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# Studies of solvation of ketocyanine dyes in homogeneous and heterogeneous media by UV/Vis spectroscopic method

Parimal Kumar Das, Ramkrishna Pramanik, Debashis Banerjee<sup>1</sup>, Sanjib Bagchi<sup>\*</sup>

> Department of Chemistry, Burdwan University, Burdwan 713 104, India Received 15 May 2000; accepted 25 May 2000

#### Abstract

Solvation characteristics of ketocyanine dyes (I–VI) have been investigated in pure solvents and heterogeneous media by absorption and fluorescence studies. The dyes are good reporters of solvent polarity. In protic solvents they exist as equilibrium mixtures of bare and hydrogen-bonded form in the ground state (S<sub>0</sub>), the latter being the emitting species. In aprotic solvents of low polarity association of the S<sub>1</sub> state of the dye takes place. In aqueous micellar media the dye resides at the micelle–water interface. The binding constant for dye–micelle interaction has been determined. Fluorescence data in  $\beta$ -cyclodextrine solution resemble that for that neutral micellar solution indicating that the interaction between the -OH group of the heterogeneous part (micelle/cyclodextrine cavity) and the carbonyl oxygen of the dye is important in both the cases. © 2000 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Optical response of molecules showing an intramolecular charge transfer (ICT) has been found to be dependent on the immediate environment [1]. As such these molecules act as micropolarity reporters probing the local environments in simple solutions or complex biomimicing system [2-5]. Of these, the fluorescent polarity probes are more advantageous compared to the non-fluorescent probes because of their widespread applicabiology tion in [6]. In our laboratory symmetrically substituted ketocyanine dyes I & II (Fig. 1), which show unique solvatochromic properties in both absorption and emission, have been used extensively for studying solvation interaction [7-9]. It was found that in homogeneous media the dyes are good reporters of hydrogen-bond donating ability of protic solvents. The micropolarity and dielectric constant at the micelle-water interface may also be obtained from the study of the fluorescence characteristics of the dyes [10]. Solvent effect on the photophysics of two other structurally similar dyes III & IV of which III is symmetrically substituted have also been studied by other workers [11,12]. In the present paper we

<sup>\*</sup> Corresponding author. Tel.: +91-342-60810; fax: +91-342-64452.

*E-mail address:* burchdsa@cal.vsnl.net.in bsanjibb@yahoo.com (S. Bagchi).

<sup>&</sup>lt;sup>1</sup> Present address: Department of Chemistry, Haldia Government College, Haldia, Midnapore, India.

present extensive studies on absorption and emission spectral characteristics of two other related dyes V & VI along with the dyes III & IV in various homogeneous media. All these compound show ICT transition between aniline nitrogen and the carbonyl oxygen. The possible ground state complexation in alcohol solvents, aggregation of the solute in non-polar media and contribution of various modes of solute-solvent interaction towards solvation interaction has been addressed. Comparison among the dyes (I–VI) has been made. Studies have also been made on the spectral characteristics of the dyes III–VI in several heterogeneous aqueous media, viz., cationic, anionic and neutral micelles and aqueous  $\beta$ -cyclodextrine solution. Semiempirical molecular calculation at AM1 level have been carried out to provide the optimised geometry, charge distribu-



Fig. 1. Dyes used in the present investigation. The charges on N and O atom have been indicated. The dipole moment of the dye in the  $S_0$  state as calculated by AM1 method is also given.

tion and the dipole moment in the ground state of the dye molecules.

## 2. Materials and methods

Ketocyanine dyes (I & II) were synthesised as describe in the literature [13]. Purity of the prepared dyes were checked by IR, UV/Vis absorption, and fluorescence spectral data. The compound III was synthesised from cyclopentanone and 4-(dimethylamino)-benzaldehyde. Cyclopentanone was dissolved in ethanol and sodium ethoxide was added to it. 4-(Dimethylamino)benzaldehyde was added to the above mixture and refluxed for 1 h. It was then cooled and filtered. The product was recrystallised from ethanol. Compounds IV, V, and VI were synthesised similarly by the condensation of indanone acetophenone, and  $\alpha$ -tetralone, respectively, with 4-(dimethylamino)benzaldehyde. The compounds were recrystallised from dry ethanol. Purity of the prepared compounds was checked by IR and C, H, N analysis.

All the solvents used were the best grade available commercially. They were distilled from calcium hydride immediately before use to ensure the absence of peroxides and oxidising agents. Mixed solvents were prepared by carefully mixing the components so as to minimise contamination by moisture. Sodium dodecyl sulphate (SDS), cetyl-trimethylammonium bromide (CTAB) and Triton X-100 were received from Sigma and used without purification. For preparing a micellar medium the required amount of the surfactant was added to triply distilled water, and the contents kept in a ultrasound sonicator (JENCONS, U.K., Model T 80) for a considerable period. Solutions of the solutes in the micellar media were prepared by adding the dye to the micellar media with proper sonication.  $\beta$ -cyclodextrine ( $\beta$ -CD) was received from Aldrich and was used without purification.

The UV/Vis absorption spectra were measured on a SHIMADZU UV 1020 PC spectrophotometer fitted with a temperature controlled unit (Model TB-85 Thermobath, SHIMADZU). The fluorescence spectra (emission & excitation) were taken on a HITACHI F4500 fluorescence spectrophotometer equipped with polarisation accessory and a temperature controlled cell holder. For measurement at different temperatures water was made to circulate through the cell holder from a constant temperature bath (HETO HOLTEN, temperature range -30-100°C).

The emission anisotropy at a wavelength  $\lambda$  was calculated from the following relationship [4],

$$r_{\rm em}(\lambda) = [I_{\rm VV}(\lambda) - G(\lambda)I_{\rm VH}(\lambda)] / [I_{\rm VV}(\lambda) + 2G(\lambda)I_{\rm VH}(\lambda)]$$
(1)

where  $I(\lambda)$  denotes the fluorescence intensity at the wavelength  $\lambda$  and the first and the second subscripts H and V respectively refer to the horizontal and vertical setting of excitation and emission polarisers.  $G(\lambda)$  is an instrumental factor representing the polarisation characteristics of the photometric system and is given by,  $G(\lambda) = I_{\rm HV}(\lambda)/I_{\rm HH}(\lambda)$ , the subscripts having the same meaning. Excitation anisotropy  $(r_{\rm ex})$  were calculated similarly.

Dimroth–Reichardt empirical solvent polarity parameters  $E_{\rm T}(30)$  [14] for the neat solvents were taken from the literature [15]. Some of the values were determined from the wavelength of maximum absorption ( $\lambda_{\rm max}$ ) of the indicator dye, viz., 2,6-diphenyl-4-(2,4,6,-triphenyl-1-pyridino) phenolate, in the solvent according to the relation,

 $E_{\rm T}(30)$  (kcal mol<sup>-1</sup>) = 28 590/ $\lambda_{\rm max}$  (nm)

## 2.1. Theoretical calculations

Semi empirical MO calculations at the AM1 [16,17] level using the MOPAC PC program were carried out for the dyes III–IV on a PC. The initial optimisation of the ground state geometries of the dye molecules was achieved using a molecular mechanics program followed by unrestricted geometry optimisation. Fully optimised geometry, charge distribution, and the dipole moment for the dye molecules in the  $S_0$  state are shown in the Fig. 1.



Fig. 2. Representative modified absorption spectrum  $[\epsilon(\tilde{v})/\tilde{v} \text{ vs. } \tilde{v}]$  and modified fluorescence spectrum  $[I(\tilde{v})/\tilde{v}^3 \text{ vs. } \tilde{v}]$ . (a) Dye VI in benzene; (b) dye VI in acetonitrile; (c) dye V in 1,2-dichloroethane, and (d) dye V in ethanol.

### 3. Results and discussions

#### 3.1. Pure solvents

The absorption and fluorescence band maxima in various pure solvents have been summarised in Table 1. There is in general an overall red shift of the Vis absorption band as the polarity of the solvent increases. Fig. 2 shows some representative absorption spectra. The absorption spectra in all the aprotic solvents show similar structures  $(1700-1900 \text{ cm}^{-1})$ , which loose their prominence as the polarity of the solvent is increased. The polar solvents are expected to interact with the carbonyl oxygen, the negative end of the dipolar dye molecule and the structure may be explained as due to carbonyl vibration. Plots of the maximum energy of absorption, E(A), versus the polarity parameter  $E_{\rm T}(30)$  is shown in the Fig. 3. The E(A) values are rather insensitive towards a change in  $E_{\rm T}(30)$  values. A linear correlation with the  $E_{\rm T}(30)$  scale of solvent polarity indicates that the nature of transition for the dyes under study

and the indicator dye for the  $E_{\rm T}(30)$ scale is the same. Thus, the longest wavelength band of the dyes are of intramolecular charge transfer (ICT) origin. In this context it may be noted that the Vis absorption band for dyes III and IV has been assigned by other workers [11,12] as due to an ICT from the nitrogen of the dimethylamino group to the carbonyl oxygen.

A red shift  $(2-4 \text{ kcal mol}^{-1})$  is observed as we go from aprotic to alcohol solvents. Moreover, the band shifts dramatically due to an addition of a very small amount of alcohol. In some cases an isosbestic point is clearly observed. Study of absorption band in *n*-hexane + ethanol mixed solvent (1:1 mole ratio) at different temperatures also indicate the existence of isosbestic point. All these facts point to exothermic formation of a ground– state complex of the solute with alcohols possibly through hydrogen bond formation with the carbonyl oxygen. The  $\Delta H$  values are in the order of dye V  $\approx$  dye VI ( $\approx 1.2 \text{ kcal mol}^{-1}$ ) and dye III  $\approx$  dye IV ( $\approx 0.9 \text{ kcal mol}^{-1}$ ). This parallels the AM1 charge densities on the carbonyl oxygen.

Table 1 Absorption and 1	fluorescence char	acteristics of the d	lyes in pure solvent	s at 298 K					
Solvents	Dye III		Dye IV		Dye V		Dye VI		
	$E(\mathbf{A})$ (kcal mol <sup>-1</sup> )	E(F) (kcal mol <sup>-1</sup> ) <sup>a</sup>	E(A) (kcal mol <sup><math>-1</math></sup> )	E(F) (kcal mol <sup>-1</sup> ) <sup>a</sup>	E(A) (kcal mol <sup>-1</sup> )	E(F) (kcal mol <sup>-1</sup> ) <sup>a</sup>	E(A) (kcal mol <sup>-1</sup> )	$E(F (kcal mol^{-1})^a)$	
Water	54.98	48.46	67.27	51.98	68.07	51.52	66.49	51.98	
Methanol	59.69	49.83 (0.17)	66.49	53.74 (0.30)	68.07	52.65 (0.27)	68.56	53.95	
Ethanol	59.81	50.02 (0.26)	66.57	54.05 (0.26)	68.40	52.95 (0.29)	68.24	54.25	
1-Propanol	60.13 50.04	50.07 (0.19) 50.04 (0.19)	66.49 66.34	54.05 (0.24) 54.05 (0.25)	68.15 67 01	52.95 (0.20) 53 07 (0.27)	68.24 68.07	54.56 (0.28) 54 88 (0.25)	
1-Dutation	59.80	50 46 (0 15)	66.18	54 25 (0 17)	16.70 68.07	53 34 (0.0.23)	00.07 68 24	55 52 (0 29)	
1-Octanol	60.07	50.89 (0.17)	66.65	54.77 (0.23)	68.73	53.90 (0.19)	68.73	51.61 (0.30)	
Acetic acid	59.56	50.96	65.58	54.98	67.90	56.02	68.07	56.39	
Acetone	62.84	52.56	68.73	54.98	70.42	54.56	70.25	54.88	
Butan-2-one	63.11	53.34	68.73	55.73	70.33	55.67	70.95	54.96	
Acetonitrile	62.43	51.33 (0.08)	68.56	53.84 (0.08)	70.08	53.54 (0.10)	70.60	52.95 (0.10)	
Propionitrile	62.29	51.98 (0.04)	68.56	54.67 (0.02)	70.08	54.46 (0.17)	70.42	53.24 (0.08)	
Benzonitrile	60.83	52.06 (0.09)			(0.03)		(0.02)	(0.12)	
1,4-Dioxane	63.39	57.97	69.23	59.82	71.12	59.32	71.48	59.69	
Tetrahydrofuran	63.11	56.04	68.89	58.28	70.60	58.11	71.28	57.53	
Anisole	61.89	55.62	68.07	57.95	69.90	57.53	06.69	57.88	
Benzene	62.84	58.73	68.40	58.83	70.60	61.03	71.09	60.73	
Toluene	63.11	59.07	68.73	61.22	70.95	61.43	71.12	61.75	
Ethylacetate	63.54	52.80	69.31	56.68	70.95	55.91	71.48	57.57	
Dichloromethane	62.49	52.71	68.07	56.28	69.65	56.04	70.42	55.41	
1,2-Dichloroetha	61.75	53.38	68.24	56.08	69.40	55.84	70.42	55.41	
ne									
<i>n</i> -Hexane	73.31	64.66	71.66	63.54	74.85	63.11	75.04	62.43	
Propylenecarbon	61.42	51.28	67.75	53.60	68.98	53.44	69.56	52.95	
ate 2,2,2-Trifluoroeth anol	ו 57.41	46.86	64.39	52.56	65.88	52.46	66.80	52.85	
10110									

<sup>a</sup> The figures in the bracket indicate the anisotropy values.

For benzene, toluene, 1,4-dioxane, and tetrahydrofuran the maximum energy of absorption comes up at a lower value although these solvents are characterised by lower polarity in the  $E_{\rm T}(30)$ scale. This suggests that the nature of interaction of the dyes with these solvents is somewhat different from that in the case of indicator solute for the  $E_{\rm T}(30)$  scale. It appears that these solvents goes into a stronger interaction with the dyes than predicted by the polarity parameters. This is also reflected by the high solubility of these dyes in these solvents.

The emission band may be characterised by  $S_1 \rightarrow S_0$  transition. For most of the solvents the bands appear as structureless at 298 K. The fluorescence band is roughly symmetrical with respect to the absorption band (Fig. 2), the absorption band being wider in all the cases. The fluorescence maximum shows strong sensitivity towards a change in solvent polarity, the band shifting to the red as the polarity increases. This is intelligible in terms of an increase in the dipole

moment on excitation. The value of  $\mu_1$ , the dipole moment in the S<sub>1</sub> state, may be obtained from the solvatochromism of the absorption and the emission band. Using the formalism developed by Marcus [18–21] one can partition E(A) and E(F)as follows

$$E(\mathbf{A}) = \Delta G(\text{solv}) + \lambda_1 \tag{2}$$

$$E(\mathbf{F}) = \Delta G(\text{solv}) - \lambda_0 \tag{3}$$

Where  $\Delta G(\text{solv})$  is the difference in free energy of the ground and equilibrium (relaxed) excited state in a given solvent and  $\lambda$  represents the reorganisation energy. The suffixes '0' and '1' denote the ground and excited state, respectively. Under the condition that  $\lambda_0 \approx \lambda_1 \approx \lambda$  one gets [22]

$$E(\mathbf{A}) + E(\mathbf{F}) = 2\Delta G(\text{solv}); \ E(\mathbf{A}) - E(\mathbf{F}) = 2\lambda$$
(4)

 $\Delta G(\text{solv})$  and  $\lambda$  may be calculated using the Onsager reaction field model. Thus, the final equation is as follows.



Fig. 3. Plots of E(A) and E(F) vs.  $E_T(30)$ . (a) Dye III; (b) dye IV; (c) dye V, and (d) dye VI.



Fig. 4. Representative plot of (a) E(A) + E(F) and (b) E(A) - E(F) as a function of dielectric function for dye V.  $f(\varepsilon) = [2(\varepsilon - 1)/(2\varepsilon + 1)]$  and  $f(\varepsilon, n^2) = [2(\varepsilon - 1)/(2\varepsilon + 1) - 2(n^2 - 1)/(2n^2 + 1)]$ .

$$E(A) + E(F) = [(\mu_0^2 - \mu_1^2)/a^3][2(\varepsilon - 1)/(2\varepsilon + 1)] + 2\Delta G(gas) + \Delta(sp)$$
(5)

and

$$E(\mathbf{A}) - E(\mathbf{F})$$
  
=  $[(\mu_1 - \mu_0)^2 / a^3][2(\varepsilon - 1)/(2\varepsilon + 1) - 2(n^2 - 1)/(2n^2 + 1)]$  (6)

where  $\varepsilon$  and *n* are the dielectric constant and the refractive index of the solvent,  $\Delta G(\text{gas})$  is the value and  $\Delta G$  in the gas phase and *a* is the cavity radius. These equations are valid for aprotic solvents where specific interactions are absent. Fig. 4 shows representative plots of  $E(A) \pm E(F)$  versus the appropriate dielectric function. Note that the

ratio of the dipole moments in the S<sub>1</sub> and S<sub>0</sub> state  $(\mu_1/\mu_0)$  may be obtained from the ratio of the slopes of such plots. From this one can calculate the  $\mu_1$  using the  $\mu_0$  values obtained from the semiempirical AM1 calculation. Note that this method does not require the value of the cavity radius, 'a'. The calculated  $\mu_1$  values for the dyes are 9.5, 10.2, 9.9, and 9.9 D for dye III, IV, V, and VI, respectively.

Fig. 3 shows also plots of E(F), the energy of fluorescence maximum, versus the  $E_{T}(30)$  parameter. A double linear correlation is found for all the dyes. Alcohol solvents fall on a separate line (having a lower slope) indicating that the nature of the emitting state is different for these class of solvents. The enhanced solvent sensitivity of E(F)compared to E(A) may be explained in terms of increased solute-solvent interaction in the excited state due to an increased in the dipole moment upon excitation. For alcohols, apart from dipolar interaction tighter hydrogen bonding is expected in the excited state of the solvent as a result of increased charge density on the carbonyl oxygen on excitation. Thus, the emitting state in the case of protic solvent is a strongly hydrogen-bonded solvated complex. For dye IV a proton transfer across the hydrogen bond has been suggested [12]. The stronger solvent-solute interaction for alcohols may also be inferred from the anisotropy (r) of fluorescence. A higher value for alcohol solvents (Table 1) indicate a slower rotational motion of the transition dipole in an alcohol cage.

In order to investigate the role of non-specific dipolarity interaction and specific hydrogen bonding ability of solvents a multiple linear regression analysis [23] was made. A linear correlation of E(F) was sought with the Kamlet–Taft parameter [24]  $\pi^*$ ,  $\alpha$ , and  $\beta$  representing the dipolarity–polarisability interaction, the hydrogen–bond donating, and acceptance ability of solvents. The following regression equations have been obtained for the dyes.

For dye III:  $E(F) = 63.99 - 5.29\alpha - 5.00\beta - 11.25\pi^*,$ n = 24, r = 0.96. r = 0.90.

For dye IV:  $E(F) = 64.50 - 3.24\alpha - 4.57\beta - 9.19\pi^*, n = 20, r = 0.94.$ For dye V:  $E(F) = 64.30 - 3.05\alpha - 3.71\beta - 9.36\pi^*, n = 20,$ 

For dye VI:  $E(F) = 64.30 - 3.60\alpha - 5.50\beta - 8.50\pi^*$ , n = 20, r = 0.94.

For all the dyes the coefficient of the  $\pi^*$  term is greater than that of the  $\alpha$  or  $\beta$  term, indicating that the dipolarity/polarisability interaction is more important for the dyes especially for the unsymmetrical dyes IV–VI. This behaviour is different for the dyes I and II where an opposite trend is observed [7,8]. For these dyes an increase in the electron density on the carbonyl oxygen



Fig. 5. Fluorescence spectrum of dye I in (a) dilute solution ( $\leq 10^{-6} \mod 1^{-1}$ ) and (b) concentrated ( $\geq 10^{-5} \mod 1^{-1}$ ) solution at 288 K. (c) Fluorescence spectrum of the concentrated solution at 308 K; (d) and (e) are the difference of the spectrum in concentrated and dilute solution at 288 and 308 K respectively.

Table 2 Fluorescence characteristics of the dyes in heterogeneous media at 298  $\mbox{K}$ 

leads to an extension of conjugation modifying the energy levels as pointed out by Kessler and Wolfbeis [13]. The constant term in the above equation represent the E(F) value in a non-polar media, e.g. n-hexane where solute-solvent interaction is not present. For all the dyes the value appears at  $\approx 64$  kcal mol<sup>-1</sup>, which is in good agreement with the experimental value (Table 2). The dyes are practically insoluble in water and so the direct measurement of E(F) for water is not possible. However, when water is added to an ethanol solution of the dye the fluorescence maximum shifts to higher wavelength. Plot of the E(F)values against the mole fraction of water gives a straight line from which the E(F) value for pure water may be found out by extrapolation. The values thus obtained have been tabulated in the Table 1.

In aromatic hydrocarbons (benzene, toluene) and cyclic ethers (1,4-dioxane, tetrahydrofuran, 2-methyltetrahydrofuran) the fluorescence band is found to be structured. When n-hexane is added to these solvents a gradual blue shift is observed and the structures become more prominent. Fluorescence in these solvents are also concentration dependent, the higher wavelength band is more prominent at higher concentration. Fig. 5 shows a representative plot. For example, in a dilute solution ( $\approx 10^{-6}$  M) the two bands around  $\lambda = 525$ and 545 nm were obtained for the dye I, the relative intensities of the bands do not change significantly as the temperature is changed in the range 288-318 K. But in concentrated solution the relative intensity of the 550 nm band increases at lower temperature. Difference of the spectra in concentrated and dilute solution indicates a broad band with maxima at  $\approx 550$  nm. The overall intensity of the band increases as the temperature

Environment	Dyes												
	III			IV			V			VI			
	$\frac{E(F)}{(\text{kcal mol}^{-1})}$	Anisotropy (r)	<i>K</i> (mol 1 <sup>-1</sup> )	E(F) (kcal mol <sup>-1</sup> )	Anisotropy (r)	<i>K</i> (mol 1 <sup>-1</sup> )	E(F) (kcal mol <sup>-1</sup> )	Anisotropy (r)	$K \pmod{1^{-1}}$	E(F) (kcal mol <sup>-1</sup> )	Anisotropy (r)	$\frac{K}{(\text{mol } 1^{-1})}$	
SDS	49.55	0.12	_	52.46	0.30	1860	52.95	0.32	732	51.98	-	340	
CTAB	49.29	0.25	-	52.95	0.28	5000	52.95	0.28	20 000	52.95	0.30	-	
TX-100	49.38	0.21	-	54.46	0.28	51 300	54.46	0.24	129 000	53.95	0.23	26 000	
$\beta\text{-cyclodextrine}$	51.89	0.33	-	54.25	0.27	-	54.88	0.30	-	54.98	0.31	-	



Fig. 6. Fluorescence spectra of dye VI in CTAB (a); SDS (b) and TX-100 (c) micelles (conc. of micelle 4 CMC). The dotted line indicates the spectrum when the surfactant concentration is 0.25 CMC. (d) Representative plot of the Eq. (8) for dye VI in CTAB.

intensity of the band increases as the temperature is lowered. No such change, however, has been observed in the excitation or the absorption spectrum. These facts points to an aggregation of the dye in the excited state in a concentrated solution (concentration  $\geq 10^{-5}$ ) in these non-polar solvents. In a polar solvent the chromophore individually interacts with solvent dipoles and are no longer free to form aggregates.

### 3.2. Heterogeneous media

The absorption and fluorescence characteristics of the dyes III–VI in heterogeneous media have been summarised in Table 2. The dyes are only slightly soluble in water. This is perhaps due to the presence of hydrophobic part of the dye. The solubility of the dye III in micellar media is also small, but for the other dyes solubilisation is higher. Increased solubility in micellar media indicates dye–micelle interaction. Measurements of emission polarisation gives high values of fluorescence anisotropy (Table 2). This indicates a slower rate of rotational motion of the transition dipole in micellar environment, meaning a significant dye-micelle interaction. Fig. 6 is a representative plot, showing the fluorescence characteristics of the dyes in a solution of a surfactant. Below the critical micelle concentration (CMC) of the surfactant the intensity of fluorescence is small and the band shows a structure. The structure becomes less prominent as the concentration of the surfactant is increased beyond the CMC value and practically vanishes at higher CMC. The structure is possibly indicative of the carbonyl vibration, which smoothes out as the dye-micelle interaction is increased. For fixed concentration of dye the intensity of maximum emission increases as the concentration of micelle is increased and reaches a limiting value at a very high concentration of micelle (when micellisation of the dye is complete). For a particular concentration of the micelle the intensity of fluorescence increases as the temperature is decreased. All the observations point to the existence of the equilibrium

$$D + M \rightleftharpoons D...M$$
 (7)

Where D and M represent the dye and the micelle respectively and D...M represent the dye bound with micelle.

The fluorescence band maximum of the dye bound to the ionic micelles appear below the extrapolated E(A) value for water and is in the order SDS > CTAB. For the neutral micelle Triton X 100 (TX-100) the maximum of emission appear around  $\lambda = 525-530$  nm for all the dyes that are similar to the E(A) value in alcohol solvent. These observations suggest that the immediate environment of the dye is a polar one. This rules out the possibility of the dye being located inside the micelle. It has been observed by earlier workers [24-26] that a part from the head group and counter ions only water and alkyl chains contribute to the polarity of the micellewater interface and as such alcoholic solvents are better model solvents to describe the region. Thus, we infer that the dyes are located in the micellewater interface.

The negative charge density of the carbonyl group of the dye in the  $S_1$  state will be involved in the electrostatic interaction with the polar head group of the ionic micelles. Besides this, hydrophobic interaction of the hydrocarbon like wing of the dye with the micelle also plays a part as reported by other workers [27] for different dyes. In the cationic micelle (CTAB), the positively charged head group will attract the negative charge density of the carbonyl oxygen and the dye will be in a more hydrophobic environment. This is particularly more important in the S<sub>1</sub> state of the dye. Thus, the possibility of hydrogen bonding interaction will be reduced. On the other hand, for anionic micelles (SDS) the chromophoric part of the dye will be more exposed to hydrophilic environment and more effective hydrogen bonding will take place. This is also reflected in the fluorescence band maximum of the dyes in the micelles as discussed earlier. The non-ionic surfactant TX-100 consists of bulky phenyl head groups and a long polyoxyethylene chain, which terminates in an -OH group. The fluorescence maximum in TX-100 micelle appear around the same region as in alcohols. This is true for other nonionic micelles. For example, in brij-35 and tween 80 the band for V appears at  $\lambda = 530$  and 525 nm,

respectively. Thus, the dye-micelle interaction is similar to the dye-alcohol interaction for these micelles.

A quantitative estimate of the binding constant (K), i.e. the equilibrium of the process Eq. (7), the equation proposed by Almgren et al. [28,29] can be used. Thus,

$$(I_{\infty} - I_0)/(I - I_0) = 1 + (K[M])^{-1}$$
(8)

where  $I_{\infty}$ ,  $I_0$ , and I are the fluorescence intensities under complete micellisation of the dye, in absence of micellisation, and at any intermediate micelle concentration, respectively. [M] represents the concentration of the micelle, which is given by [M] = ([Surf] - CMC)/N and [Surf] represents the surfactant concentration and N is the aggregation number. For the calculation of M the values of Nare 62, 60, and 143 for SDS, CTAB, and TX-100, respectively. The measured K values (+10%) are given in the Table 2.  $\Delta H$  values may also be obtained similarly. Our experimental results indicate that  $|\Delta H|$  values (1–2 kcal mol<sup>-1</sup>) are in the order CTAB  $\approx$  TX-100 > SDS. For the cationic micelle (CTAB) the electrostatic interaction between the carbonyl oxygen and the positive charged micelle is the major contributing factors towards  $\Delta H$  values. In SDS, however, the positive end of the dye  $(S_1 \text{ state})$ , i.e. the N atom of the dimethylamino group goes into interaction with the micelle. But the charge of N atom is somewhat shielded by the methyl group. Thus, the electrostatic interaction is less. There is however a hydrogen bonding interaction between the carbonvl oxygen and water molecules. The results indicate that for SDS the overall interaction energy becomes less than that for the CTAB micelle. It is important to note that the dye-micelle interaction for symmetric ketocyanine dyes (I-III) is less than for the unsymmetric dyes (IV-VI). For unsymmetric dyes, one end of the dipolar dye (positive or negative) may remain attached to the micelle interface keeping the other end (negative or positive) part away from the micelle, thus minimising the electrostatic interaction. But this is not possible for the symmetric structure, making the dye-micelle interaction weaker.

Table 2 also lists the spectral features in aqueous  $\beta$ -cyclodextrine ( $\beta$ -CD) solution. Strong

dye- $\beta$ -CD interaction is indicated by high values of fluorescence anisotropy. It appears that the fluorescence characteristics in the medium is very similar to those in the neutral micelles, e.g. TX-100, brij 35, or tween 80, pointing to the fact that interaction of the dyes in these media are very similar. Thus, the dye is located near the  $\beta$ -CD bucket and the interaction of the carbonyl part of the dye with the hydroxyl groups in  $\beta$ -CD are important.

### 4. Conclusion

Ketocyanine dyes are good indicators of solvent polarity. In protic solvents they exist as an equilibrium mixture of bare and hydrogen bonded form, the later being the emitting species. In aprotic solvents of lower polarity the  $S_1$  state of the dye exists in associated form in equilibrium with the solvated monomer. The unsymmetric dyes show greater micelle-dye interaction. The binding constant and the heat of binding can also be determined from fluorimetric studies.

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