jected to vacuum distillation. At 3 mm. pressure a few drops of liquid distilled below 200°, the main product distilling from 200–225° as a red-brown viscous liquid which soon crystallized. The residue (9.0 g.) could not be distilled or crystallized. After recrystallization from acetone and petroleum ether, the volatile portion weighed 9.3 g. (34%) and was found to be 2-*p*-methoxystyryl-3-methylquinoxaline (m. p. 124–125°).

Of the starting materials 0.041 mole of anisaldehyde and 0.038 mole of dimethylquinoxaline are unaccounted for; thus the 9.0 g. of undistillable residue probably consists of a polymeric 1:1 condensation product.

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The Critical Concentration of Dodecanesulfonic Acid

BY H. F. WALTON

The writer recently measured the activity of 1-*n*-dodecanesulfonic acid in aqueous solution at two temperatures by an electromotive force method, and concluded from the results that the critical concentration, above which the association of negative ions to form micelles begins, is 0.0064 *M* at 25°, and 0.003 *M* at 0°. These values, especially that at 0°, are at variance with those found by other methods, as in Table I.

TABLE I

CRITICAL CONCENTRATION OF DODECANESULFONIC ACID

Method	Critical concn., molar 0°	25°	Ref.
E. m. f.	0.003	0.0064	1
Conductivity	.010	.0072	2, 3
Freezing point	.010	....	3
Indicator	.0095 (4°)	.0075	This work

This note describes measurements of the light absorption by a dissolved indicator dye, thymol blue. This indicator normally changes from red to yellow in the *p*H range 1.2-2.8, but in 0.01 *M* dodecanesulfonic acid it is a darker red than in 2 *M* hydrochloric acid. The position of the absorption bands of the indicator is not changed appreciably by the colloidal electrolyte, but their intensity is increased, and the red form appears to be solubilized or stabilized in some way. Solubilization is a property of micelles rather than simple molecules, as Hartley showed,[4] and the concentration where solubilization first occurs is approximately equal to the critical concentration of the colloidal electrolyte.[4,5,6]

Experimental

Solutions of the yellow form of thymol blue in water and in 0.02 *M* dodecanesulfonic acid were prepared, the indicator concentration being the same in both. The optical density of the sulfonic acid solution was measured at 550 mμ, using a Beckman spectrophotometer with 1-cm. cell. Five hundred and fifty mμ is the peak of the main absorption band of the red form; the yellow form absorbs hardly at all at this wave length. The sulfonic acid concentration was progressively reduced by diluting a measured volume of solution with the aqueous indicator solution added from a buret; the indicator concentration thus remained constant. Runs were made with two different indicator concentrations, 10 p. p. m. (2.1×10^{-5} *M*) and 2.5 p. p. m. (5.2×10^{-6} *M*), and at two temperatures, 25 and 4°; the 4° measurements were made in the cold room. The results are shown in the graph, with comparative data for the indicator in hydrochloric acid. The curves for the lower indicator concentration show the sharper inflections. Since the concentration of indicator is so much less than that of the acid, the effect of the indicator in promoting micelle formation must be very small, and these inflections, coming at 0.0095 *M* at 4° and 0.0075 *M* at 25°, probably represent the critical concentrations of sulfonic acid for micelle formation. If so, they agree well with conductivity and freezing point measurements, as is shown in Table I. Why the electromotive force method should give different results is still not apparent.

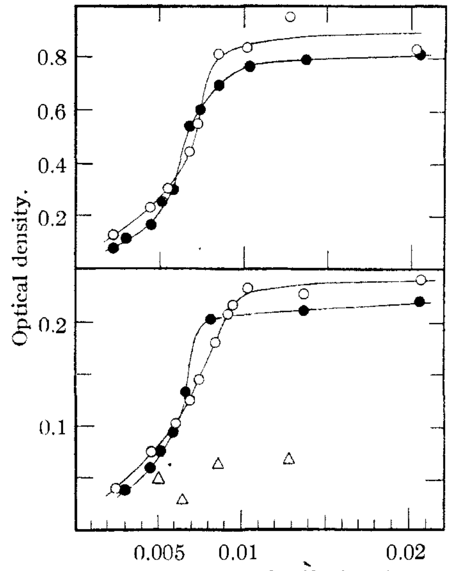

Fig. 1.—Optical density *versus* acid concentration: upper curves, 10 p.p.m. thymol blue; lower curves, 2.5 p.p.m. thymol blue; open circles, 4°; filled circles, 25°; triangles, hydrochloric acid plus 2.8 p.p.m. thymol blue at 25°.

A comparison of the optical densities in hydrochloric acid and in dodecanesulfonic acid shows that the red indicator color is considerably enhanced by the sulfonic acid even below the critical concentration. At 25°, the optical density rises approximately with the square of the sulfonic acid concentration, suggesting that a binary complex, such as $(C_{12}H_{25}SO_3)_2^=$, is formed which associates with the indicator.

(1) Walton, THIS JOURNAL, **68**, 1180 (1946).
(2) Brady, Thesis, Stanford University, 1944.
(3) McBain, Dye and Johnston, THIS JOURNAL, **61**, 3210 (1939).
(4) Hartley, *J. Chem. Soc.*, 1968 (1938).
(5) Sheppard and Geddes, *J. Chem. Phys.*, **13**, 63 (1945).
(6) Corrin, Klevens and Harkins, *ibid.*, **14**, 216 (1946).

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Note on the Darzens–Claisen Reaction

BY MELVIN S. NEWMAN AND BARNEY J. MAGERLEIN

On attempting to alkylate cyclohexanone by treating its sodium enolate with the *p*-toluenesulfonic acid ester of ethyl glycolate, the main prod-