Effect of pH on the Critical Micelle Concentration of Sodium Dodecyl Sulphate

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Synopsis

Critical micelle concentration (CMC) of sodium dodecyl sulphate (SDS) at various pH's between 2 and 10 has been studied using three methods as dye absorption, conductance, and light scattering measurement. At low pH (below pH 4) the CMC decreases whereas at higher pH it remains constant.

INTRODUCTION

The CMC is the concentration at which the micelle make their appearance.[1] Various workers, using different methods have measured the CMC of SDS, but no reference to the effect of pH on this basis has been found. In the present work the influence of pH on CMC of SDS has been investigated.

EXPERIMENTAL

Materials

Sodium Dodecyl Sulphate: This was obtained from Sigma Chemical Co., St. Louis, Mo. The solution was prepared by dissolving it in deionized water. The purity of this emulsifier was specified at 99.9%.

Pinacyanol Chloride (1,1,-Diethyl-2,2′-carbocyanine chloride): This was obtained from Koch-Light Laboratories, Ltd. This was prepared with deionized water and a purple color dye solution was obtained.

The pH of the SDS solution was adjusted with a pye pH meter with a combination electrode.

METHODS

Three methods were used for the determination of CMC of SDS at various pH between 2 and 10.

Dye Absorption Measurement

For the dye absorption measurement the solution of SDS was prepared with dye, pinacyanol chloride. The purple color of the dye solution changed to blue when the sodium dodecyl sulphate solution was added to it. The change of the

* Deceased.

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color is due to the formation of salt[2] between dye cation and the anion of SDS. The dye spectrum possesses two absorption bands with water as solvent, at 550 and 600 nm. These bands disappear when SDS is added and a new band is formed with a maximum at wavelength 606 nm. This wavelength remains unchanged during the various measurements of the absorption spectra of the dye solutions in the presence of different concentration of SDS at different pH's. The absorbances of the different concentration of SDS for each pH was determined with the Cecil CE 272 Spectrophotometer using the wavelength 606, plotted against the concentration. The CMC was determined from the intersection of two straight lines for each pH.

Conductance Measurement

In the conductance measurements the value of the conductance (G) (Ω^{-1}) was obtained from the slide wire reading (S) divided by the value on the range switch[3] for various concentrations and pH's. In each case the value of the conductance was obtained.

$$G = (S/R)\Omega^{-1}$$

These values were plotted against concentration, and CMC in each case was obtained as above.

Light Scattering Measurement

For light scattering measurement deionised water used as solvent was purified by distilling twice and filtering several times through Millipore 0.22 μ, 44 mm membrane filters. The millipore filters were used to remove dust.[4] The filtration of the solution SDS was performed in the same way as for the solvent. For measuring scattering ratios, unpolarized light wavelength 436 nm was used. The ratio of light scattered at 90° to the light transmitted at 0° was determined from the deflections of the galvanometer. The determination of CMC from light scattering measurement was obtained by plotting Rayleigh ratio[5] at 90° (R90°) against the concentration of SDS at pH's 3, 5, 7, 8.5, and 10.

The CMC values thus obtained were plotted against pH.

RESULTS AND DISCUSSION

The CMC of SDS measured by the absorption, conductance, and light scattering techniques at various pH's are shown in Table I and plotted in Figure 1. The CMC obtained by these methods are slightly different. Such differences may originate from the kind of data which is plotted.

The CMC's of SDS, reported by previous workers, are represented in Table II, but the pH range for the CMC measurements was not mentioned. In the present work it has been found that pH of the various concentration of SDS solution used remained within the range 9.2–9.5. So, it has been assumed that the CMC's, shown in Table II, have been measured at pH 9.2–9.5. The CMC value shown in Table III cover a considerable range. The values of CMC from the present work agree quite well with higher range of reported values.

It is observed from Figure 1 that at low pH CMC decreases. The decrease at

TABLE I
CMC of SDS, Determined by Dye Absorption, Conductance, and Light Scattering Measurement at Various pH's

pH	Dye absorption measurement (CMC)	Conductance measurement (mol/dm^3)	Light scattering measurement (mol/dm^3)
2	0.0065	0.007	—
3	0.008	00075	0.0085
4	0.009	0.0085	—
5	0.0095	0.01	0.009
6	0.0095	0.01	—
7	0.0095	0.01	0.009
8	0.0095	0.01	—
8.5	—	—	0.009
9	0.0095	0.01	—
10	0.0095	0.01	0.009

CMC of SDS in the present study may arise either from the replacement of heavier ions with the lighter ion or a decrease of the charge density at the surface. In the present work, however, the replacement of sodium ion with hydrogen ions at lower pH is not sufficient to bring about a significant change. An ionic micelle bears changes on its surface, and these may be influenced by additional electrolyte. The concentration of electrolyte (sodium hydroxide solution) in the present work was so low that it is unlikely to have any effect on the CMC.

However, hydrogen ions, because of their special properties, may have an effect at quite low concentration. They may decrease the electrostatic repulsion of

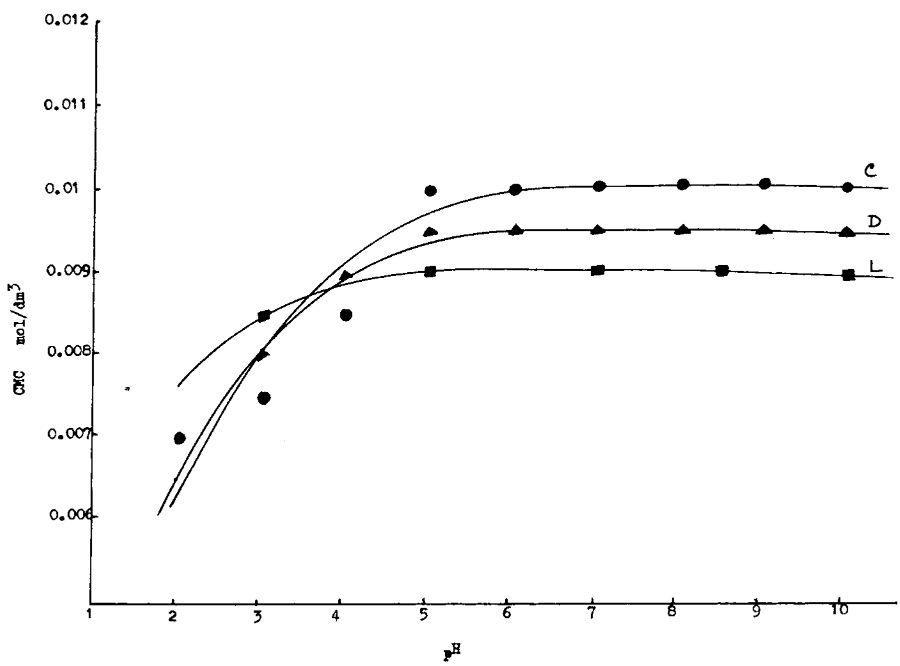

Fig. 1. CMC of SDS, determined by dye absorption (D), conductance (C), and light scattering (L) measurement determined at various pHs.

TABLE II
CMC's of SDS for Various Workers

Method	CMC (mol/dm^3)	Authors
Light scattering	0.008125	Mysels and Princen[6]
Light scattering	0.008	Tartar[7]
Light scattering	0.008	Oko and Venable[8]
Light scattering	0.008	Parfitt and Wood[9]
Conductance	0.00827	Shirahama and Kashiwabara[10]
Spectral-dye	0.00163	Gin and Harris[11]
Conductivity	0.004	Gin and Harris[11]
Stopped blow (spectral dye)	0.0057	Yasunaga, Takada, and Harada[2]
Dye absorption	0.0095	Present work
Conductivity	0.01	Present work
Light Scattering	0.09	Present work

the charge heads by decreasing the charge density on the surface of the micelle, thus changing the stability of micelle.

Klevens and Raison[12] measured the effect of pH on the CMC of perfluoro hexancic acid for various mole fractions of acid in mixture of acid and its salt using spectral-dye method. A marked change in CMC with pH was observed in the case of perfluorohexanoic acid. Although the present study does not go to such a low pH, the results are approximately similar to Klevens and Raison.[12]

It may be concluded that, within experimental error, CMC is independent of pH between 5 and 10 and is dependent below pH 4.

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