Studies on Foams. IV. The Effect of Electrolyte on the Foam Formation of Congo Red Solution

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The foams may be classified into two groups, namely hydrophobic or less stable foam and hydrophilic or more stable foam. The less stable foam is obtained by the aqueous solutions of alcohols, fatty acids and electrolytes and it has shorter foam duration than 30 seconds. The more stable foam is obtained by soaps, dyes, proteins and various detergents. According to O. Bartsch[1] the less stable foam behaves like the negatively charged hydrophobic colloid and easily unstabilized by the addition of electrolyte, while the more stable foam hardly affected by the electrolyte. The present author considers, however, that such a conclusion is not quite correct, especially in the case of the more stable foam. In order to study on this problem the foam formation of congo red solution in the existence of electrolytes has been measured.

(1) O. Bartsch, *Kolloid-Beih.*, **20**, 1 (1925).

The foam formation was determined by the shaking test. Twenty cubic centimeters of solution was taken into a test tube of 40 cc. in capacity and 1.8 cm. in diameter, providing a glass stopper. This was shaken up and down for 30 seconds at the rate of 3 times per second and at the amplitude of 25 cm. Soon after the shaking, the height of the foam zone becomes maximum (usually less than 5 seconds). The height of the maximum foam zone A_m is read, which is taken as a measure of foaminess of the solusion. The foam, then, gradually collapses untill at last a part of free liquid surface appears. Let the time required for the appearance of free liquid surface be t, which is taken as the measure of the foam duration. The change of the height of foam zone with time is also recorded. The strength of foam, τ, is calculated as the reciprocal of the collapsing velocity of foam zone for the initial 30 seconds, thus,

$$\tau = \frac{30}{A_m - A_{30}} \left(\frac{\text{sec.}}{\text{cm.}}\right) \quad \text{for} \quad t > 30 \text{ sec.}$$

where A_{30} denotes the foam height read at 30 seconds after the the maximum height of foam zone is attained.

The stock solution of dye has been prepared in the following manner. Four grams of congo red (Merck's sample) was boiled with distilled water for several minutes and then adjusted accurately to one litre in volume after cooling. Just before the measurement, this solution was diluted with distilled water or some electrolyte solution untill the concentration of dye became 3.20 grams per litre. In order to avoid the effect of aging of solution, measurements have been undertaken just at one week after the preparation of the stock solution.

The general feature of the change of foam formation of congo red solution by the addition of sodium chloride is shown in Fig. 1. A prominent maximum is found in the curve of the foam duration at relatively low concentration of electrolyte, and also a maximum is seen in the curve of foam strength, while no maximum is observed in the curve of the foaminess. It is usually said that the foaminess and foam duration or foam strength of a solution are independent of each other. As an example the solutions of saponin and n-butyl alcohol are often cited, the former produces a more stable but less voluminous foam than the latter. This example, however, is not suitable in this case, for the foam stability of saponin solution may be due to some special reason, such as the formation of an insoluble film. In fact, foaminess and foam duration change, in most cases, similarly with each other, by the change of concentration. This is valid as far as the viscosity of solution is not extremely large, as discussed in the previous paper[2] on the less stable foams. This does not seem, however, to be true for the finely dispersed, long lasting foam.

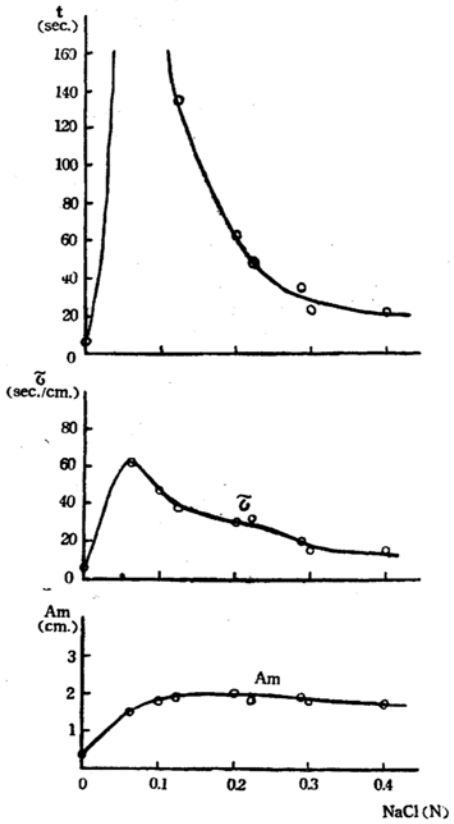

Fig. 1.—The effect of NaCl on the foam formation of congo red solution.

Such a steep maximum in foam duration of 3.20 g./l. congo red solution is also found by the addition of $NaNO_3$, NaOH, HCl, and $BaCl_2$. It is notable that a good peptization agent NaOH, a strong precipitation agent $BaCl_2$, and an acid HCl behave in the same manner as NaCl and $NaNO_3$, though the concentration for the maximum of foam duration is different from each other. As it is well known, acid precipitates blue congo acid from the solution of congo red. The concentrations of these electrolytes at the maximum point of foam strength are shown in Table 1.

One plausible explanation of the maximum of foam formation may be the peptization of dye particles by the electrolyte. Wo. Ostwald [3] and R. Tanaka[4] found the phenomenon that the congo acid is peptized by the addition of small amount of electrolyte. W. Schramek and E. Götte[5] stated from diffusion data, and T. H. Morton[6] from ultra-filtration experiments,

(2) M. Nakagaki, This Bulletin, **21**, 30 (1948).

(3) Wo. Ostwald, *Ber.*, **62**, 1194 (1929).
(4) R. Tanaka, *Kolloid-Z.*, **54**, 156 (1931).
(5) W. Schramek and E. Götte, *Kolloid-Beih.*, **34**, 218 (1932).
(6) T. H. Morton, *Trans. Faraday Soc.*, **31**, 262 (1935).

that the particle size of dye became minimum by the addition of small amount of electrolyte. C. Robinson,[7] E. Valkó[8] and S. M. Neale,[9] however, recognized no minimum point on their curves of particle size to concentration of added electrolyte. The same conclusion was obtained by the present author. It will be reported in another paper. After all, peptization may be an action to disperse a precipitated mass into colloidal particles, scarcely affecting the size of particles already dispersed in sol state.

In spite of little change of particle size, the foam formation shows a steep maximum with the addition of the small amount of electrolyte. This is explained by the idea presented in the preceding paper,[10] that the foam formation is mainly predominated by the separately dispersed ions rather than the portion of dye dispersed in colloidal aggregates, and that the surface chemical porperties of dye ions are determined by the balance of its hydrophilic and hydrophobic character. The addition of electrolyte decreases the affinity of the polar part of dye ions to solvent, and this results in the increase of the surface activity of solute. In fact, the specific surface tension to water measured by du Nouy's tensiometer for 3.20 g./l. of congo red solution decreases from 0.98 for pure dyestuff solution to 0.96 for solution containing 0.48 *N* of sodium chloride. The increase of surface activity, from which the increase of foam formation is explained, is regarded as a presage of salting out. When the concentration of electrolyte is further increased, the affinity of polar group of dye ion to solvent becomes weaker, till the dye ions coagulate and precipitate from the solution. The decrease of foam duration may be related to this process. The coagulation value will have a certain connection with the electrolyte concentration of maximum foam strength, as a measure of the ability of electrolyte to enfeeble the affinity between dye and solvent.

Table 1
Maximum Foam Formation and Coagulation Value.

Electrolyte	Concn. of electrolyte for max. foam strength, *N**.	Coagulation value**, *N*.
NaOH	0.17	0.73
$NaNO_3$	0.11	1.07
NaCl	0.062	0.71
$BaCl_2$	0.0043	0.0056
HCl	0.0028	0.0043

* Concentration of congo red is 3.20 g./l.
** Concentration of congo red is 2.00 g./l.

The coagulation value of 2.00 g./l. congo red solution has been measured, and the result is cited in Table 1. Since the coagulation of congo red is a "Slow Coagulation," the coagulation value is varied with time, and coagulation is observed in fairly dilute solution of electrolyte after a long time. In this report, the coagulation value is defined as the minimum concentration of electrolyte necessary to make solution turbid after 24 hours. Comparing the concentration of electrolyte for maximum foam strength with the coagulation value, the general drift coincides with one another.

Summary

The changes of foaming power of the solution of congo red by the addition of electrolytes have been estimated. There is a prominent maximum in the foam duration by the change of the concentration of electrolyte, while no such maximum is seen in the foaminess. The electrolyte concentration, at which the foam strength becomes maximum, and the coagulation value changes in the same trend from an electrolyte to the other. This is accounted for the fact that the affinity of polar part of dye ion to solvent is weakened by the addition of electrolyte.

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(7) C. Robinson, *Proc. Roy. Soc.* (*London*), **A148**, 681 (1935); *Trans. Faraday Soc.*, **31**, 277 (1935).
(8) E. Valkó, *Trans. Faraday Soc.*, **31**, 231, 278, (1935).
(9) S. M. Neale, *Trans. Faraday Soc.*, **31**, 282 (1935).
(10) M. Nakagaki, This Bulletin, **22**, 200 (1949).