

The change of electrical charge and molecular structure of crystal violet have been discussed conclusively by Adams and Rosenstein⁽⁷⁾ by means of absorption spectra. According to them, dye ions having electrical charge 0, +1 + 2, + 3 and + 4 are colorless, violet, yellow, green and colorless, respectively. These ions coexist in chemical equilibrium in the solution. When pH of solution decreases, the mean value of electrical charge increases.

The surface activity of dye ion increases, as stated in the preceding paper,⁽²⁾ when the hydrophilic character becomes weaker or hydrophobic character becomes stronger. Since the radical having an electrical charge has the strong hydrophilic character, both of the hydrophilic property of ion and the surface tension of the solution increase when pH of solu-

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(2) M. Nakagaki, this Bulletin, **23**, 47 (1950)

(3) W. Pauli and F. Lang, *Monatsh.*, **67**, 159 (1936).

(4) M. Nakagaki, this Bulletin, **22**, 200 (1949).

(5) Wo. Ostwald, *Kolloid-Z.*, **10**, 97; 132 (1912); **24**, 67 (1919).

(6) A. Hantzsch, *Kolloid-Z.*, **15**, 79 (1914); *Ber.*, **48**, 158 (1915).

(7) E. Q. Adams and Rosenstein, *J. Am. Chem. Soc.*, **36**, 1452 (1914).

tion becomes smaller. This conclusion coinsides with the data cited in Fig. 1. The foam formation may be accounted under the consideration of the shift of equilibrium (micelle) $\rightleftarrows$ (ion), and of the variation of surface activity of dye ion. The equilibrium displaces to ion side when the hydrophilic character of ion increases. Since the foam formation of solution is thought to be mainly contributed from the portion dispersed in single ion state, the foam formation will increase when pH of solution decreases and the hydrophilic character of ion increases. When pH of solution became small enough, the foam formation begins to decrease owing to the decrease of surface activity of dye ion. By these two factors, the foam formation becomes maximum at the concentration 0.00917 N of hydrochloric acid.

Analogous explanation will be valid also for soap solutions. The variations of foam formation with pH for sodium salts of palmitic, myristic, and lauric acid are measured by G. D. Miles and J. Ross.(8) A maximum of foam formation has been observed on alkaline side, in opposition to the case of crystal violet and brilliant green. This is reasonable, since soaps are sodium salts of fatty acids and dyes are hydrochlorides of organic amines.

Summary

Effects of sodium chloride, hydrochloric acid, and sodium hydroxide on the surface tension and foam formation of solutions of crystal violet and brilliant green were measured. By the addition of sodium chloride surface tension decreases and foam formation shows a maximum. In the cases of hydrochloric acid and sodium hydroxide, surface tension increases with the decrease of pH and foam formation shows a maximum at about $p\text{H} = 2$. These results were accounted by the change of surface activity of dye ion and the displacement of the equilibrium (micelle) $\rightleftarrows$ (ion).

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(8) G. D. Miles and J. Ross, *J. Phys. Chem.*, **48**, 280 (1944).