Spectroscopic Study of Cationic Hemicyanine Dyes in Lithium Dodecyl Sulfate Solution

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Hemicyanine dyes are effective voltage sensitive probes in biomembranes (Loew *et al* 1979; Ephardt and Fromherz 1989). The probing of rapid changes of electrical potential in biological membrane has been studied in the light of spectroscopic behaviour of these dyes (Ephardt and Fromherz 1993). The physical behaviour of surfactant micelle can be viewed upon as a pseudo model for biomembranes to study the interactions of biological systems with various additives, for instance anesthesiatics.

Unlike homogeneous solvents, micelles posses a gradient of polarity, ranging from polar interfacial area to non-polar micellar interior (Heindl *et al* 1993). The solubilization of an additive, therefore, is affected not only by the charge present on the additive but also depends upon its hydrophobicity (Shah *et al* 1998a). Previously, we studied the interactions of both zwitterionic and cationic hemicyanine dyes with various surfactant systems (Shah and Awan 1996; Shah *et al* 1997; Shah *et al* 1998a; Shah *et al* 1998b). The present work describes the spectroscopic behaviour of homologous cationic hemicyanine dyes (Fig 1) in lithium dodecyl sulfate (LDS) solutions. This involves, examining the effect of increasing surfactant concentrations on the electronic spectra of the dyes and determination of approximate number of dye molecules incorporated into a single micelle.
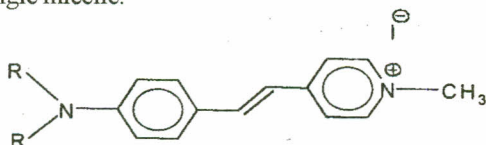
Fig 1. Hemicyanine dyes (1 R = CH_3, 2 R = C_2H_5, 3 R = C_3H_7, 4 R = C_4H_9).

Ultraviolet-Visible absorption spectra of the hemicyanine dyes, 1-4 (Shah *et al* 1998a) with and without lithium dodecyl sulfate (Fluka) were recorded on Shimadzu double beam UV-265 type spectrometer. The electronic spectra of 1.0×10^{-5} mol dm^{-3} dye solutions containing surfactant in the concentration range 10^{-3} to 10^{-2} mol dm^{-3} were recorded at 25.0 ± 0.1 °C. The critical micelle concentration (CMC) of lithium dodecyl

sulfate (LDS) was determined from the plot of specific conductance versus surfactant concentration. The specific conductance was precisely measured with Microprocessor Conductivity Meter (WTW), LF 2000/C, Germany at 25.0 °C.

Fig 2 shows the effect of increasing surfactant concentration (C_s) on the λ_{max} values of the dyes (**1-4**). In the premicellar region, i.e., at very low surfactant concentrations, a blue shift is observed in the electronic spectra of the dyes (**2-4**). This blue shift may occur due to complexation of additive dye with the negatively charged head of the surfactant (Reeves *et al* 1973; Minch and Shah 1979). The magnitude of this blue shift is greater for more hydrophobic dyes. This indicates that the formation of complex is favoured by the increasing hydrophobicity, i.e., the dye molecule orients itself into more favourable position to interact with the surfactant when it contains longer dialkyl chains as in the case of dye **4**.

Near its critical micelle concentration (CMC), beyond which the surfactant molecules self associates to form clusters or micelles, the increasing concentration of LDS caused red shift in the electronic spectra of the dyes (**1-4**) which shows a continuous change of environment around the oriented chromophore of the dyes. When the concentration of the surfactant (LDS) is well above its CMC, the values of λ_{max} become nearly constant, showing the incorporation of large number of dye molecules within the micelles of LDS (Minch and Shah 1979). In case of less hydrophobic dyes **1** and **2**, the λ_{max} values doesn't become uniform even in the micellar region of the surfactant. This accounts for the fact that the less hydrophobic dyes are not completely solubilized into the surfactant
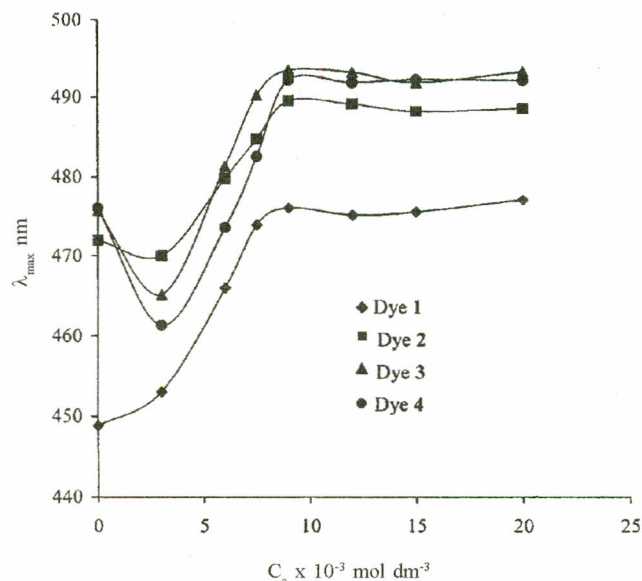

Fig 2. Effect of LDS on λ_{max} of cationic hemicyanine dyes.

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Table 1

Relation between experimental data and approximate number (n) of dye molecules incorporated per micelle at $C_s = 9.0 \times 10^{-3}$ mol dm^{-3}

Dye	R	A_o	$\varepsilon_m \times 10^3$ dm^3 mol^{-1} cm^{-1}	$C_m \times 10^{-6}$ mol dm^3	n
1	CH_3	0.106	23.9	8.72	5
2	C_2H_5	0.218	35.8	9.86	6
3	C_3H_7	0.277	42.6	9.80	6
4	C_4H_9	0.291	46.3	9.82	6

micelles. Since the strong interaction present between the negative head of the surfactant and the positively charged pyridinium moiety of the dye does not allow the dye molecules to penetrate deeply into the micelles. Therefore, most of the time the dye molecules remain oriented near the surface of the micelles and hence absorb the light more favourably than in the bulk of the aqueous solution similar to merocyanine dyes (Minch and Shah 1979).

The approximate number of the dye molecules incorporated into a single micelle can be calculated by using the following equation (Miyashita and Hayano 1981; Wang and Verrall 1994)

$$n = \frac{C_m}{M}$$

where C_m is the concentration of the dye solubilized within the micelles and the micellar concentration M can be computed as follows

$$M = \frac{C_s - CMC}{N}$$

where C_s is the total surfactant concentration and N is the mean aggregation number of the surfactant micelles, which is taken as reported, i.e., 63 (Leibner and Jacobus 1997).

The concentration of solubilized dye (C_m) is determined by using the following relation (Minch and Shah 1979)

$$C_m = \frac{A_o - A}{\varepsilon_o - \varepsilon_m}$$

where A_o is the absorbance of the dye in the absence of surfactant, A is the absorbance at the same wavelength in the presence of surfactant. The molar extinction coefficient, ε_o, is calculated from A_o and ε_m is determined at higher surfactant concentration above CMC, where the absorbance of the dye-surfactant solution becomes nearly constant.

Table 1 shows some experimental and calculated data including the number of dye molecules incorporated per micelle at 25.0 °C. Unexpectedly the increasing hydrophobicity of the dyes showed insignificant effect on the number of dyes molecules incorporated per micelle. This can be explained by keeping in view that the dye hydrophobicity, even in the case of more hydrophobic dye **4** is not high enough to overcome the electrostatic interactions present between the surfactant head group and the cationic dye molecules. Therefore, the dye molecules are present most of the time near the interfacial region of the micelles.

Key words: Anionic surfactant, Hydrophobic interactions, Hemicyanine dyes.

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