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Dye–surfactant interaction: chain folding during solubilization of styryl pyridinium dyes in sodium dodecyl sulfate aggregates

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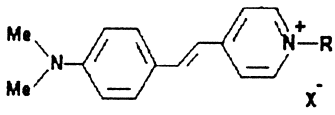
Abstract

Cationic dyes are known to interact with membranes and, therefore, are used as membrane probes. The alkyl chains of the dyes play a role in modifying the environment of the chromophore and affect the nature of interaction with the micelle. A number of cationic dyes with varying alkyl chains (C_1 to C_{18}) have been synthesized and their interaction with sodium dodecyl sulfate (SDS) is reported. From the absorption, fluorescence spectra and binding constant values it has been proposed that: (a) C_1–C_8 dyes solubilize in the micelle and the chromophore occupies a methanolic/ethanolic environment, (b) C_{10}–C_{14} dyes exist both as an extended monomer and as folded species in presence of SDS, which is reflected in two Gaussian peaks, (c) the experimentally obtained absorption spectra for C_{16} and C_{18} dyes can be explained by three Gaussian peaks due to monomer ⇋ dimer in the absence of surfactant and two such peaks due to monomer and folded monomer in the presence of surfactants. The binding constant and fluorescence intensity values support this proposition.

Keywords: Solubilization; Cationic dye; Chain folding; Hydrophobic patch; Binding constants; Surfactant

1. Introduction

Transportation of various solutes through cellular membranes has generated interest in studying the structure of carrier proteins linked with membranes. Cell membranes have charged interfaces separating the water compartments by a hydrophobic sheath formed by the tails of lipid bilayers. *N*-methyl-4-(*p*-*N*, *N*-dimethylamino styryl) pyridinium iodide (**I**, $n = 1$) in 10% MeOH–H_2O is found to stain chromatin material in laboratory mouse indicating its capacity to penetrate cell membranes [1]. The proteins containing both hydrophobic and hydrophilic groups orient themselves to form intrinsic, extrinsic or transmembrane proteins [2]. Extrinsic proteins are exposed to water, whereas, intrinsic proteins are buried in lipid membrane where the protein globule has a hydrophobic coat of its own.

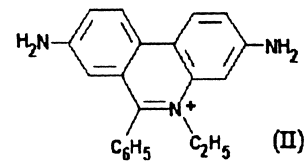


(I)

X = Br, I (R = CH_3)

R = C_nH_{2n} (n = 1, 3, 5, 6, 8, 10, 12, 14, 16, 18)

Sodium dodecyl sulfate (SDS) in aqueous medium forms micelle which mimic biological membrane system as a model of globular protein and capable of solubilizing hydrophobic molecules resulting in a high local concentration. Interaction of various solutes with the micellar phase and encapsulation of molecules inside micelle are studied as models to see the nature of interaction between the anionic phosphate groups of DNA and cationic heterocyclic dyes such as ethidium ion (**II**) [3].



(II)

We present here a spectral study of cationic dyes (**I**) with systematic structural variation in the chain in presence of SDS micelle and the surfactant assisted topological change occurring in its long quaternary chain.

2. Experimental

2.1. Materials

N-alkyl-4- (*p*-*N*,*N*-dimethylamino styryl) pyridinium bromides were prepared by the method reported earlier

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Table 1
Characterisation of data of the dyes (C_1–C_{18})

Carbon chain in the dye	Molecular formula	Melting point (°C)	Yield (%)	%C Found (Calc.)	%H Found (Calc.)	%N Found (Calc.)
C_1	$C_{16}H_{19}N_2I$	256	84	52.32 (52.47)	5.13 (5.23)	7.57 (7.65)
C_3	$C_{18}H_{23}N_2Br$	272	75	61.93 (62.25)	6.47 (6.68)	7.93 (8.07)
C_5	$C_{20}H_{27}N_2Br$	254	70	63.72 (64.0)	7.04 (7.25)	7.31 (7.46)
C_6	$C_{21}H_{29}N_2Br$	236	70	64.42 (64.78)	7.41 (7.50)	6.88 (7.19)
C_8	$C_{23}H_{33}N_2Br$	232	60	65.89 (66.18)	7.62 (7.97)	6.52 (6.71)
C_{10}	$C_{25}H_{37}N_2Br$	234	65	67.11 (67.40)	8.18 (8.37)	6.02 (6.29)
C_{12}	$C_{27}H_{41}N_2Br$	228	65	68.15 (68.48)	8.38 (8.73)	5.57 (5.91)
C_{14}	$C_{29}H_{45}N_2Br$	239	60	68.91 (69.44)	8.65 (9.04)	5.13 (5.58)
C_{16}	$C_{31}H_{49}N_2Br$	230	75	69.88 (70.19)	9.21 (9.33)	5.10 (5.29)
C_{18}	$C_{33}H_{53}N_2Br$	240	70	70.61 (70.93)	9.21 (9.58)	4.71 (5.02)

[4,5]. 4-Methyl pyridine was quaternized with alkyl bromide of varying chain length and was then condensed with *p-N,N*-dimethylamino benzaldehyde in ethanol in the presence of one drop of piperidine. The reaction mixture was concentrated by evaporation of ethanol. Red solid was separated by cooling on ice. The product was crystallized from absolute ethanol. Purity of the compound was checked by TLC (silica gel, eluent mixture of methanol–acetone, 3 : 1 v/v) and the extinction coefficient after each crystallization. Generally, 2–3 crystallizations were required for obtaining a constant value of molecular extinction coefficient. The analytical data of the dyes are given in Table 1. The dyes are referred to as C_n according to the number (n) of carbon atoms in the alkyl chain (**I**).

Sodium dodecyl sulfate (SDS, Sisco-Chem, spectroscopic grade) was crystallized twice from ethanol and dried in vacuo over P_2O_5. Triple distilled water was used throughout the experiment.

2.2. Spectroscopic measurements and techniques

A concentrated (ca. 1 mM/l) stock solution was prepared separately for each dye by dissolving required amount of the dye in methanol. The solution for spectral measurement was prepared by adding 0.1 ml of the above stock solution to a 5 ml volumetric flask containing freshly prepared solution of the surfactant in triply distilled water. Aliquots (3 ml) of these solutions were taken in quartz cuvettes thermostated at 25°C. Absorption spectra were obtained on Shimadzu 160 spectrophotometer and emission spectra were obtained on a Shimadzu RF-5000 spectrofluorophotometer. The broad absorption spectra were fitted with two and three Gaussians respectively, with the help of Gaussian curve fitting programme to study the location sites of dyes in aqueous micellar solution.

3. Results

We have measured the absorption spectra and emission spectra of the dyes in 2% methanol–water (v/v) and in microheterogenous micellar media like anionic SDS.

3.1. Absorption spectra

It is seen that the λ_{max} values of C_1–C_8 dyes increase on addition of SDS to a plateau with a break at 4.2 mM of SDS, which is taken as the CMC of SDS (Fig. 1). This value of CMC however, is lower than the reported value (8.1 mM) of SDS [6], may be because of electrostatic interaction with the dyes. The absorption bands of C_{10} to C_{18} dyes are broad and are not symmetric. In order to quantify the change, the spectra have been fitted as a sum of Gaussian peaks with the help of a Gaussain curve fitting programme. Curve fitting with two Gaussians (three in few cases) yields a solution with a minimum amount of error. The half line widths, area under the curve and height of each peak with corresponding frequencies (ν_{max} and λ_{max}) are given in Table 2 for different dyes. Representative spectra of C_{12} dye indicating the observed peak and Gaussian peaks are given in Fig. 2. On the basis of absorption data the dyes can be placed in three categories: (i) C_1–C_8 dyes absorb at about 450–455 nm in the absence of surfactant and show a bathochromic shift to about 485 nm at [SDS] > CMC (Fig. 1). The C_8 dye shows broad and asymmetric spectrum when [SDS] < CMC, which on deconvolution (Fig. 3) give two gaussian peaks at 493 and 436 nm, (ii) C_{10}–C_{14} dyes show two Gaussian peaks at 461–471 nm and 392–420 nm in the absence of SDS. On addition of surfactant the peaks undergo bathochromic shift, (iii) the nature of spectra of C_{16} and C_{18} dyes in the absence of surfactant are same, which are explained by three Gaussian peaks at 472, 418 and 403 nm (Fig. 4 for C_{16} dye). On addition of SDS, both 472 and 418 nm peaks undergo bathochromic shift and the 403 nm peak no longer exists (Fig. 5). Since the dyes are not soluble in hydrocarbon solvents, λ_{max} values in butanol–hexane (or decane) mixtures were determined and a plot of λ_{max} vs. mol% of butanol gives a straight line which on extrapolation to zero butanol concentration gives a λ_{max} value of about 441 nm (Fig. 6).

On the basis of the solubility behaviour in 2% MeOH–H_2O (v/v) solvent system and SDS surfactant solution in 2% MeOH–H_2O (v/v) the dyes can be classified into four categories: (i) C_1 dye is soluble in water and at all concentration of SDS, (ii) C_3 and C_5 dyes are soluble in water

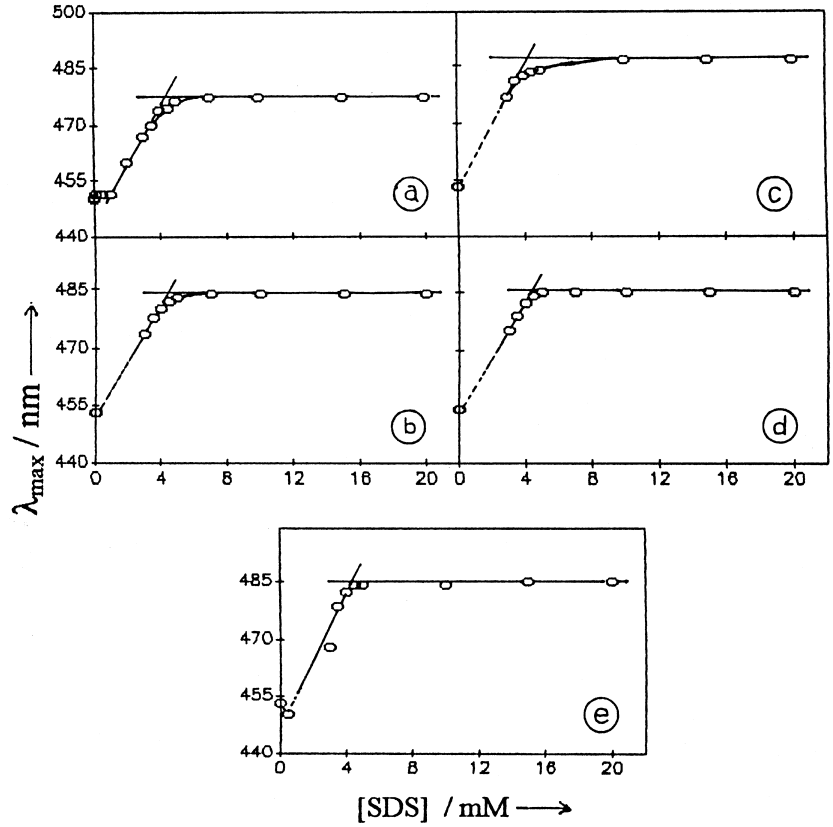


Fig. 1. Plot of λ_{max} of the dyes vs. [SDS]: (a) C_1, (b) C_3, (c) C_5, (d) C_6, (e) C_8. Turbidity Zone (– – –); [Dye] = 0.02 mM.

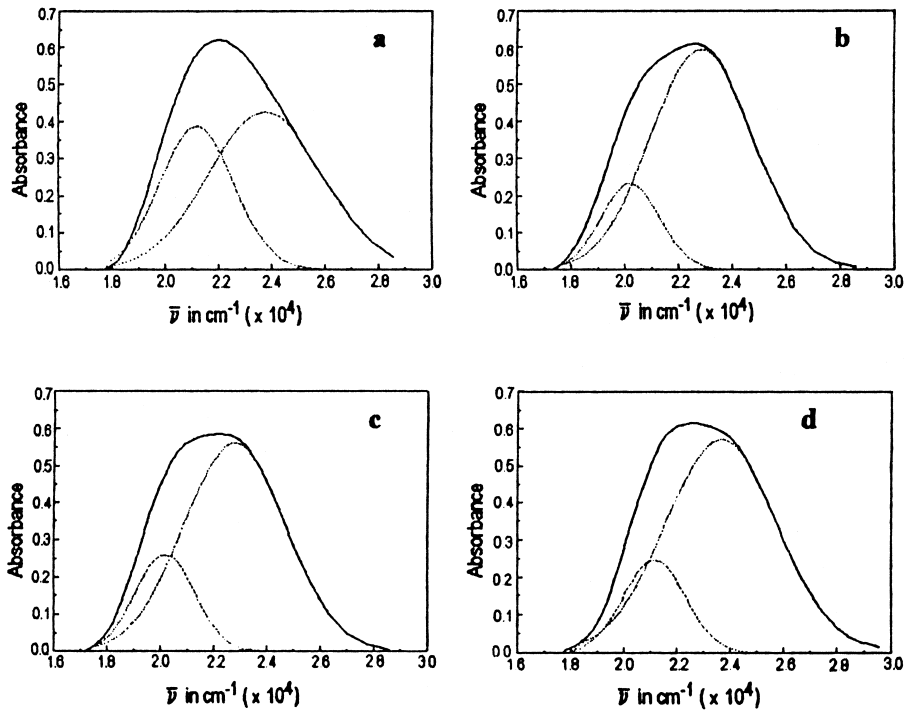


Fig. 2. Deconvoluted absorption spectra of C_{12} dye in SDS. ([SDS]: (a) 0, (b) 1, (c) 5 and (d) 20 mM respectively; [Dye] = 0.02 mM).

Table 2
The area of the curve, half band width, absorption maxima and height of the peak obtained from Gaussian curve fitting analysis of absorption spectra

Dyes (C_n)	SDS (mM)	Peak	Area	Width	$\bar{\nu}$ (cm^{-1})	λ_{max} (nm[a])	Height
C_{10}	0	1	1236.1	2815.2	21303	469	0.350
		2	2209.8	4549.8	23909	418	0.387
	1	1	499.0	2249.1	20274	493	0.177
		2	2123.6	3763.0	22934	436	0.450
	5	1	978.01	2322.6	20247	493	0.336
		2	1938.9	3881.5	22605	442	0.398
	20	1	1565.9	2575.3	20390	490	0.485
		2	1896.0	4383.3	22863	437	0.345
C_{12}	0	1	1338.3	2764.4	21202	471	0.386
		2	2282.5	4258.8	23792	420	0.427
	1	1	634.97	2175.7	20235	494	0.233
		2	2803.9	3767.3	22878	437	0.594
	5	1	725.66	2206.0	20181	495	0.262
		2	2681.4	3814.0	22791	438	0.561
	20	1	706.81	2267.5	20261	494	0.249
		2	2965.5	4142.6	22659	441	0.571
C_{14}	0	1	1551.4	3437.8	21673	461	0.360
		2	1411.8	5835.7	25454	392	0.193
	1	1	358.73	2155.2	20250	493	0.133
		2	2249.9	4056.5	22780	438	0.442
	5	1	441.68	2319.7	20278	493	0.155
		2	2460.1	4374.0	22784	438	0.449
	20	1	484.31	2270.0	20278	493	0.170
		2	2396.1	4585.9	22664	441	0.417
C_{16}	0	1	844.07	3131.0	21144	472	0.215
		2	472.46	2888.7	23913	418	0.130
		3	465.46	2651.3	24756	403	0.140
	1	1	556.44	2399.7	20288	492	0.185
		2	2330.2	4098.0	23250	430	0.453
	5	1	616.11	2259.5	20282	493	0.217
		2	2451.8	3857.9	22981	435	0.507
	20	1	582.22	2191.8	20204	494	0.212
		2	2524.5	4074.2	22898	436	0.494
C_{18}	1	1	309.88	2375.4	20398	490	0.104
		2	2421.7	4692.4	22998	434	0.412
	5	1	320.19	2387.3	20404	490	0.107
		2	2555.1	4797.5	22919	436	0.425
	20	1	265.88	2104.7	20347	491	0.100
		2	2570.3	4748.1	22806	438	0.432

[a] λ_{max} values have been calculated from $\bar{\nu}$.

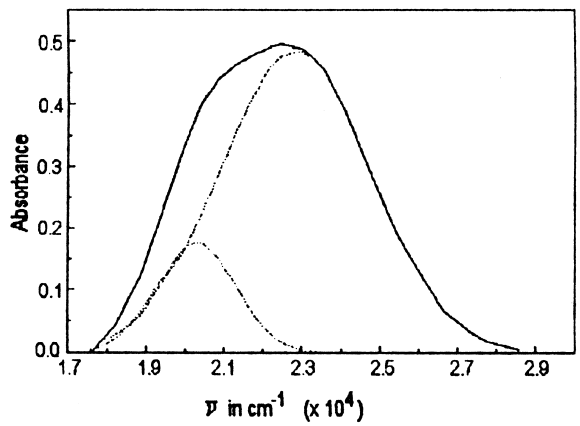


Fig. 3. Deconvoluted absorption spectra of C_8 dye in 1 mM of SDS.

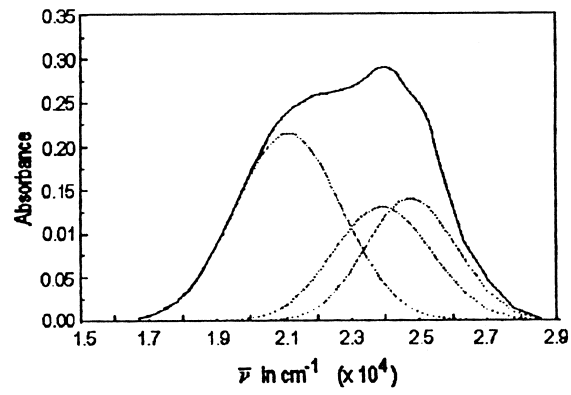


Fig. 4. Deconvoluted absorption spectra of C_{16} dye in 2% MeOH–water (v/v) system. [Dye] = 0.02 mM.

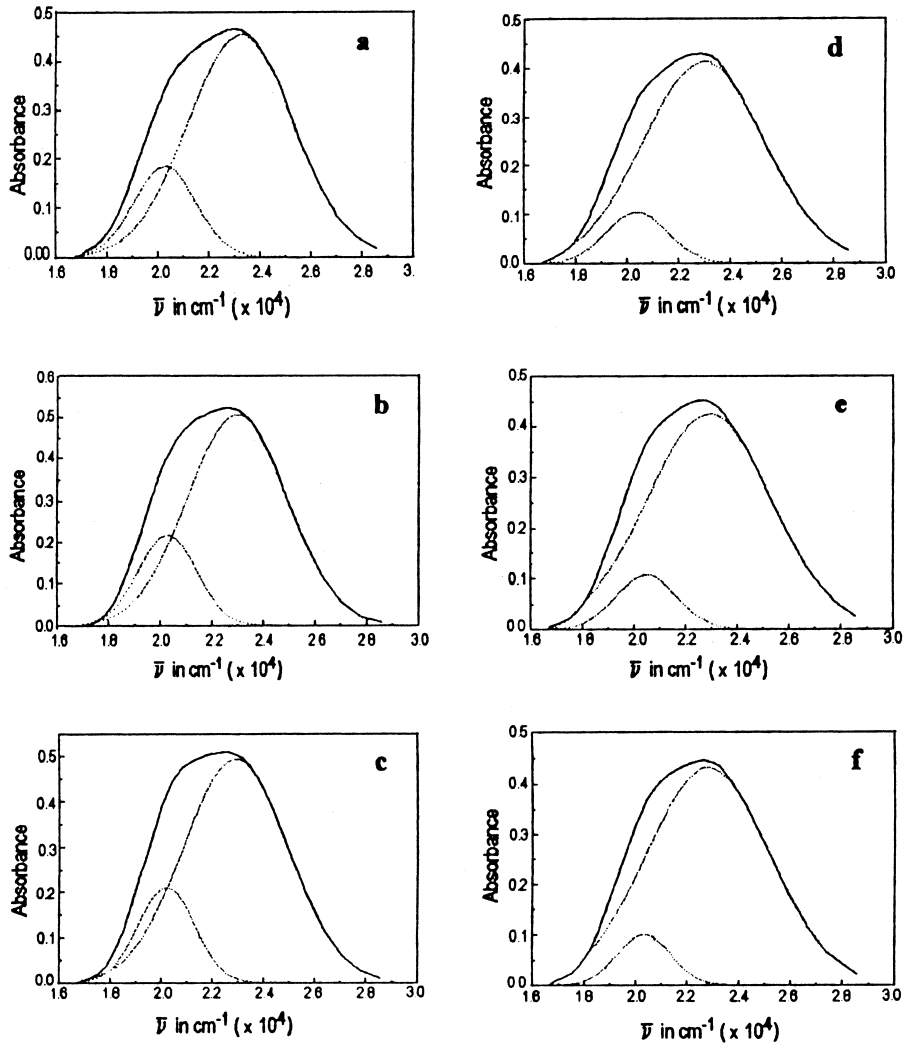


Fig. 5. Deconvoluted absorption spectra of C_{16} (a, b, c) and C_{18} (d, e, f) dyes in SDS. [SDS] = (a) 1 mM, (b) 5 mM, (c) 20 mM, (d) 1 mM, (e) 5 mM (f) 20 mM.

and form turbidity within a certain range of SDS concentration. On further addition of SDS complete solubilisation occurs, (iii) C_6–C_{12} dyes are insoluble in water, but are soluble in 2% MeOH–H_2O system. The solution in MeOH–H_2O exhibits a turbidity zone within a certain concentration range of SDS and then goes into complete solution on further addition of SDS, (iv) C_{14}–C_{18} dyes are insoluble in water and solution of these dyes in 2% MeOH–H_2O do not form any turbidity with SDS. The appearance of turbidity with C_3 to C_{12} dyes at [surfactant] < CMC (Table 3) is probably due to immobilization of the dyes

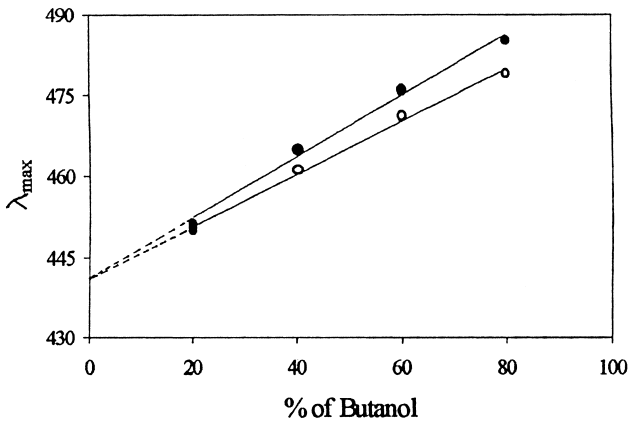


Fig. 6. Plot of λ_{max} vs. mol% of butanol of C_{10} dye in butanol–hexane/decane mixture. (○) butanol–hexane; (●) butanol–decane.

Table 3
Range of [SDS] for the turbidity zone along with the number of surfactant molecules required for the formation of an immobilised material

Dyes (C_n)	[SDS] in turbidity zone (mM/L)	Number of surfactant/dye molecules
C_3	0.06–2	3–100
C_5	0.06–2	3–100
C_6	0.02–1	1–50
C_8	0.02–0.1	1–5
C_{10}	0.02–0.05	1–2.5
C_{12}	0.02–0.03	1–1.5

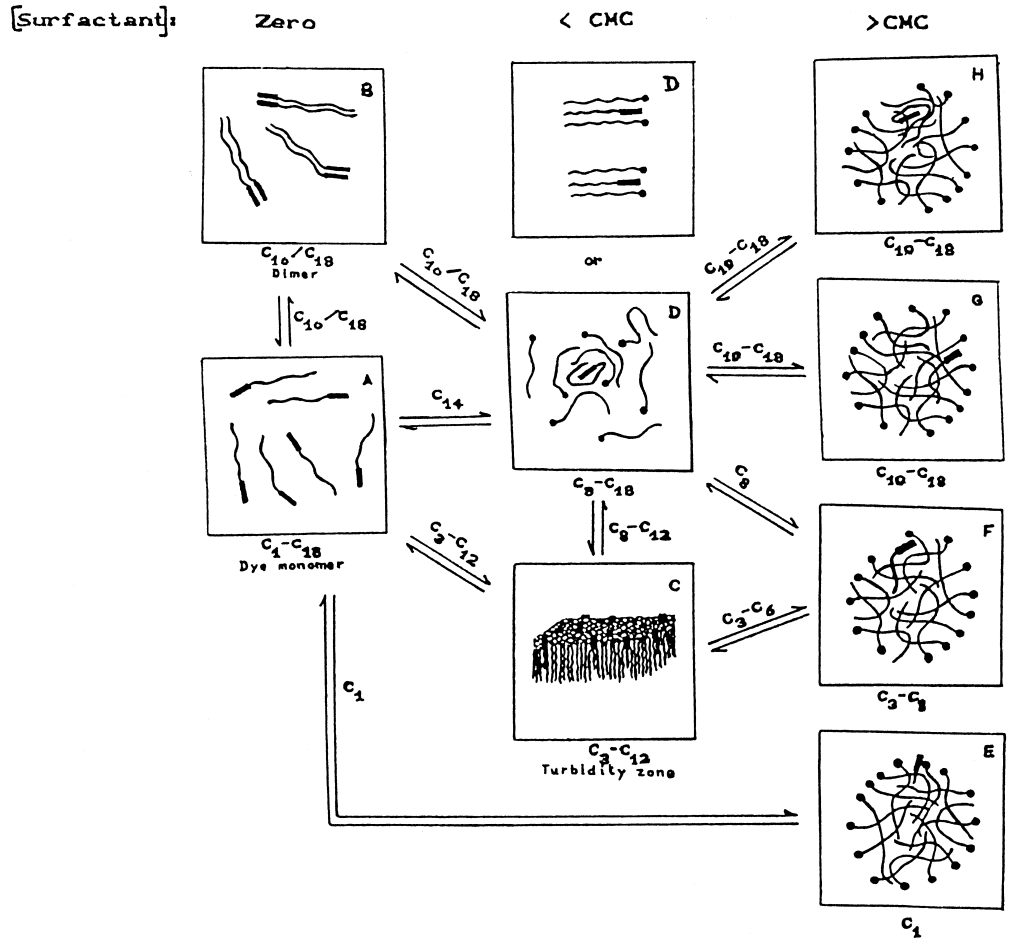


Fig. 7. Structural hierarchy of the dyes (C_1–C_{18}) in the presence of SDS. Cationic dye molecules with varying chain length: ▬∿∿∿ Surfactant molecules (SDS): ●∿∿∿.

(Fig. 7(C)) in SDS matrix resulting in partial or complete charge neutralization of the species. Oliveira et al. [7] have observed turbidity for cationic pyrene derivatives (Pyrinylmethyl tri-*n*-butylphosphonium bromide) in SDS and have explained it by proposing aggregation between the two. This situation is comparable to the formation of an ionic crystal. The number of surfactant molecules per dye molecule required for the formation of such a material, and the SDS concentration range for the turbidity zone are given in Table 3. The C_3 and C_5 dyes, being soluble in water, require a large number of surfactant molecules to be partitioned into the surfactant phase. As the solubility of the dye decreases with increasing chain length, the number of surfactant molecules required to form the turbidity zone decreases sharply.

3.2. Emission spectra

The influence of SDS on the emission intensity of the dyes is shown in Fig. 8. Linear curves are obtained with break points at 4.2 mM, which is same as that obtained from absorption spectra. The appearance of a single symmetric peak in the emission spectra of all the dyes clearly indicates the existence of a singular species in the excited state. On the basis of the λ_{em} values, the dyes can be categorized as: (i) C_1 to C_6 dyes show a constant λ_{em} value at 581 nm at all concentrations of SDS, (ii) C_8 to C_{14} dyes show a hypsochromic shift from 581 nm to about 560 nm followed by a bathochromic shift to about 578 nm, with increasing [SDS], (iii) C_{16} and C_{18} dyes under similar condition show a hypsochromic shift from 590–580 nm to 564–570 nm throughout the concentration range of SDS. Similarly, on the basis of the intensity of emission values the dyes can be classified as: (i) C_1 to C_{10} dyes show a shift in intensity from 8–9 in the absence of surfactant to 130–152 in 20 mM of SDS (Fig. 8(a–f)), (ii) the intensity values of emission of C_{12} to C_{14} dyes increase from 8–9 to 42–46 in the same range of SDS (Fig. 8(g–h)), (iii) C_{16} and C_{18} dyes show negligible intensity (0.1–0.5) in the absence of surfactant and the intensity increase to a value of about 17–18 at 20 mM of SDS.

The ground state association constant (K_M) for the association of the dye and the micelle to give the association species (MD) has been determined from the equilibrium.

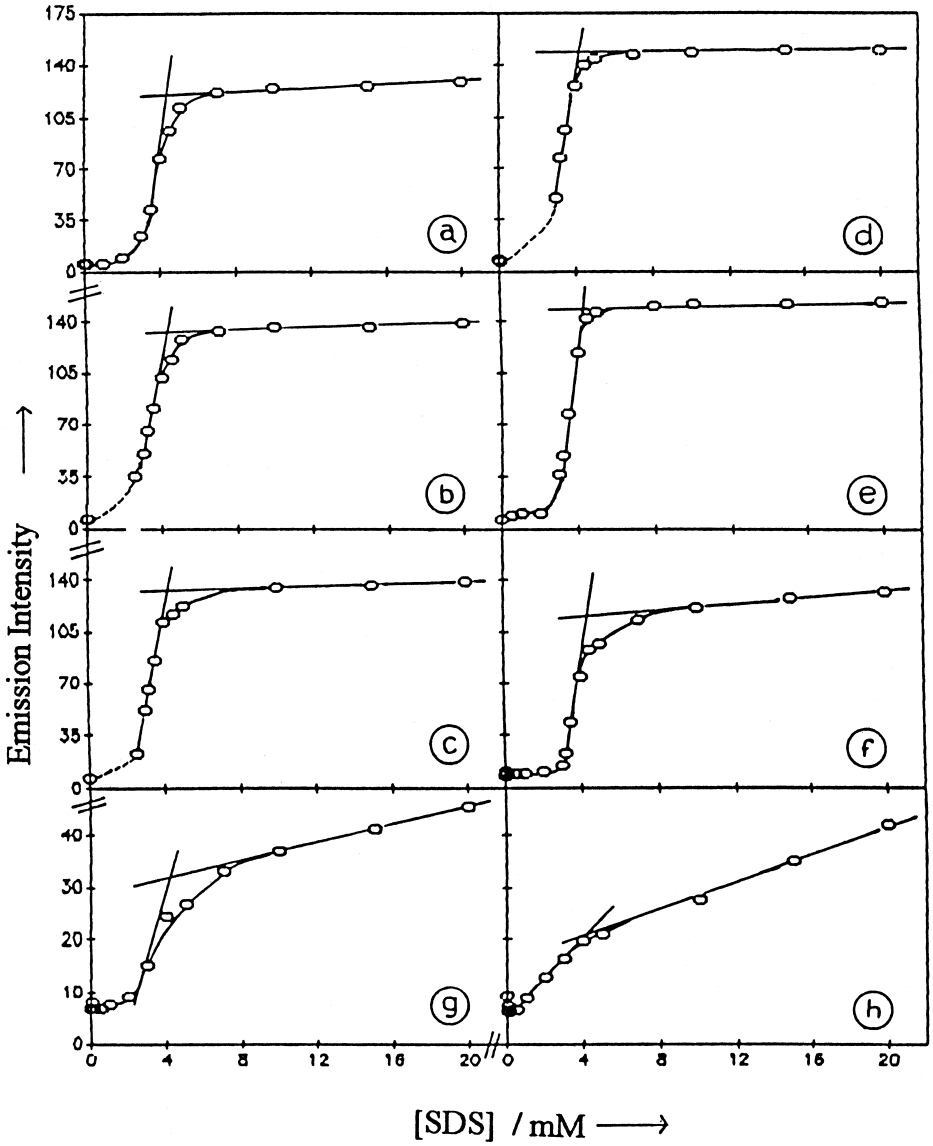


Fig. 8. Plot of fluoroscence intensity (I) of dyes vs. [SDS]: (a) C_1, (b) C_3, (c) C_5, (d) C_6, (e) C_8, (f) C_{10}, (g) C_{12}, (h) C_{14}. Turbidity zone (– – –); [Dye] = 0.02 mM.

$$M + D \overset{K_M}{\leftrightharpoons} MD$$

So,

$$K_M = \frac{[MD]}{[D][M]} \quad (1)$$

The photo events resulting in the excitation of D and MD are assumed to occur much faster than the time taken for the equilibrium to be attained. Since the dye molecules are distributed between bulk solvent and micellar phases, the fraction of micellized and aqueous solutes are given by $K_M[M]/(1 + K_M[M])$ and $1/(1 + K_M[M])$ respectively. Let I_t refer to the intensity of dyes (C_n) in a solution at a given concentration of micelle, I_m and I_w represent, respectively, the luminescence intensities in a micellized solute and of the solute where the interaction of the dye with surfactant starts, and [M] is the concentration of the micelle, calculated using [M] = ([S]-CMC)/N. The value of N for SDS is taken as 62 [6,8]. Then,

$$I_t = \frac{I_w}{1 + K_M[M]} + \frac{I_m K_M[M]}{1 + K_M[M]} \quad (2)$$

The association constant, K_M, has been calculated by using Eq. (2).

The observed intensity values at high and low micellar concentration approximate to I_m and I_w, respectively. Table 4 lists the binding constants for C_1 to C_{14} dyes with micellar SDS at 25°C.

The binding of a solute to an ionic micelle is electrostatic only when the strength of the interaction is determined by

Table 4
Association constant (K_M) of the different dyes with SDS micelles at 25°C and ratio of association constant of dayes (K_M) with respect to $K_{C_{14}}$

Dyes (C_n)	K_M in M^{-1} ($\times 10^5$)	$K_M/K_{C_{14}}$
C_1	1.65	23.6
C_3	1.52	21.7
C_5	1.76	25.1
C_6	4.27	61.0
C_8	4.41	63.0
C_{10}	0.65	9.30
C_{12}	0.34	4.90
C_{14}	0.07	1.00

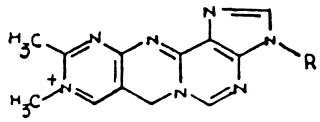
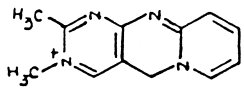
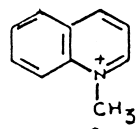
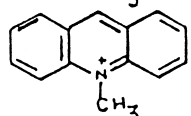
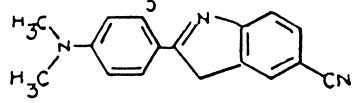
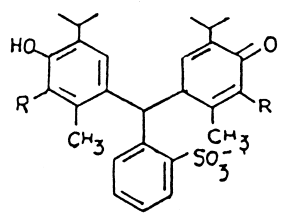
the charge density of the solute. The association constant of SDS micelles with some inorganic cations (purely electrostatic), organic molecules (hydrophobic) and some cationic organic molecules are given in Table 5.

4. Discussion

The styryl dyes are positively charged having alkyl chains with increasing hydrophobicity. Mishra et al. [5] have evaluated the length of the polyene chain of the chromophore of the dyes containing the positive charge to be about 12.1 Å. They have proposed dimerization of the C_{16} dye which explains the absorption maximum at 403 and 418 nm for C_{16} dye in the absence of surfactant. Various workers [9–12] have also attributed the hypsochromic shift in the absorption spectra to the dimerization of cyanine dyes.

The C_1 to C_8 dyes exist as monomers with λ_{max} values around 450–455 nm at the experimental concentration in 2% (v/v) methanol–water system (Fig. 7(A)). The bathochromic shift associated with C_1 to C_8 dyes on addition of surfactants and enhancement of emission intensity indicate the passage of the fluorophore from polar aqueous medium to a rela-

Table 5
Association constants of some inorganic ions, hydrophobic and organic cations with SDS micelles at/or near 25°C

		K, M^{-1}	Reference
1.	Ag^+	1.3×10^3	9
2.	Cu^{+2}	2.0×10^3	10
3.	Ni^{+2}	2.4×10^3	11
4.	Naphthalene	2.0×10^4	12
5.	Anthracene	4.0×10^5	12
6.	Pyrene	1.7×10^6	12
7.		$(9.69 \pm 0.31)10^3$	3
8.		$(1.86 \pm 0.06)10^3$	3
9.		4.80×10^4	3
10.		$(1.38 \pm 0.1)10^5$	3
11.		3.8×10^3	13
12.		R=Br 4.19×10^3 =H 0.485×10^3	14 14

tively nonpolar site in micellar environment. The C_1 dye ($\lambda_{max} = 478$ nm) has an environment corresponding to an $E_T(30)$ value of 57.5 (Fig. 7(E)) whereas that of C_3–C_8 dyes ($\lambda_{max} = 484$ nm) have a less polar environment ($E_T(30) = 52.4$) (Fig. 7(F)). The fluorescence intensity (Fig. 8) and the K_M values of C_1–C_8 dyes (Table 4) are in conformity with the current view that the longer the hydrophobic alkyl chain of the dyes, the deeper is their penetration into the hydrophobic interior of the micelle, and less polar is the solubilisation site. Maiti et al. [13] have found the average radius (hydrodynamic radius) of SDS to be 16.7 Å (20.7 Å). Recent studies [14–19] have revealed that the periphery of SDS micelles is a 'wet' shell of thickness 6–9 Å comprising of polar head groups, the counterions and considerable amount of water of less mobility of solvation dynamics in the 180–550 ps [20] time scale (pure water - = 310 fs [21]). Abraham et al. [22] have also reported that the SDS pseudophase is heavily hydrated. The absorption spectra of C_8 dye when [SDS] < CMC and that of C_{10} to C_{18} dyes in the presence and absence of surfactant can be explained by two (or three) Gaussian peaks. The emission intensity values of C_{12} to C_{18} dyes at 20 mM of SDS are far less than that of C_1 to C_{10} dyes indicating that the microenvironment around the fluorophores of C_{12}–C_{18} dyes are less polar than water. Since the extrapolated value of absorption maxima of the dyes in hexane/decane is 441 nm, it is proposed that a fraction of the dyes occupies a hexane-like environment and the other fraction occupies an environment of $E_t(30)$ value of 47–49.7.

The hexane-like environment in the surfactant assembly is provided by the 'dry core' of the micelle. The incorporation of the cationic dye into the 'dry core' would be against the attractive force of the micellar surface and further the long alkyl chain would experience steric effect [23] of the disordered 'dry core'. Just as a milliped retracts into a coil by a stimulation, the long chain of the dye, similarly, may be folded such that the chromphoric group enjoys a hydrocarbon-like environment. It is difficult to propose at this stage the exact nature of this conformation. Abraham et al. [22] have also noted that polar molecules are solubilized either in the micelle palisade layer or at the micellar surface. Our results show that the interface of the micelle is not homogeneous which is in conformity to the views of Almgren and Swarup [24]. Some molecules of the probe experience a hydrocarbon-like environment, and others, a polar environment at the micellar surface. This argument fits in to both Fromherz and Menger micelles with hydrophobic patches at the interface. Further addition of surfactant does not produce any perceptible change in the spectrum. The roughness of the micellar surface can be decreased by increasing the aggregation number and shape of the micelle, which can be ascribed by the addition of sodium chloride [25]. Sodium chloride is also known to denature an enzyme [26,27]. As expected, the extent of folding (436–441 nm) for C_{10}–C_{18} dyes decreases with respect to the extended species (492 nm) on addition of 0.2 M of sodium chloride. Mishra et al. [28] have assigned 472 nm peak to the monomeric, 418 and 403 nm peaks to the dimeric (Fig. 7(B)) species of the C_{16} and C_{18} dyes. The two and three Gaussian peaks for C_{10} to C_{18} dyes are, therefore, ascribed to the presence of monomer $\leftrightharpoons$ dimer in the absence of surfactant. With addition of surfactant a competition between homomolecular and heteromolecular interaction sets in, as a result, the dissociation of the dimer occurs resulting in a broadening of the spectrum, which separates into two Gaussian peaks (Table 2). These two species continue to exist till 20 mM of SDS.

As C_{10}–C_{18} dyes exist in two different states in SDS medium and in 2% (v/v) methanol–water system (C_{16} and C_{18} dyes in 2% (v/v) methanol–water system exists in three different states), the total peak area corresponding to the dye molecule in presence and absence of SDS is the sum of the peak area of different states of the dye. Thus, if we consider the individual peak areas to be G_1, G_2 and G_3 then the total peak area is given by

$$G_{Total} = G_1 + G_2 + G_3$$

If P_1 fraction corresponds to the monomer and P_2 and P_3 fractions correspond to the dimer or coiled form of the dye molecules respectively existing in various environments, then their values can be calculated from the following relations and are given in Table 6. It is interesting to note that P_2 (or $P_2 + P_3$) fraction is always higher than P_1 fraction.

$$P_1 = \frac{G_1}{G_T}; \qquad P_2 = \frac{G_2}{G_T}; \qquad P_3 = \frac{G_3}{G_T}$$

The binding properties of the cationic dyes are of intrinsic interest since their binding to SDS has both an electrostatic and a hydrophobic component. The cationic dyes have

Table 6
Fraction of the dye present in different environment of the SDS surfactant system

Dyes (C_n)	Fraction	SDS (mM)			
		0	1	5	20
C_8	P_1	–	0.16	–	–
	P_2	–	0.84	–	–
C_{10}	P_1	0.36	0.19	0.33	0.45
	P_2	0.64	0.81	0.67	0.55
C_{12}	P_1	0.37	0.18	0.21	0.19
	P_2	0.63	0.82	0.78	0.81
C_{14}	P_1	0.52	0.14	0.15	0.17
	P_2	0.48	0.86	0.85	0.83
C_{16}	P_1	0.47	0.19	0.20	0.19
	P_2	0.27	0.81	0.78	0.81
	P_3	0.26	–	–	–
C_{18}	P_1	0.48	0.11	0.11	0.09
	P_2	0.29	0.89	0.89	0.91
	P_3	0.23	–	–	–

hydrophilic head group of 12.1 Å length and hydrophobic chain length varying from 1–21 Å as the carbon chain changes from C_1 to C_{18}. Zolhewicz and Munoz [3] have observed that the presence or absence of the positive charge on the solubilizate has little influence on the magnitude of the binding constant to SDS. In the present case each dye has a delocalized positive charge and alkyl chain of increasing hydrophobicity. The K_M values instead of increasing with the carbon number decrease steeply for C_{10} to C_{14} dyes and are negligible for C_{16} and C_{18} dyes as compared to other dyes. If the Fromherz [29] model for the micelle is considered for the binding of the dye then the distribution of the dye not only occurs in the spherical ionic surface but also occurs in the hydrophobic pocket on the surface of the micelle. The distribution of these pockets in the micelle determines the penetration of the dye into the micelle. The Menger micelle [30] predicts the distribution of cationic dye in a large region surrounding the relatively small hydrophobic core. Our experimental results can be explained by both these models. The binding of C_1 to C_8 dyes at the interface is both electrostatic and hydrophobic in nature (Fig. 7(E) and Fig. 7(F)). The C_{10} to C_{18} dyes appear to exist in two different environments in the ground state when [SDS] < CMC, which is reflected in the absorption spectra (Table 2). These two environments are due to the folded or sandwiched form of one of the species with the surfactant (Fig. 7(D)) and presence of the other in a more polar environment of SDS. On further addition of SDS, micellisation occurs and one fraction of the dye most probably remains in a folded form to a large extent and occupies the hydrophobic patch of the micellar surface (Fig. 7(H)), and another in the polar region of the micellar surface (Fig. 7(G)). A surfactant-assisted folding process has also been reported by Maltesh and Somasundaran [31] while studying the interaction of PEG in the presence of SDS. Bao et al. [32] have proposed folding of the long alkyl chain of tetradecyl benzyl dimethylammonium chloride in the micellar structure by studying the hydrophobic interaction between pyrene and the tetradecyl compound. Saroja and Samanta [8] have proposed folding of the long alkyl chain of 11-(4-aminopthalimido) undecanoic acid to explain its location in the micelles. Similar folding phenomena of polymethylene chain in micellar environments is reported by Worsham et al. [33]. Since the folded form is expected to have a hydrophobic surface, the 'open structure' of the micelle adsorbs it at the hydrophobic patch of the surface rather than move deep into the micellar interior. The driving force behind such an arrangement is due to the ionic nature of the dye. A negligible binding constant indicates the decrease of both coulombic and hydrophobic force of attraction for C_{16} and C_{18} dyes. Zana et al. [34] have observed that spacers containing 8 methylene groups lie flat at the interface adopting a stretched conformation. This study, therefore is a unique example of surfactant-assisted folding phenomenon occurring in dyes containing long alkyl chains. However, the values of the association constant do not unambiguously state the localization sites of the dyes within the micelle.

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