Use of Alizarin Red S for Determining Critical Micelle Concentration of Cationic Surfactants

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Abstract

The critical micelle concentrations of cetyl trimethyl ammonium bromide and cetyl pyridinium bromide have been calculated by a spectral-dye method. Alizarin red S at pH 9.12 was found to be suitable for these two cationics. Two shifts in the dye maximum, one due to complex formation (500 mμ or 525 mμ) and the other due to the dye-surfactant complex solubilized in the micelles of the cationics were realized. The critical micelle concentration was represented by the point of intersection of two curves at wavelength 500 mμ and 550 mμ for cetyl pyridinium bromide and 525 mμ and 550 mμ for cetyl trimethyl ammonium bromide.

Introduction

IT HAS BEEN KNOWN for more than thirty years that indicator dyes have their colors altered when present in solution along with surfactants (1,2). Fajans (3) investigated the effect of dye adsorption on ionic surfaces. Deutsch (4) described striking examples of effects on indicators when adsorbed at oil-water interfaces. In 1934, Hartley (5) studied the effects of anionic, cationic and nonionic detergents on a large number of dyes. The work of Sheppard and Geddes (6) on the spectrum of pinacyanol and cationic detergents was further extended by Corrin et al. (7), whose investigations led them to develop a method

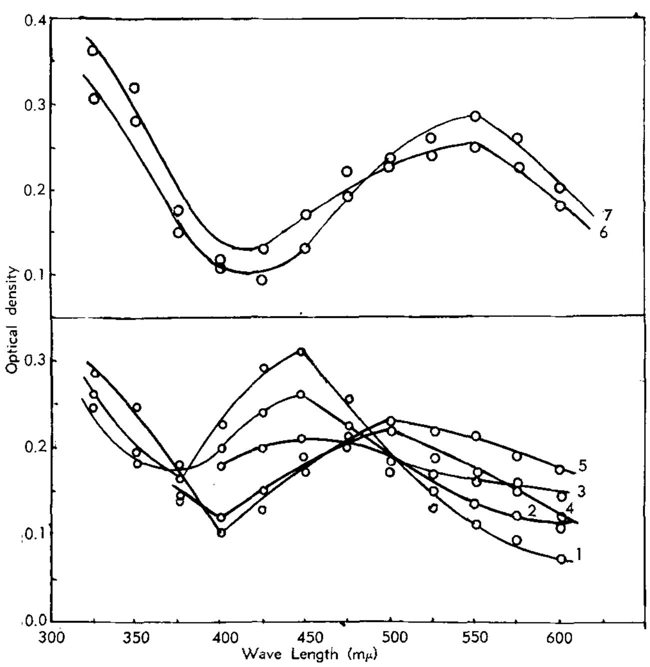

FIG. 1. Absorption spectra of 6.7×10^{-5}M alizarin red S for different concentrations of CPB.
Curve 1—6.7×10^{-5}M dye + 3.3×10^{-4}M CPB
Curve 2—6.7×10^{-5}M dye + 6.6×10^{-4}M CPB
Curve 3—6.7×10^{-5}M dye + 10.0×10^{-4}M CPB
Curve 4—6.7×10^{-5}M dye + 13.3×10^{-4}M CPB
Curve 5—6.7×10^{-5}M dye + 33.3×10^{-4}M CPB
Curve 6—6.7×10^{-5}M dye + 53.3×10^{-4}M CPB
Curve 7—6.7×10^{-5}M dye + 80.0×10^{-4}M CPB

(8) for determining the critical micelle concentration (cmc). Hiskey and Downey (9), Mysels and Mukerjee (10), Herzfeld (11), Ginn and Harris (12), etc., also used this technique to determine the cmc of some cationic and anionic surfactants.

The apparent simplicity of the above methods of providing color changes has been used to determine the cmc values of cetyl trimethyl ammonium bromide and cetyl pyridinium bromide by employing alizarin red S. This dye is more sensitive than the other dyes so far employed in the study of cationic surfactants.

Experimental

Reagents

Cetyl trimethyl ammonium bromide (CTMAB) and cetyl pyridinium bromide (CPB) were obtained from British Drug House and were recrystallized from acetone. The stock solutions were prepared in doubly distilled water (all glass). Alizarin red S used in this study was also a BDH product and was used without further purification. The buffers, Walpole, McIlavine and borax, were prepared in the laboratory.

Apparatus

A Bausch and Lomb Spectronic 20 was used for the absorption measurements and the pH of the solutions were measured by a Cambridge Bench Type pH meter.

Samples

Following sets of solutions were prepared from 10^{-3}M dye stock solutions: (a) 15 ml buffers containing 0.1 to 1.0 ml of dye solutions; (b) 1 ml dye in 15 ml buffer containing 1 to 12 ml of cationic surfactant solutions. Buffers of pH 2.00, 7.00 and 9.12 were used in both sets.

Results and Discussion

The spectrum of alizarin red S solution changes very markedly with increasing concentration of cationic surfactants. At pH 9.12 the shift in the maximum of the dye in presence of cationic surfactant is very large (445 mμ to 550 mμ) in comparison to those observed at the other two pH values. At pH 7.00 in the initial concentrations of the surfactant, precipitation occurs which might be attributed to a dye-surfactant complex. However, on further addition of surfactant the precipitate redissolves and the dye gives the same maximum as in the alkaline range, the shift being from 515 mμ to 550 mμ. At pH 2.00 no appreciable shift in dye maximum could be observed (415 mμ to 425 mμ). Figure 1 represents some typical data to illustrate the effect observed with gradual addition of cetyl pyridinium bromide.

We have shown in another communication (13) that in dilute surfactant solutions the binding ratio between the surfactant and the dye molecule is 1:1. This ratio, however, changes with the increase in the surfactant concentration due to the appearance of micelles in the solution. At pH 9.12 two maximum

TABLE I

Influence of CTMAB on the Absorption Maximum of Alizarine Red S

Conc. of surfactant $\times 10^{-5}$M	Absorption maximum at different pH values (2.00)	(7.00)	(9.12)
0.00	415 mμ	515 mμ	445 mμ
3.3	415 mμ	515 mμ	525 mμ
6.6	415 mμ	......	525,540 mμ (ill-defined)
10.0	415,425 (ill-defined	......	525,540 mμ (ill-defined)
13.3	425 mμ	...	550 mμ
33.3	425 mμ	550 mμ	550 mμ
53.3	425 mμ	550 mμ	550 mμ
80.0	425 mμ	550 mμ	550 mμ

Influence of CPB on the absorption maximum of alizarine red S

Conc. of surfactant $\times 10^{-4}$M	Absorption maximum at different pH values (2.00)	(7.00)	(9.12)
0.00	415 mμ	515 mμ	445 mμ
3.3	415 mμ	515 mμ	445 mμ
6.6	415 mμ	......	445 mμ
10.0	415 mμ	......	500 mμ
13.3	415 mμ	......	500 mμ
33.3	425 mμ		500 mμ
53.3	425 mμ	550 mμ	550 mμ
80.0	425 mμ	550 mμ	550 mμ

shifts are observed, viz., from 445 mμ to 525 mμ and 525 mμ to 550 mμ in presence of cetyl trimethyl ammonium bromide. The first shift takes place with surfactant concentration 6.66×10^{-5}M while the second one is observed by increasing a little beyond this concentration. In the case of cetyl pyridinium bromide the shift in the maximum is from 445 mμ to 500 mμ for the concentration 13.3×10^{-4}M and the second maximum, i.e., 550 mμ is observed after this concentration (Table I). The maximum at 550 mμ remains unaffected by further addition of the surfactant.

We believe that the first change in maximum is due to the compound formation between the surfactant and the dye and that the next change in maximum occurs because the dye-surfactant complex is solubilized in the micelles of the surfactant. This complex is soluble at pH 9.12 but insoluble at pH

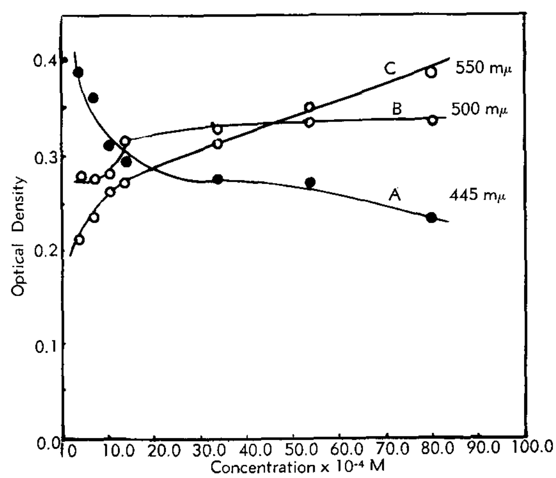

FIG. 2. Concentration (CPB) vs. optical density (dye-surfactant mixture) pH 9.12.

TABLE II

Comparative cmc Values of Cetyl Trimethyl Ammonium Bromide and Cetyl Pyridinium Bromide from Different Methods

Method	Critical micelle concentration CTMAB $\times 10^{-5}$M	CPB $\times 10^{-4}$M
Spectrophotometric	26.0	42.0
Conductometric	25.0	53.0
Emf measurements method	23.8	38.0

7.00, with the result that the maximum 525 mμ (or 500 mμ) at pH 9.12 is not observed here. Further addition of the surfactant results in its dissolution with the formation of micelles giving a maximum at 550 mμ.

The color of the alizarine red S changes from red to violet on addition of surfactant and this change is spectrophotometrically characterized.

The Transition Region

Figure 2 shows typical changes in absorbance in the dye-surfactant mixtures. The optical densities of the dye-surfactant mixtures are plotted vs. surfactant concentration at 445 mμ, 500 mμ and 550 mμ for cetyl pyridinium bromide and at 445 mμ, 525 mμ and 550 mμ for cetyl trimethyl ammonium bromide. Curve A decreases at an accelerated rate. Curve B of the violet solution increases simultaneously and flattens out at higher concentrations of the surfactant. Curve C is similar to B but does not flatten until far beyond the point corresponding to micelle formation. The intersection of B and C is taken as the cmc point. This provides a proof of the fact that micelles are formed in the color transition region.

The values of cmc are given in Table II.

The value for CPB is comparable to those reported in the literature but the cmc value of CTMAB is considerably lower than that reported by others. Confirmatory evidence on CTMAB has been obtained with conductometric and emf measurements (14). The spectrophotometric method is not precise and gives the range of values rather than the true cmc value, but its simplicity compensates this limitation.

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