Spectrophotometric determination of critical micelle concentration of surfactants with dye indicators

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The absorbance of a series of mixtures of dye-surfactant solutions with dye concentration constant and increasing surfactant concentration has been measured. The $\lambda_{\text{max}}$ against surfactant concentration show either maximum or minimum corresponding to CMC of the surfactants which can be explained on the basis of micellisation and solubilization or the formation of adsorption aggregates of dye surfactants.

It is believed that micelle exists in equilibrium with monomer molecules or ions$^1$. Many dyes, polynuclear hydrocarbons, proteins and lipophilic substances are stabilized in presence of micelles, while displaying marked spectral and colour changes$^2$.$^-^4$. It has also been reported that the maximum colour changes occur when the charge on the detergent micelle is opposite to that of the indicator ions in the study of the effects of anionic, cationic and non-ionic surfactants. The addition of relatively small amount of ceteryltrimethylammonium bromide or cetaryltrimethylammonium bromide to alkaline blue solution of methyl thymol blue causes marked colour changes representing dissociation of the blue solution.$^5$

Fluorescence studies have indicated that initially both cationic and non-ionic surfactants bring about a decrease in fluorescence intensity of ethyl eosin which increases with further addition of surfactant$^6$. A considerable work on micellisation and aggregation of block copolymers and other surfactants has been recently done by means of light scattering, viscosity and fluorescence quenching measurements$^7$.

In the present note the absorbance of the pure dye solution has been measured as the standard and then the absorbance at this $\lambda_{\text{max}}$ in each case of dye-surfactant system measured with the increase in surfactant concentration, dye concentration being kept constant. When such absorbance is plotted against increasing surfactant concentration, the graphs indicate maxima or minima corresponding to the respective CMC values of the surfactants.

Experimental

A Shimadzu digital double beam spectrophotometer UV 150 was used for spectral measurements. The surfactants selected were: cationic-cetyltrimethylammonium bromide (CTAB), tetradecyltrimethylammonium bromide (cetramide); anionic-sodium oleate (Na-oleate); sodium cholate (Na-cholate) and sodium dodecyl benzene sulphonate (Na-DBS); non-ionic-triton X-100 and tween-80. The dyes under investigation were: cationic-malachite green, crystal violet, methylene blue; anionic-eosin, methyl orange, amaranth; non-ionic-fluorescence and 2,4-dichlorofluorescein.

Results and discussion

When both the surfactant and dye bear the same charge, the absorbance against increasing surfactant concentration rises rapidly reaching a maximum. As the surfactant concentration approaches CMC value with the formation of micelles, dye aggregates will be dissociated from polymeric to monomeric form and solubilization of dye will increase rapidly due to micellization; thus the intensity will reach maximum at CMC. However, with further increase in surfactant concentration colloidal particles (called neutral colloid) are formed with consequent aggregation and adsorption of dye molecules resulting in decrease in the absorbance; the maximum intensity indicating CMC value of the surfactant (Fig. 1A, a - d).

When the dye and surfactant are oppositely charged, dye surfactant aggregates will be formed due to preferential interaction resulting in decrease of the absorbance below CMC. However, with increasing surfactant concentration, micelle formation will progressively increase, resulting in disaggregation and also solubilization of dye molecules. This will bring about an increase in absorbance reaching a limiting value. The transition stage, the minimum in the graph is indicative of CMC of the surfactant (Fig. 1A, e - h). In case, the surfactant is anionic and dye non-ionic, the curve shows increasing intensity reaching a peak value and then resulting in decrease with increasing surfactant concentration. However, when the surfactant is cationic and dye non-ionic, there is first minimum and then increase in intensity.
The electrokinetic studies have indicated that anionic agents make electrokinetic potential at the interface more negative, while cationic agents make it less negative or even positive. Therefore, correlating adsorption with change in potential, cationic agents being adsorbed strongly, show decrease in intensity before CMC, while anionic agents show increase in intensity before CMC due to lesser adsorption caused by both micellization and solubilization. Tween-80 shows an increase in the absorbance before CMC against anionic methyl orange, while triton X-100 shows decrease in intensity before CMC against cationic malachite green, in accordance with previous results (Fig. 1B, d, e).

As seen from plots and Table 1, it is observed that using absorbance of the solution at $\lambda_{\text{max}}$, the CMC values of the surfactants come out within narrow range in almost all the cases, exception being that of tween-80.

Acknowledgement
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References

Table 1—Critical micelle concentration values

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Literature</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTAB</td>
<td>6.8 x 10^{-5} M to 2.0 x 10^{-4} M</td>
<td>1.5 x 10^{-3} M</td>
</tr>
<tr>
<td>Cetramide</td>
<td>0.9 x 10^{-3} M to 2.0 x 10^{-3} M</td>
<td>3.5 x 10^{-3} M</td>
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<tr>
<td>Na-DBS</td>
<td>1.0 x 10^{-3} M to 0.4 x 10^{-3} M</td>
<td>4.2 x 10^{-3} M</td>
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<tr>
<td>Na-cholate</td>
<td>2.5 x 10^{-3} M to 2.5 x 10^{-3} M</td>
<td>5.0 x 10^{-3} M</td>
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<tr>
<td>Na-oleate</td>
<td>0.8 x 10^{-3} M to 2.2 x 10^{-3} M</td>
<td>2.64 x 10^{-3} M</td>
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<tr>
<td>Triton X-100</td>
<td>1.5 x 10^{-4} M to 2.4 x 10^{-4} M</td>
<td>3.2 x 10^{-4} M</td>
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<tr>
<td>Tween-80</td>
<td>4.2 x 10^{-4} M to 7.0 x 10^{-4} M</td>
<td>4.0 x 10^{-4} M</td>
</tr>
</tbody>
</table>

*Adapted from: Critical micelle concentration of aqueous surfactant systems by P Mukharji and K J Mysels (NSRDS-NBS 36).
*Adapted from: Customer/Technical Service (Sigma’ Chemical Company, St. Louis, USA), 1989.