Studies on Foams. III. The Foam Formation of Some Dyestuff Solutions.

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It has been reported, in the preceding paper[1], that the abilities of foam formation of some mixtures of organic liquids are correlated with the volume contraction on admixture, and the latter may probably be related with the amphipathy of solute molecules. That is to say, the balance between the polar and non-polar portion of the molecule has been considered as an essential factor governing the foam formation. If this might be true also of dyestuff solutions known as "micelle colloids", some connection may be found among the foam formation, surface activity, and molecular structure of the dyestuffs.

The foam formation and the surface tension have been measured on the aqueous solutions of congo red and five triphenyl methane dyes: methyl violet 5 B, brilliant green, malachite green (crystallized), crystal violet (chemical pure), and Hofmann's violet. E. Merck's dyes have been used without further purification, excepting congo red, which has been purified by the sodium acetate-alcohol method. Dyestuff solutions were preserved for 1 to 36 weeks as the solution of 1 g./l., and diluted just before the measurements.

The foam formation was measured by the shaking test; 20 c.c. of the solution was taken into a test tube, 40 c.c. in capacity, and 1.8 cm. in diameter and provided with a glass stopper. This was shaken up and down for 30 seconds at the rate of 3 times a second and at the amplitude of 25 cm. The maximum foam zone height A_m (cm.) is considered as a measure of the foaminess of the solution. The foam strength τ(sec./cm.) is defined as the reciprocal of the collapsing velocity of foam within the initial thirty seconds. Thus,

$$\left.\begin{array}{lll} & \tau = 30/(A_m - A_{30}) & \text{for } t > 30, \\ \text{or} & \tau = t/A_m & \text{for } t < 30, \end{array}\right\}$$

where A_{30} is the foam height after 30 seconds from the instant of maximum foam height, and t is the foam duration in seconds. The foaming ability (F) of the solution (Fig. 1) is defined as the products of foaminess (A_m) and foam strength (τ). The surface tension was measured by du Nouy's tensiometer. The viscosities of these solutions were also measured, and concluded that they have no appreciable effects on the foam formation, since the values relative to water are 1.00 to 1.02.

(1) The second paper, This Bulletin, **22** (1949), 21.

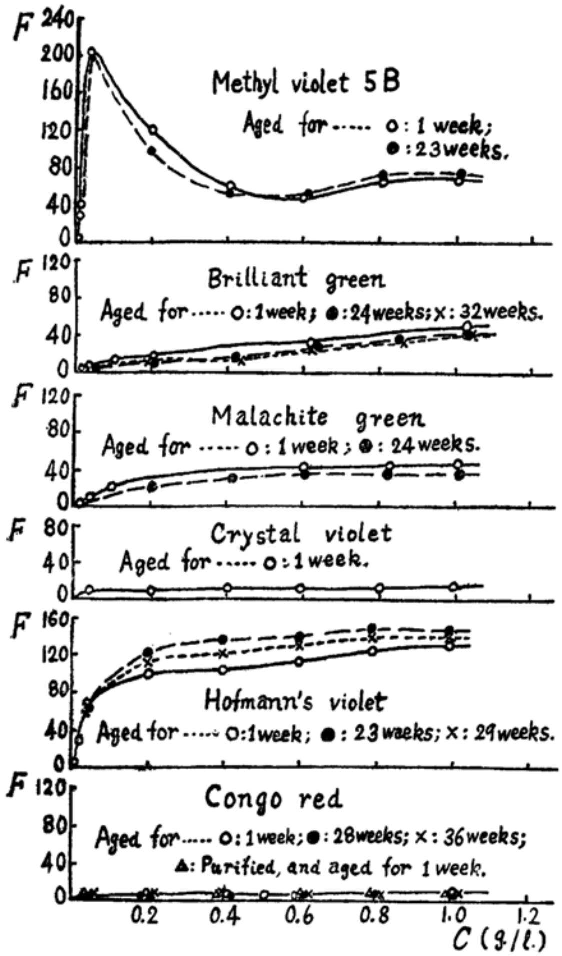

Fig. 1. Foaming Abilities.

The effect of aging of the solution on the foam formation is not serious, and the change of foam formation by the purification of dye is also insignificant.

It is shown in Table 1 that the solution of large foaming ability has small surface tension excepting Hofmann's violet. Such a relation may be interpreted as follows. The ion of crystal violet, e. g., undergoes quantum mechanical resonance among three equivalent structures, and in consequence, the molecule takes the shape of a regular triangle, and three nitrogen atoms equally have 1/3 of the positive charge as the average. This was stated by E. Hückel(2) and G. N. Lewis and M. Calvin(3), and the symmetrical structure interpreted satisfactorily the absorption spectra obtained by G.E.K. Branch and M. Calvin.(4) On the other hand, malachite green or brilliant green has a phenyl radical which lacks the amino group, and this part of the molecule shows distinct hydrophobic character. Then, the molecule having both polar and non-polar parts in the molecule was named by G. S. Hartley(5) as "amphipathic" molecule. Such a molecule is adsorbed to the surface of the solution, turning the polar part to water and the non-polar part to air, and lowers the surface tension and increases the foam formation; the degree of which is greater when the hydrophobic character of the non-polar part is more distinct or the hydrophilic character

(2) E. Hückel, *Z. Elektrochem.*, **43** (1937), 827.

(3) G. N. Lewis and M. Calvin, *Chem. Rev.*, **25** (1939), 273.

(4) G.E.K. Branch and M. Calvin, "The Theory of Organic Chemistry," pp. 179, New York (1941).

(5) G. S. Hartley, "Aqueous Solutions of Paraffin-Chain Salts", Chapter 7, Paris (1936).

Table 1. Properties of Dyestuff Solutions. (Aged for one week).

Dyestuff	Concentration		Specific surface tension	Foaming ability	Foaminess	Foam strength	Foam duration
				F	A_m	τ	t
	(g./l.)	(mol/l.)	γ/γ_w		(cm.)	(sec./cm.)	(sec.)
Methyl violet 5B	1.01	0.00209	0.86	71	5.1	14	>200
Brilliant green	1.03	0.00214	0.90	47	3.7	12.7	>200
Malachite green	0.827	0.00227	0.94	42	3.1	13.5	42
Crystal violet	0.796	0.00196	0.96	11	8.9	2.8	11
Hofmann's violet	0.988	0.00235	0.96	187	4.7	27	>200
Congo red	1.52	0.00218	0.99	3.4	1.4	2.5	3.4

of the polar part is weaker. This is a qualitative generalization of Traube's rule, which has been applied to homologous series of alcohols and fatty acids by O. Bartsch(6) and T. Sasaki(7), but no one attempted hitherto to apply this idea to more complex substances. From this standpoint, however, it is thought to be reasonable that the surface activity and foaming ability of crystal violet, having positive charges on every apex of the regular triangular melecule, are smaller than that of brilliant green or malachite green, having no charge on one of the apexes. Then, comparing the amino group of brilliant green and malachite green, the former is ethylated and the latter is methylated, so that the hydrophilic nature of the former is weaker than the latter. It is, therefore, reasonable that the surface activity and the foaming ability of the former is greater than that of the latter. As to methyl violet 5B, the surface activity and foaming ability are very large, and the foaming ability becomes maximum at a relatively low concentration (Fig. 1), since one of the amino groups is connected with a very large hydrophobic group. One exception is Hofmann's violet, whose surface activity is small while the foaming ability is large. This is thought to be due to the strong interaction between amino groups which are only partially ethylated.

The sequence of the foaming ability of triphenyl methane dye solutions is thus interpreted with their structural formulae. Since the dominant factor is the properties of the molecule itself, it is supposed that the single molecule is mainly concerned with the foam formation and micelle plays no significant role.

Summary

The foam formations of the aqueous solutions of methyl violet 5B, brilliant green, malachite green, crystel violet, Hofmann's violet and congo red have been measured. The foaming ability, that is the product of foaminess and foam strength, is considered as the measure of the

(6) O. Bartsch, *Kolloid-Z.*, **38** (1926), 177.
(7) T. Sasaki, This Bulletin, **13** (1938), 517.

foam formation. This scarcely changes by the long period's storage of the solution. The foaming ability of them is nearly parallel with the surface activity. This is interpreted with structural formnlae of dyestuffs.

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