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Interaction of *N*-alkyl styryl pyridinium dyes with TX-100 in aqueous medium: Role of the alkyl chain during solubilisation

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Abstract

Interaction of a series of *N*-alkyl styryl pyridinium dyes having varied alkyl chain (C_n) with nonionic surfactant (Triton X-100) solution has been studied by using absorption and emission techniques. The binding constants of the dyes (C_1–C_{18}) with the surfactant aggregates have been calculated and found to increase with increasing alkyl chain length of the dyes. A decrease in the CMC value of TX-100 in presence of the dyes with increasing chain length has been observed and the phenomenon is attributed to the increasing hydrophobicity of the additive. The relative $E_T(30)$ values of the local environment of the dyes in TX-100 micelles with respect to standard solvents have been determined. A solubilisation strategy of the micelle for the dyes has been reported where the cationic head group remains in the oxyethylene cage of the micelle and the hydrophobic tail remains buried in the micellar core due to pulling effect.

Keywords: Styryl pyridinium dyes; Alkyl chain; TX-100 micelle; Hydrophobicity; $E_T(30)$

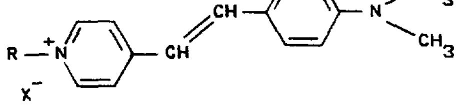
1. Introduction

Micelles have the potential to mimic membrane system and to interact with various neutral and charged molecules. We have studied the solubilisation characteristics of a number of *N*-alkyl styryl pyridinium dyes of varying hydrophobicity in cationic and anionic surfactant (CTAB and SDS) systems [1,2]. The difference in spectral behaviour of the dyes in the ionic surfactants has been explained by proposing a hydrophobic force field (F_H) in and around the micelles and coiling–decoiling phenomenon of the dyes. Besides the dyes are found to form a turbid zone in various concentration of these surfactants. Generally, for hydrocarbons and polar compounds, the order of solubilisation capacity of micelles appears to be nonionic > cationic > anionic, for surfactants with the same carbon chain length [3]. The interface of nonionic micelle provides a large space to entrap the dye molecules by adsolubilisation. Parida and Mishra [4] have recently studied the adsolubilisation behaviour of styryl pyridinium dyes in polyethylene glycol (PEG) adsorbed to silica surface and have found that the dyes are encapsulated inside the cage of the PEG unit. Hence the present study is proposed to study the interaction of a series of cationic dye (*I*) with TX-100 micelle and to see the effect of alkyl chain length during solubilisation.

2. Experimental details

2.1. Materials

N-Alkyl-4-(*p*-*N*,*N*-dimethylamino styryl) pyridinium bromides were prepared by the method reported earlier [5,6]. The dyes are referred to as C_n according to the number (n) of carbon atoms in the alkyl chain (*I*).



(I) $X^- = Br^-, I^-$ ($R = CH_3$)

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

Triton X-100 (Qualigen, spectroscopic grade) was used as received. Triple distilled water was used throughout the experiment.

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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 added to 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.

3. Results and discussion

3.1. Absorption spectra

Unlike SDS and CTAB in which turbidity appears within a narrow concentration range of the surfactants during the solubilisation process of the dyes [1,2], TX-100 does not produce any turbidity. All the dyes except C_{16} and C_{18} show λ_{max} values within 450–457 nm in 2% (v/v) MeOH–H_2O. Both the C_{16} and C_{18} dyes exhibit λ_{max} values at 416 nm with shoulders at 400 and 475 nm (Fig. 1). On dilution the structureness of the spectrum disappears and a broad peak is obtained (Fig. 1). The characteristic of the spectrum does not alter (Fig. 1) on increasing the concentration of the dyes. Sahay et al. [7] have characterized the peak at 400 and 475 nm due to the dimer and monomer of the dyes respectively. Hence the peak at 416 nm with a shoulder at 400 nm can be ascribed to the dimer of the dyes. These dyes remain in the dimer form mostly because of the hydrophobic interaction of the long alkyl chains. The shoulder at 475 nm indicates a relatively low concentration of the monomer in the solvent system. On addition of TX-100 the peak due to the monomer only is obtained at 473 nm which indicates the interaction of the monomeric form of the dyes with the hydrophillic head group of the surfactant resulting in the shift of the dimer $\rightleftharpoons$ monomer towards the monomer. Further addition of TX-100 results in a bathochromic shift in the absorption maximum of

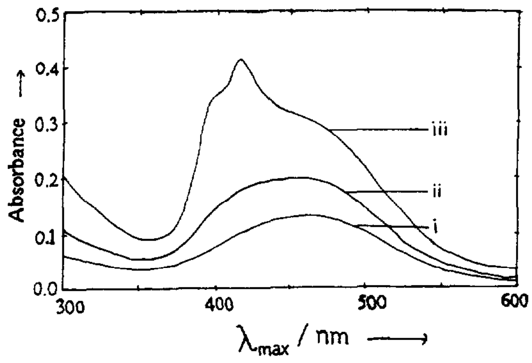


Fig. 1. Absorption spectra of C_{16} dye in 2:98 (v/v) MeOH–H_2O system at 25°C. [dye] = (i) 0.005, (ii) 0.01 and (iii) 0.02 mM.

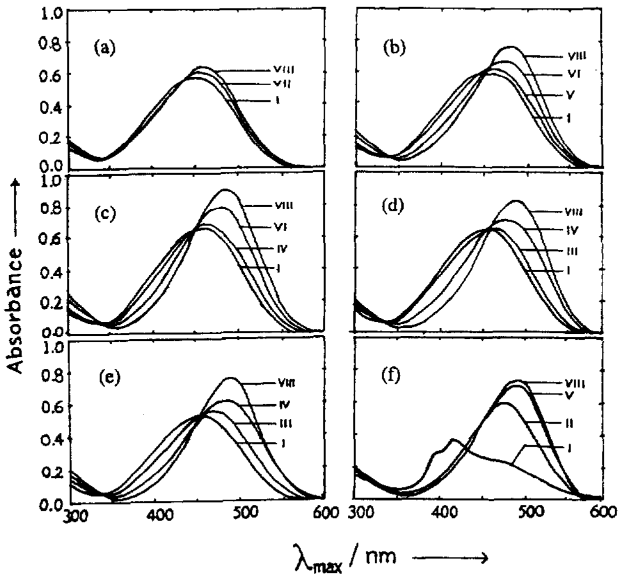


Fig. 2. Absorption spectra of dyes (a) C_1, (b) C_6, (c) C_8, (d) C_{10}, (e) C_{12}, (f) C_{16} in various [TX-100]. [TX-100] = i: 0, ii: 0.074, iii: 0.147, iv: 0.442, v: 0.589, vi: 1.473, vii: 2.947 and viii: 11.79 mM; [Dye] = 0.02 mM.

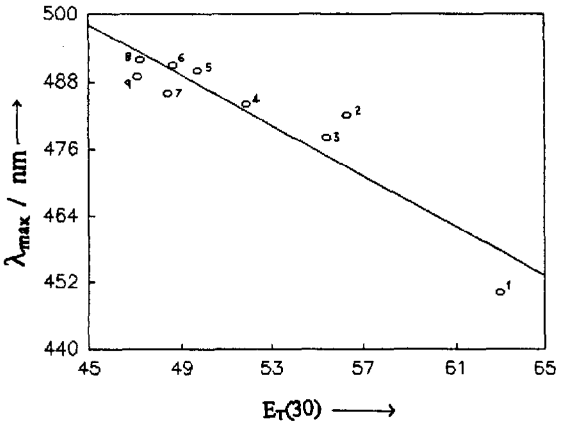


Fig. 3. A plot of λ_{max} of the C_3 dye as a function of microscopic solvent polarity parameter $E_T(30)$. 1: Water, 2: Ethylene glycol, 3: Methanol, 4: Ethanol, 5: Butanol-1, 6: Isobutanol, 7: Propanol-2, 8: Cyclohexanol, 9: Butanol-2.

Table 1

The values of the concentration of TX-100 at which break points are obtained from the plots of λ_{max}/emission intensity (I_{em}) of the dyes vs. [TX-100]

Dye	Break point (λ_{max}) in mM	Break point (I) in mM	Dielectric constant (D)	$E_T(30)$
C_1	5.36	6.36	71.5	64.20
C_3	4.85	4.72	62	61.37
C_5	4.70	4.45	39	56.35
C_6	2.87	2.67	32.5	54.40
C_8	1.50	1.50	24	51.40
C_{10}	0.80	1.09	18.5	50.00
C_{12}	0.363	1.09	17.8	49.10
C_{14}	0.363	1.00	17.8	49.10
C_{16}	0.236	1.00	17.8	49.10
C_{18}	0.236	1.00	17.8	49.10

The probable derived dielectric constant and $E_T(30)$ values for the location of the dyes in TX-100 environment. [TX-100] = 0–11.79 mM; [Dye] = 0.02 mM; Solvent = 2:98 (v/v) MeOH–H_2O; Temp. = 25°C.

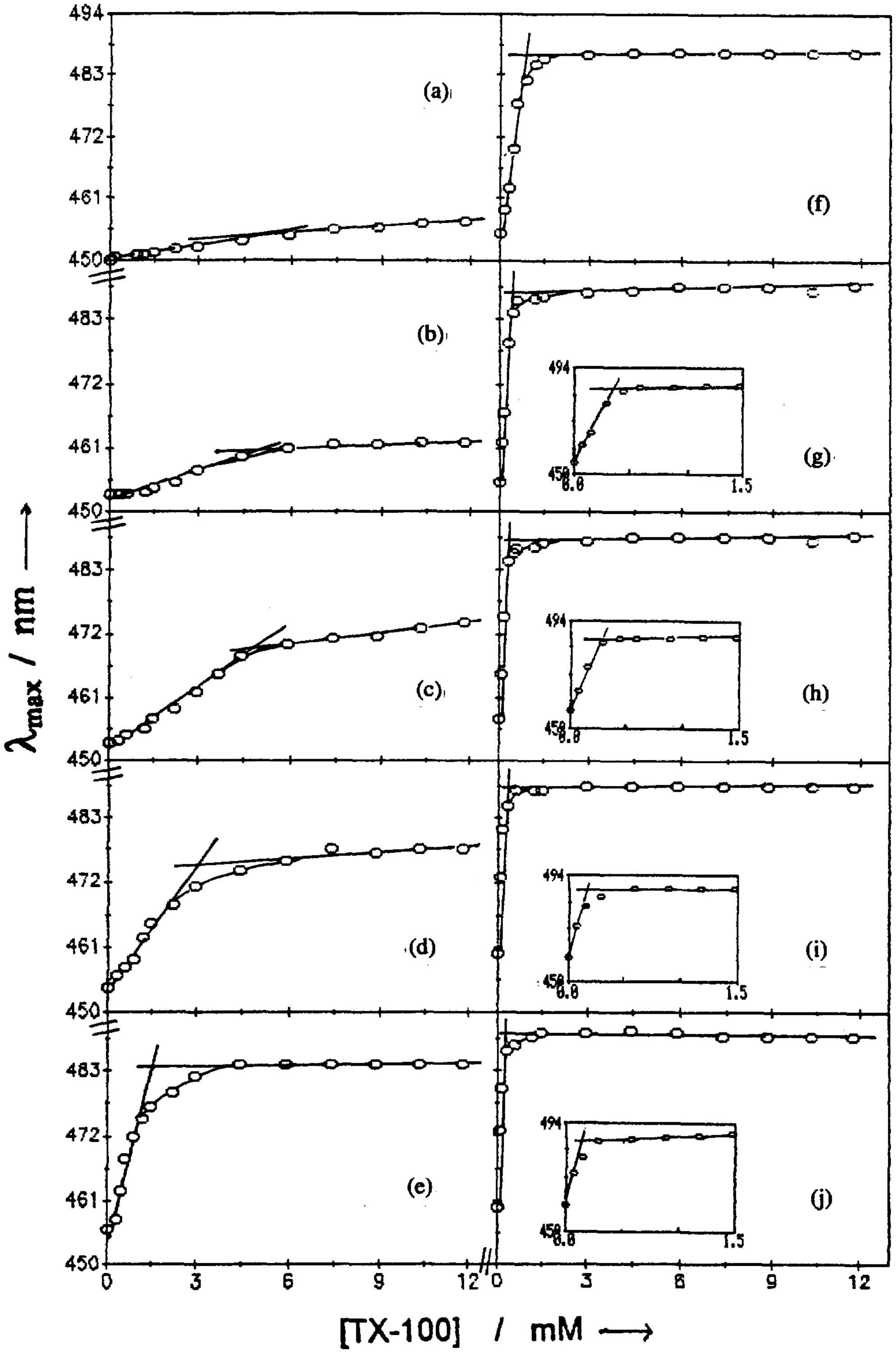


Fig. 4. Plot of λ_{max} of dyes (C_n) vs. [TX-100] in 2:98 (v/v) MeOH–H_2O at 25°C. [Dye] = 0.02 mM. (a) C_1, (b) C_2, (c) C_4, (d) C_6, (e) C_8, (f) C_{10}, (g) C_{12}, (h) C_{14}, (i) C_{16}, (j) C_{18}.

all the dyes. The λ_{max} values for all the dyes however attain constant values after a certain concentration of the surfactant. Some representative spectra at [TX-100] = 0, <CMC, >CMC are given in Fig. 2. These λ_{max} values are fitted to a standard curve of λ_{max} of dyes in various solvents and their $E_T(30)$ values. Since the λ_{max} values of the dyes (C_1–C_{18}) do not change in any solvent, a representative plot of the λ_{max} of C_3 dye vs. $E_T(30)$ values of various solvents is given in Fig. 3. The average $E_T(30)$ values of the micellar environment in which the dyes are located are given in Table 1. The $E_T(30)$ value is found to decrease linearly with increasing C_n up to about C_{10} and then remains constant. Thus the incor-

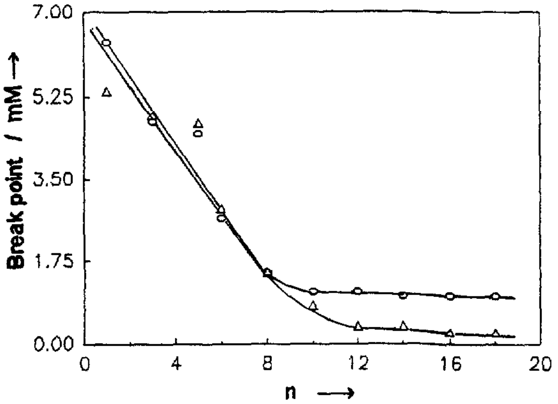
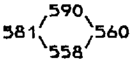


Fig. 5. Plot of break points in Figs. 3 and 6 vs. number of carbon atoms in the alkyl chain of the dye (I) (Break point for λ_{max} curve: Δ and for I_{em} curve: 0).

Table 2
Absorption and emission maxima and fluorescence intensity of the dyes (C_1–C_{18}) in TX-100

Dye	λ_{max} in nM	$\Delta\lambda_{abs}$	λ_{em} in nM	$\Delta\lambda_{em}$	Intensity
C_1	450–457	7		21	3.85–146.62
C_3	453–464	11	581–589–562	19	6.78–203.45
C_5	453–474	21	581–588–568	13	6.84–275.75
C_6	454–478	24	581–586–571	10	8.12–331.70
C_8	455–484	29	581–583–575	6	7.1–339.9
C_{10}	455–487	32	581–584–580	1	7.93–333.5
C_{12}	455–489	34	581–585–578	2	7.98–309.24
C_{14}	457–489	32	584–582	2	9.00–303.1
C_{16}	400		584–584	0	3.91–304.15
	416–489	–			
	475	–			
C_{18}	400		581–582	0	0.55–301.4
	416–489	–			
	475	–			

[TX-100] = 0–11.79 mM; [Dye] = 0.02 mM; Solvent = 2:98 (v/v) MeOH–H_2O; Temp. = 25°C.

poration of the dyes in the micelle is consistent with the current view that the longer the carbon chain is, the greater the extent of incorporation of the dyes will be. The plots (Fig. 4) of the absorption maximum values vs. [surfactant] are bilinear with break points at specific concentration of the surfactant which decreases with increasing carbon chain in the dye. A plot (Fig. 5) of the [surfactant] at which break occurs vs. C_n is linear up to C_{10} and then it asymptotes. The break-point concentration of the surfactant due to the C_1 dye agrees with the literature CMC value of TX-100 [8]. The $\Delta\lambda_{abs}$ ($\lambda_{[S]=13.4\,mM} - \lambda_{[S]=0}$) value increases linearly to C_{10} and then it remains almost constant. The Δλ values of C_{16} and C_{18} have not been considered because of their dimerisation in the absence of surfactant.

3.2. Emission spectra

All the dyes show a maximum in the emission spectra at 581 nm in 2% (v/v) MeOH–H_2O solvent system. On addition of surfactant, a bathochromic shift by about 3–9 nm is initially noticed, followed by a hypsochromic shift by about 30–3 nm for C_1 to C_{12} dyes, the C_1 dye showing a maximum shift of 30 nm which then decreases with increasing alkyl chain of the dye up to C_{12}. The C_{14} to C_{18} dyes do not exhibit such shifts. Only the C_1 dye shows an interesting phenomenon that on addition of surfactant, initially, the emission band at 581 nm splits into two bands: one appearing at 590 nm and the other at 558 nm. Both the bands gradually converge on gradual addition of surfactant (Table 2) and a single peak at 560 nm is obtained at a surfactant concentration of 2.95 mM. The λ_{em} value of the C_1 dye in dioxane ($D = 2.209$) is 556 nm and therefore the C_1 dye is perhaps distributed in aqueous and micellar phase, the micellar phase dye shows the emission at 558 nm and the aqueous phase dye shows at 590 nm. Further addition of surfactant increases the concentration of the micellar bound dye only with a resultant decrease in the concentration of the free dye. This behaviour is not exhibited by other dyes. The plot of $\Delta\lambda_{em}$ ($\lambda_{em}^{max} - \lambda_{em}^{min}$) for all the dyes (Fig. 6) decreases linearly with increasing C_n up to C_{10} and then it asymptotes.

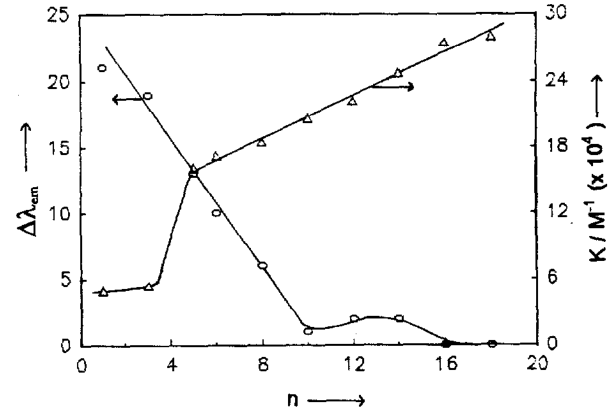


Fig. 6. Plot of association constant (K_M, Δ) and $\Delta\lambda_{em}$ (0) of the dyes in TX-100 vs. number of carbon atom (n) in the alkyl chain of the dyes.

3.3. Fluorescence intensity

All the dyes have very low emission intensity in 2% (v/v) MeOH–H_2O solvent system but on addition of the surfactant the intensity increases linearly and sharply up to a certain concentration of the surfactant. Such sharp increase in the intensity is not observed in ionic surfactants. The plots of (Fig. 7) intensity vs. [surfactant] are bilinear with a break point at decreasing concentration of the surfactant with increasing chain length of the dye. The concentration of the surfactant at which the break points is obtained correspond to the literature value of the CMC of the surfactant for C_1 dye only. The decreasing concentration of the surfactant for the break point in case of dyes with increasing alkyl chain length suggests the decrease in CMC of TX-100. This decrease may be due to a co-operative effect where the alkyl groups of the dyes incorporate hydrophobicity to the system thus increasing the micellization. The break point concentrations of the sur-

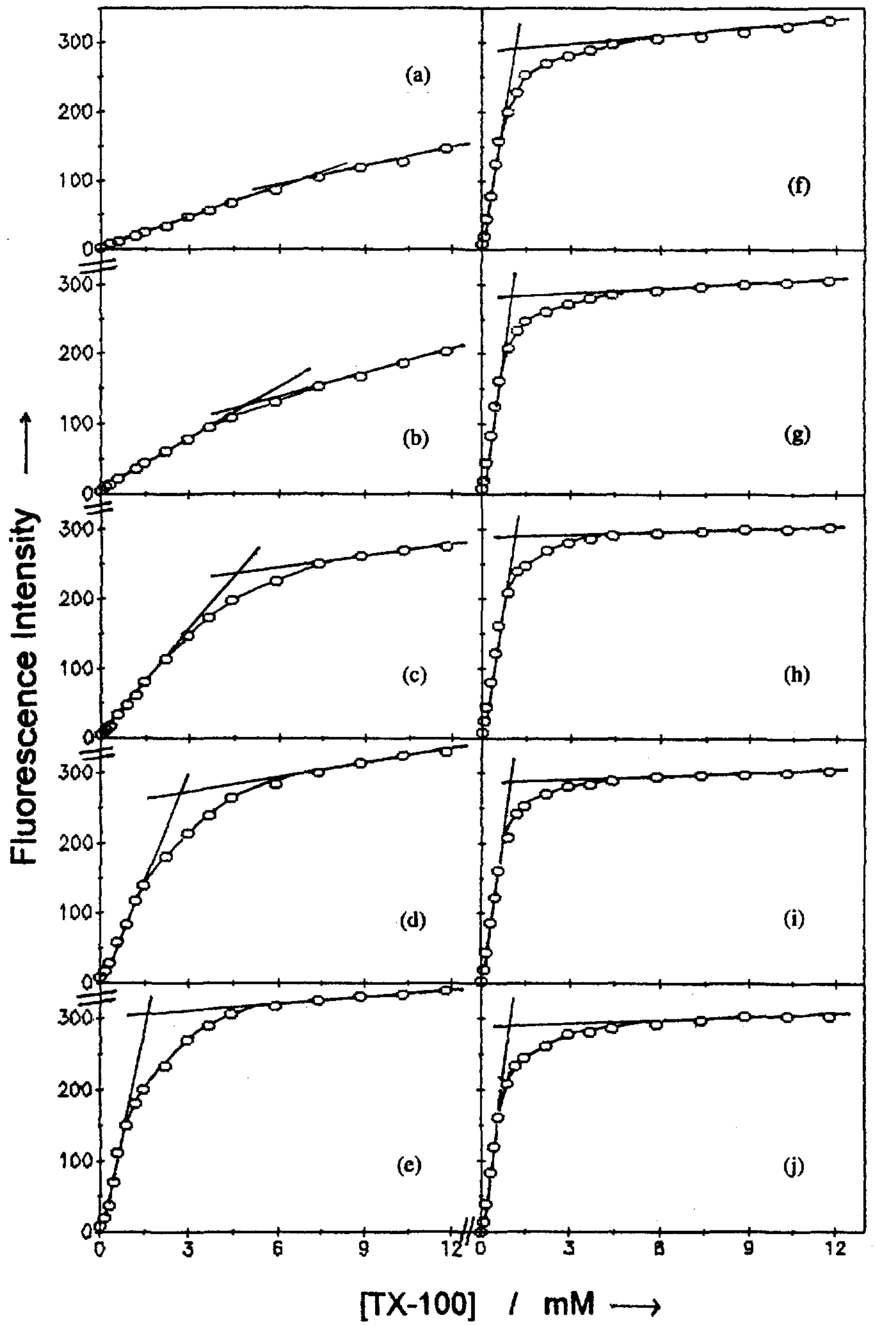


Fig. 7. Plot of fluorescence intensity (I) of dyes vs. [TX-100] in 2:98 (v/v) MeOH–H_2O at 25°C. [Dye] = 0.02 mM. (a) C_1, (b) C_3, (c) C_5, (d) C_6, (e) C_8, (f) C_{10}, (g) C_{12}, (h) C_{14}, (i) C_{16}, (j) C_{18}.

factant are plotted with the chain length (C_n) (Fig. 5) of the dye and the linear plot is found to asymptote at C_{10}. The increase of intensity on initial addition of the surfactant is found to be sensitive to the carbon chain length in the dye. The sensitivity ($S_I = I/[\text{surfactant}]$) increases with the chain length of the dye when [surfactant] < CMC and remains constant when [surfactant] > CMC. The sensitivity vs. n plot is S type which indicates that the emission intensity of the C_5 to C_{10} dye are most sensitive to changes in [TX-100], than other dyes. The curve asymptotes at C_{10}. The intensity of the dye increases due to increasing rigidity of the dye in presence of surfactant. It appears that after the CMC of the surfactant, the micellar structure does not change and therefore the dyes do not experience any change in their environment. But before the CMC, increasing concentration of the surfactant changes the structural environment of the dye. So the sensitivity parameter may be used as a measure of the structural changes of the surfactant before CMC.

TX-100 contain a polyoxyethylene chain with a terminal hydroxy group which has a crown ether like structure and the nonpolar part contains a benzene ring with branched carbon chain. The dye under consideration has a positively charged ionic group with carbon chain of increasing hydrophobicity attached to pyridyl nitrogen. Prior to the formation of the micelle, the monomeric surfactant may be aggregating to give premicellar structures which bind the dye and make it rigid as a result the intensity increases. In order to ascertain the 'open' or 'closed' environment of the dyes (D), the binding constant values of the dyes to the micelles (M) have been determined by using Eq. (3). The association of the dyes with the micelle (M) can be represented by expression (1). It is assumed that only one molecule of the dye is associated.

$$\mathrm{M}+\mathrm{D} \overset{K_\mathrm{M}}{\rightleftharpoons} \mathrm{MD} \tag{1}$$

The binding constant (K_M) can be calculated by using expression (3).

$$I_\mathrm{t}=\frac{I_\mathrm{w}}{1+K_\mathrm{M}[\mathrm{M}]}+\frac{I_\mathrm{m}K_\mathrm{M}[\mathrm{M}]}{1+K_\mathrm{M}[\mathrm{M}]} \tag{2}$$

$$K_\mathrm{M}[\mathrm{M}]=\frac{I_\mathrm{t}-I_\mathrm{w}}{I_\mathrm{m}-I_\mathrm{t}} \tag{3}$$

In this equation I_t, I_w, I_m are the intensities at any [surfactant], in water and in micellised surfactant respectively. The values of K_M are calculated and given in Table 3. It is observed that the binding constant increases with increasing carbon chain of the dyes. A plot of K_M vs. C_n (Fig. 6) is linear $R=0.994$ for C_5 to C_{18} dyes with a slope $=0.958\ \mathrm{M}^{-1}$. The point for C_1 and C_3 fall much below the line. In view of the increasing intensity of the dyes in pre-micellar surfactant and the sensitivity dependence of the intensity on the hydrophobic chain, the binding of the dyes to the surfactant (S) and the number of surfactant molecules (x) per dye has been estimated by using Eq. (3a).

$$x\mathrm{S}+\mathrm{D} \overset{K_\mathrm{S}}{\rightleftharpoons} \mathrm{S}_x\mathrm{D} \tag{3a}$$

So

$$K_\mathrm{S}[\mathrm{S}]^x=\frac{I_\mathrm{t}-I_\mathrm{w}}{I_\mathrm{s}-I_\mathrm{t}} \tag{4}$$

or

$$\log\frac{I_\mathrm{t}-I_\mathrm{w}}{I_\mathrm{s}-I_\mathrm{t}}=x\log \mathrm{S}+\log K_\mathrm{S} \tag{5}$$

The values of K_S and x are given in Table 3. The binding constant of the lower homologues of the dye increase by about 7 to 9 times on micellisation of the surfactant. But with increasing chain length the ratio ($K_\mathrm{M}/K_\mathrm{S}$) falls and almost become constant at C_{10}. Therefore, the dye molecules appear to have a strong affinity to a polyoxyethylene group and are incorporated into its exterior region. With micellisation of the surfactant the binding becomes stronger as a result the value of K_M increase by about 7 times. Increasing hydrophobicity of the dye due to increase in the chain length increases the sensitivity of interaction of the dye to the monomers or pre-micellar aggregates. The dyes may be getting adsorbed on the surface of the surfactant monomer or pre-micellar aggregate and the value of K_S does not alter on micellisation. Thus it is concluded that the hydrophobicity plays a dominant role in the interaction of the dyes with TX-100.

Table 3
Values of x (x = no. of surfactant molecules/dye molecule before micellisation), K_S (binding constant before micellisation), the sensitivity of intensities (S_I) of emission to change in [TX-100] before micellisation and the values of binding constant (K_M) of the dyes with TX-100 after micellisation

Dye	x	$K_\mathrm{S}(\times 10^4)$ in M^{-1}	Sensitivity ($S_\mathrm{I}=I/[\mathrm{TX\text{-}100}]$)	$K_\mathrm{M}(\times 10^4)$ in M^{-1}
C_1	1.5	0.662	13.90	4.93
C_3	1.4	0.552	24.10	5.38
C_5	1.6	1.787	48.90	16.15
C_6	1.8	10.397	92.25	17.28
C_8	1.7	12.23	173.17	18.45
C_{10}	1.6	24.30	236.00	20.60
C_{12}	1.6	25.88	263.32	21.19
C_{14}	1.6	27.93	261.78	24.76
C_{16}	1.6	28.49	280.45	27.42
C_{18}	1.6	17.04	283.71	27.98

[TX-100] = 0–11.79 mM; [Dye] = 0.02 mM; Solvent = 2:98 (v/v) MeOH–$\mathrm{H_2O}$; Temp. = 25°C.

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