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Dye–Surfactant Interaction: Role of an Alkyl Chain in the Localization of Styrylpyridinium Dyes in a Hydrophobic Force Field of a Cationic Surfactant (CTAB)

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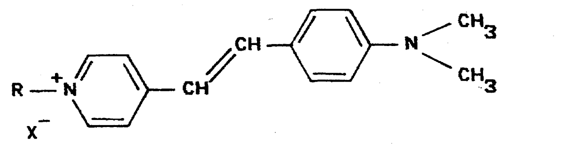
The interaction of a number of cationic dyes (I) with a varying number of methylene groups (C_n) in the alkyl chain attached to pyridyl nitrogen with a cationic surfactant (CTAB) assembly is reported. The binding constant of the dyes (C_5 to C_{18}) with the micelle have been calculated, and are found to increase with increasing carbon chain. A plot of the binding constant vs. the chain length shows a curve with a maximum for C_{16}, which is attributed to a compatibility factor. From studies of the electronic and emission spectra it is proposed that a micelle has a hydrophobic force field and that the dyes are localized in various pockets of the field.

The solubilization of an organic substrate in surfactant micelles depends on the nature of the hydrophobic group and charge in the substrate. A micellar solution provides three topographical regions i.e. inside (I), boundary (B), and outside (O), where solubilization may occur. The local concentration of the substrate in any region is controlled by the mutual charge and hydrophobicity. It has been proposed[1] that in ionic micelles these regions are known to give high ionic strength and a fairly sharp boundary between high- and low-polarity regions. This proposition has obtained support from several theoretical and semiempirical models.[1,2] Behera et al.[3] have studied the aggregation of C_{16} dye in a CTAB solution by absorption spectroscopy, and have concluded that the dye aggregates with CTAB, leading to the formation of a mixed micelle due to compatibility.[4]

Studies of the photophysical and photochemical behavior of cyanine dyes are of interest due to their wide application in photofilms, dye-lasers, photodynamic therapy, second-harmonic generation etc. Recently, Ferreira et al.[5,6] have shown that molecules like rhodamine, oxazines, and diphenylmethanes are able to penetrate into the polymer matrix, resulting in a decrease in the nonradiative pathways for deactivation. The hydrophobic group present in the dye molecules is able to pull the molecule to the hydrophobic core of a micelle. Due to this pulling effect, the hydrophilic or polar part of the molecule is localized at various regions of the micelles. We reported earlier that[7] the hydrophobic interaction between the dye and surfactant molecules plays a vital role in the orientation of the chromophoric group of the dyes at the interfacial region of an ionic micelle. The present work deals with a study of the interaction of cationic dyes (I) of various chain length with a cationic surfactant (CTAB) (Chart 1).



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

$R = CH_3$, C_3H_7, C_5H_{11}, C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$
$C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$, $C_{18}H_{37}$

Chart 1.

Experimental

Materials: *N*-Alkyl-4-(*p*-dimethylaminostyryl)pyridinium bromides were prepared by a method reported earlier.[8,9] 4-Methylpyridine was quaternized with alkyl bromide of varying chain length, and then condensed with *p*-dimethylamino-benzaldehyde in ethanol in the presence of piperidine. The reaction mixture was concentrated by evaporation of ethanol. A red solid, separated by cooling on ice, was filtered and crystallized from absolute ethanol. The 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 to obtain a constant value of the molecular extinction coefficient. The dyes are referred to as C_n according to the number (n) of carbon atoms in the alkyl chain.

Cetyltrimethylammonium bromide (CTAB) (Sisco-Chem, spectroscopic grade) was crystallized twice from a methanol–acetone mixture (3 : 1 v/v) and dried in vacuo over P_2O_5. Triple-distilled water was used throughout the experiment.

Spectroscopic Measurements and Techniques: A concentrated (ca. 1 mM, $1\ M = 1\ mol\,dm^{-3}$) stock solution was prepared separately for each dye by dissolving a weighed sample of the dye in methanol. A solution for a spectral measurement was prepared by adding 0.1 mL of the above stock solution to a 5-mL volumetric flask containing a freshly prepared solution of the surfactant in triply distilled water. Aliquots (3 mL) of these solutions were taken to quartz cuvettes thermostated at 25 °C. The absorption spectra were obtained on a Shimadzu 160 spectrophotometer and the emission spectra were obtained on a Shimadzu RF-5000 spectrofluorophotometer.

Results and Discussion

Absorption Spectra: The influence of the [surfactant] on the absorption of dyes of various chain length (C_6—C_{16}) is shown in Fig. 1. The C_1—C_5 dyes do not show any change in λ_{max} and the optical-density values in presence of varying concentrations of CTAB surfactant (up to 10 mM), whereas a change is noticed with C_6 dyes (Fig. 1). The λ_{max}–[CTAB] plots for C_8 to C_{18} dyes (Fig. 1) have distinctly three arms. The third arm for C_6 is not perceptible, even up to 30 mM of CTAB. The λ_{max} in the first arm remains almost constant, then rises at 3.5 mM CTAB, and again levels off. The range of the concentration of CTAB where λ_{max} jumps narrows along with an increase in the carbon chain in dyes up to C_{16}. The $\Delta\lambda$ (λ_{max} at 10 mM CTAB, where λ_{max} is almost constant, and where all the dye molecules are expected to be fully incorporated in the micelle—λ_{max} in the absence of surfactant) in CTAB solutions increases with increasing chain length of the dye, the increase being sharp from C_6 to C_8 and then almost becomes constant. Both C_{12} and C_{14} dyes are found to form a turbid zone within 1—3.5 mM of CTAB. Oliveira et al.[10] have also observed turbidity due to the aggregation of pyrenylmethyltributyl-phosphonium bromide (PMTP) (0.007 mM) and SDS (0.15—0.4 mM). The λ_{max} of C_{12} dye does not change in the turbidity zone, whereas that of C_{14} dye decreases to 397 nm from 457 nm. The spectrum at 3.5 mM CTAB for C_{14} shows bands of equal intensity at 398 and 474 nm ($\log \varepsilon = 4.29$ and 4.26, respectively). The peak at 398 nm is nonexistent at 4.0 mM of CTAB, and only a peak at 478 nm is obtained. Both C_{16} and C_{18} dyes show a λ_{max} value at 416 nm with shoulders at 400 and 478 nm in the absence of a surfactant. Upon the addition of a surfactant the peak at 400 nm becomes prominent at the cost of the 416 nm peak, which completely disappears at 2 mM CTAB. The 400 nm peak again disappears in favour of the 478 nm peak at 5 mM of CTAB (Fig. 2). C_{18} dye also exhibits a similar behavior like that of the C_{16} dye.

Emission Spectra: The fluorescence maxima are not affected by a change in the [surfactant]; only a shift by about 3 nm takes place. However, the intensity increases by a great deal, and is dependent on the carbon chain (*n*) of the dye. A plot of ΔI ($I_{CTAB=10\ mM} - I_{CTAB=0}$) vs. n gives an S-type plot passing through the origin (Fig. 3). Two break points, at C_5 and C_{10}, are observed. The intensity vs. [CTAB] plots

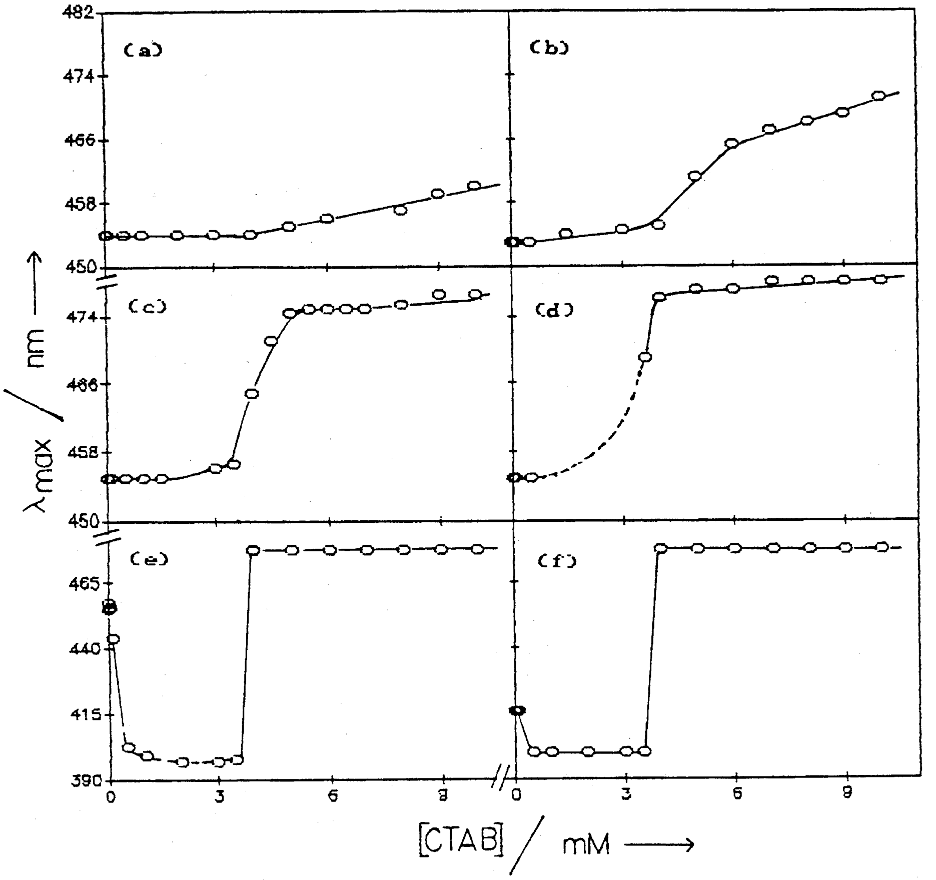


Fig. 1. Plots of λ_{max} of dyes (C_n) vs. [CTAB] in 2 : 98 (v/v) methanol–water at 25 °C. [Dye] = 0.02 mM: (a) C_6, (b) C_8, (c) C_{10}, (d) C_{12}, (e) C_{14}, (f) C_{16}. Turbidity Zone (- - -).

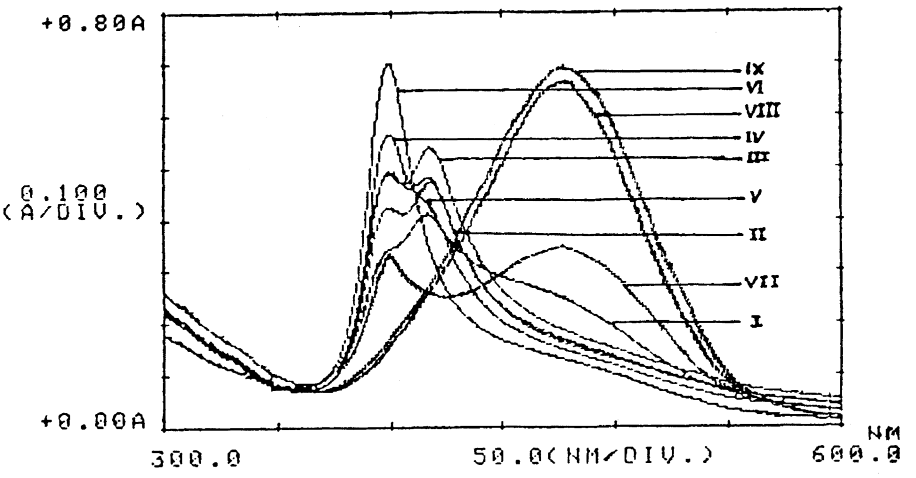


Fig. 2. Repetitive scanning of UV-vis spectra of C_{16} dye at various concentration of CTAB. [Dye] = 0.02 mM; [CTAB]/mM: (i) 0.00, (ii) 0.1, (iii) 0.5, (iv) 1.0, (v) 1.5, (vi) 3.0, (vii) 4.0, (viii) 5.0, (ix) 10.0.

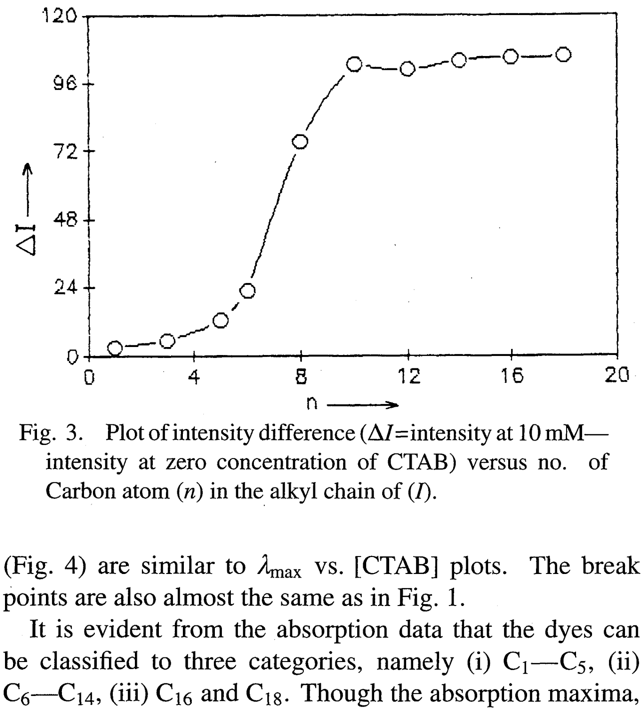


Fig. 3. Plot of intensity difference (ΔI=intensity at 10 mM—intensity at zero concentration of CTAB) versus no. of Carbon atom (n) in the alkyl chain of (I).

(Fig. 4) are similar to λ_{max} vs. [CTAB] plots. The break points are also almost the same as in Fig. 1.

It is evident from the absorption data that the dyes can be classified to three categories, namely (i) C_1—C_5, (ii) C_6—C_{14}, (iii) C_{16} and C_{18}. Though the absorption maxima, the molecular extinction coefficient and λ_{em} values do not change for C_1 to C_5 dyes, the intensities of the emission of these dyes gradually increase upon the addition of CTAB. Georges[11] has mentioned in a review article that an increase in the fluorescence intensity can be ascribed to a decrease in the radiationless relaxation processes due to a decrease in the molecular motion because of an increase in the microviscosity.

In an earlier paper Behera et al.[3] have ascribed the peaks at 478 and 395 nm to the monomeric and dimeric form of the C_{16} dye. Hence, the absorptions at around 400 and 478 nm for both C_{16} and C_{18} compounds are ascribed to dimeric and monomeric states, respectively. A temperature study of dimer $\rightleftharpoons$ monomer equilibrium for C_{16} dye in the absence of CTAB is given in Fig. 5. With increasing temperature the [dimer] decreases along with a concomitant rise in the [monomer], though the decrease/increase levels off at about 50 °C. The dimeric peak, however, disappears completely at 5 mM CTAB, indicating complete absorption of the dye as a monomer into the micelle. Therefore, no change in λ_{max} is noticed after 5 mM CTAB. The C_{14} dye also exhibits this behavior over a narrow range of the CTAB concentration (3.6—4.0 mM). No dimeric peak for C_{14} is observed at a 4.0 mM CTAB because of its complete incorporation into the micellar core. Hence, the C_{14} to C_{18} dyes are incorporated in the micelle because of near compatibility[4] of the chain lengths.

A micelle has both electrostatic and hydrophobic fields (F_H), the strengths of which decrease with the distance from the surface of the micelle. A decrease in the hydrophobic field strength is akin to a decrease in the electric field around a charged particle, and is asymptotic in nature.[12] Albeit the electrostatic repulsion of the cationic dyes due to the cationic surface of the CTAB micelle, their location around the micellar interface may be ascribed to the hydrophobic field effect on the dyes having varied hydrophobicity. Thus, the C_1—C_5 dyes occupy a region of low hydrophobic field as a result of small changes in the intensity of emission. C_6 to C_{18} dyes occupy varying hydrophobic fields in a micellar environment. Both C_{16} and C_{18} dyes remain as a dimer and form a mixed micelle with the surfactant. The region of occupation of the dyes in a CTAB micellar solution is compared with the polarity scale (E_T (30))[13] of the MeOH–H_2O system. Generally methanol/ethanol–water systems are considered for a comparison because these are better model solvents in view of the fact that, apart from the head groups and counter ion, only water and the alkyl chain contribute to the surface polarity of the aqueous micelles.[14] Accordingly, the occupation sites of the dyes in a CTAB micellar solution have been identified as: C_1—C_5: Bulk aqueous medium 2% MeOH–H_2O v/v ($E_T(30) = 62.8$), C_6: 20% MeOH–H_2O v/v ($E_T(30) = 61.0$), C_8: 37.5% MeOH–H_2O v/v ($E_T(30) = 59.2$), C_{10}: 60—70% MeOH–H_2O v/v ($E_T(30) = 57.7$—57.1), C_{12}—C_{18}: 70—90% MeOH–H_2O v/v ($E_T(30) = 57.1$—56.0). Saroja and Samanta[15] have evaluated the interface polarity of CTAB to be 56.3 on the $E_T(30)$ scale. By using ketocyanine dyes as

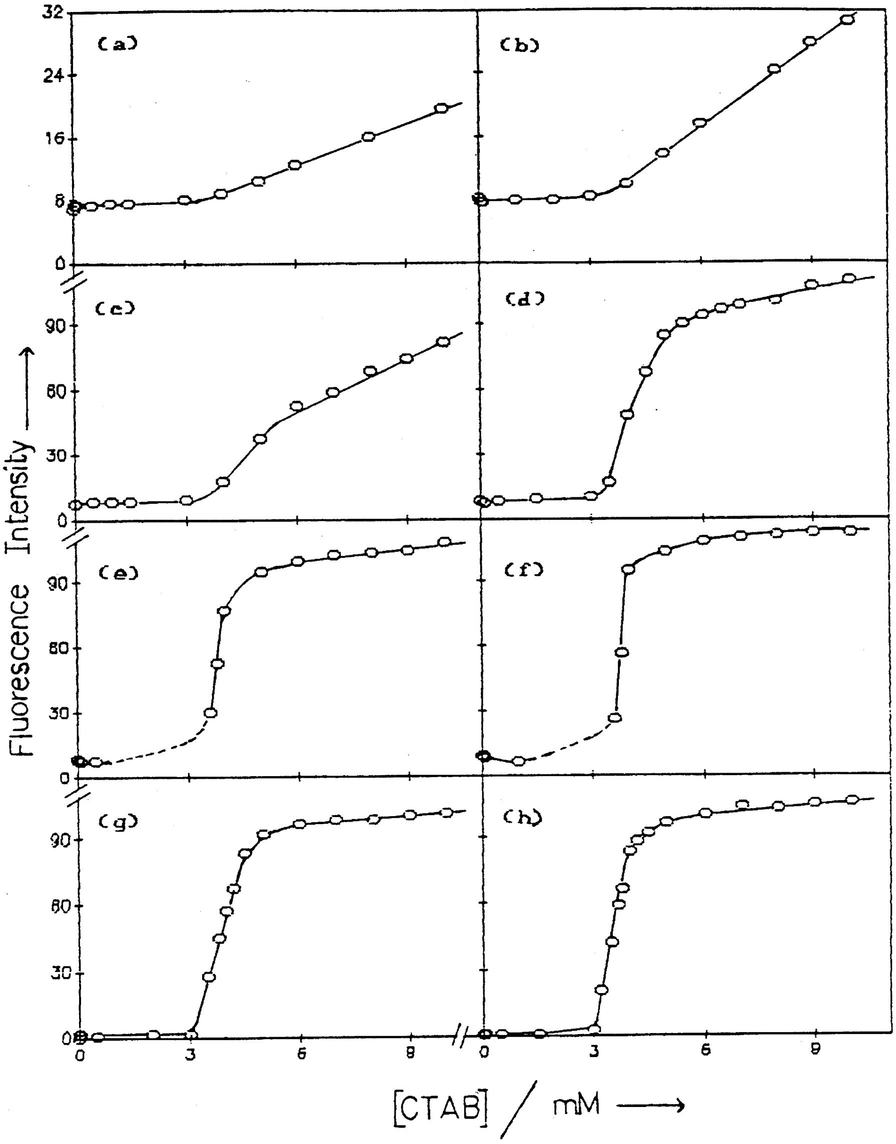


Fig. 4. Plot of fluorescence intensity (I) of dyes (C_n) vs. [CTAB] in 2 : 98 (v/v) methanol–water at 25 °C. [Dye] = 0.02 mM: (a) C_5, (b) C_6, (c) C_8, (d) C_{10}, (e) C_{12}, (f) C_{14}, (g) C_{16}, (h) C_{18}. Turbidity Zone (- - -).

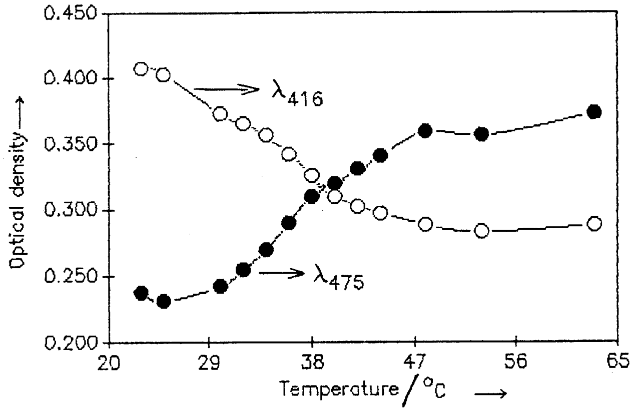


Fig. 5. Plot of optical density at λ_{475} (●) and λ_{416} (○) of C_{16} dye versus temperature. [Dye] = 0.02 mM.

indicators, Banerjee et al.[16] have also determined the $E_T(30)$ values for a series of surfactant micelles. Hence, C_{12}—C_{18} dyes are around the interfacial region. Therefore, it is possible to delineate the location sites of the dyes from both the absorption and emission spectra. The hydrophobic field (F_H) strength decreases exponentially with a function of the distance from the micellar droplet. The core of the micelle is of constant hydrophobic field corresponding to n-alkane, which than decreases with increasing distance/$E_T(30)$ from the interface of the micelle (Fig. 6).

The maximum wavelength of emission (λ_{em}^{max}) values of the dyes remain the same up to a certain concentration of CTAB (3.5 mM), after which a slight hypsochromic shift is noticed, which may be due to medium rheology. Wandelt et al.[17] have observed a linear relationship of the fluorescence quantum yield to the local viscosity of the medium of 4-dimethylamino styryl pyridinium bromide in protic solvents. The increase in the emission intensity also becomes percepti-

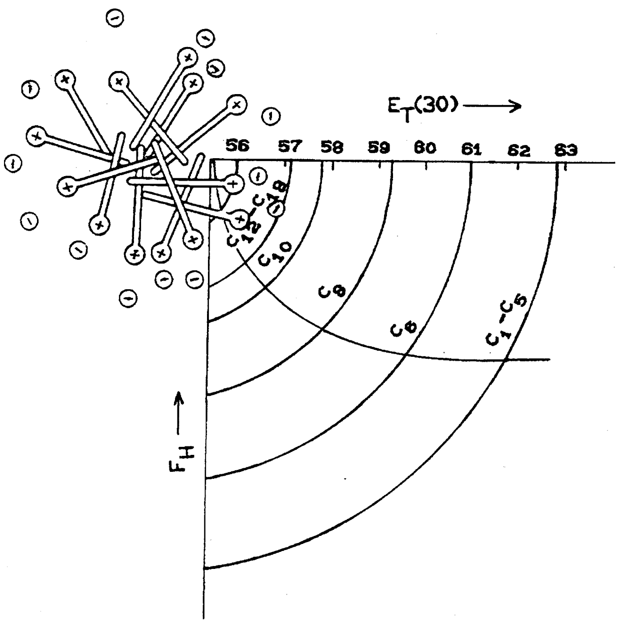


Fig. 6. Schematic representation of localization of dye in a CTAB micellar force field gradient with respect to $E_T(30)$ scale. The asymptotic curve is a quantitative representation of the decrease of hydrophobic force (F_H) field with distance.

ble from C_6 dye. It has been noticed that the intensities of the emission remain constant up to 3.5 mM CTAB. The increase in intensities of the dye molecule may be due to binding of the [D] to surfactant assembly, M (Eq. 1).

$$M + D \rightleftharpoons MD \tag{1}$$

In this equation M is the micelle and D is the dye molecule. The incorporation of only one dye molecule into the micelle is assumed.[18,19] The binding constants (K) are estimated from the fluorescence intensity data using the following equation:

$$I_t = \frac{I_w}{1+K[M]} + \frac{I_m K[M]}{1+K[M]}. \tag{2}$$

Here, I_m, I_t, and I_w are the relative fluorescence intensities under complete micellized conditions, at the intermediate surfactant concentration, and at the surfactant concentration where no interaction has occurred, respectively, and [M] is the concentration of the micelle, calculated using $[M] = ([S]-\mathrm{cmc})/N$. The value of N for CTAB is taken to be 60.[20] Plots based on the above equation are linear up to 5 mM CTAB, as has been also noticed by Saroja and Samanta.[20] The values of K have been obtained and are given in Table 1. The K value increases with increasing chain length up to C_{16}, and then decreases. A plot of K vs. C_n (Fig. 7) exhibits a maxima and fall to zero (on extrapolation) at C_3. The binding of C_{16} with CTAB is maximum due to compatibility in the chain length.[4] It is evident from the plot that the binding of the dye with the micelle becomes strong with the C_8 chain in the dye.

This study concerning the interaction of dyes with various chain lengths with the cationic surfactant (micelle) leads to the following conclusions:

Table 1. Association Constant (K) of the Dyes Reported in This Work with CTAB Micelles at 25 °C

No. of carbon in the alkyl chain	K in M^{-1} ($\times 10^4$)
C_5	1.23
C_6	1.48
C_8	2.93
C_{10}	11.9
C_{12}	26.77
C_{14}	39.94
C_{16}	43.76
C_{18}	37.07

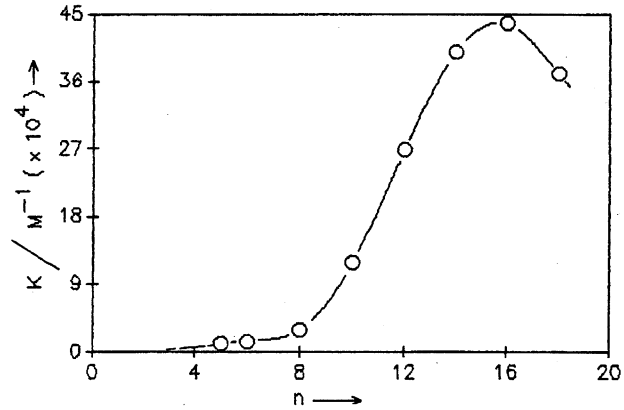


Fig. 7. Plot of association constant (K) of the dye with CTAB micelle versus number of carbon atom (n) in the alkyl chain of (*I*).

1. The hydrophobic chain in the dye plays an important role in its interaction with the micelle. The interaction is not perceptible up to C_5.
2. The dimerization of the dyes in the absence of a surfactant begins with the C_{16} dye. The C_{14} dye, however, forms a turbid zone with probable dimerization in the presence of a surfactant.
3. The binding of the dyes increases with increasing chain length with a break appearing at C_8.

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