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Steady-state fluorescence and photophysical properties of a ketocyanine dye in binary surfactant and polymer–surfactant mixture

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Abstract

Steady-state and time-resolved fluorescence studies have been done using a ketocyanine dye in heterogeneous media containing binary mixtures of sodium dodecyl sulphate (SDS) and triton X-100 (TX-100), and SDS + polyvinyl pyrrolidone (PVP). The dye molecules are found to distribute between core and interfacial region of the micelles. The band corresponding to the dye molecule in the core region exhibits red edge excitation shift. Study of lifetime in picosecond domain reveals that the de-excitation of the excited state of the dye via radiative pathway (k_r) is independent of environment. The non-radiative decay constant (k_{nr}) on the other hand has been found to depend on the nature of environment, the core region being characterised by a faster decay rate. The slower decay rate in the interfacial region has been explained as due to hydrogen bonding interaction of the carbonyl group of the dye with protic solvents. Interesting variation of k_{nr} in the core region with surfactant composition has been observed which is explained in terms of surfactant–surfactant interaction in the micelles. Microviscosities at the micelle–water interface has been determined. For binary mixture of surfactants, the value of microviscosity has been found to deviate from ideality. An index of deviation from ideality has been proposed.

1. Introduction

Ketocyanine dyes [1,2] are suitable fluorescence probes for studying solvation characteristics of a medium. The solvatochromic fluorescence behaviour of these probes has been used extensively to obtain information regarding solvation interaction in pure and mixed binary and ternary solvents [3–7]. Solvent dependence of general photophysics of the dyes in homogeneous media is also interesting. Lifetime (τ) of the dyes in a protic solvent has been found to be considerably longer than that in an aprotic solvent [8]. Although the steady-state fluorimetric studies with the dyes have been done in aqueous solution containing pure surfactants [9], a systematic study in heterogeneous media containing binary surfactant mixture or polymer–surfactant mixture has not yet been done with these dyes as probes. These heterogeneous systems are very interesting from theoretical and practical point of view and have been the subject of current interest [10–17]. Moreover, time-resolved fluorescence studies in heterogeneous media have not been done with this dye. Objective of the present paper is to explore the possibility of studying solvation and microenvironmental characteristics of heterogeneous systems using the solvent sensitive fluorescence parameters of the dyes. The steady state parameters (e.g. position of band maximum, the effect of red edge excitation on the fluorescence and anisotropy) and lifetime in the picosecond domain have been studied for the dye (1-1), (9-1)-di-1, 9-di-(2,3-dihydroindolyl)-4,6-dimethylene-nona-1,3,6,8-tetraene-5-one (Fig. 1) in aqueous solutions containing homo- and hetero-micelles formed between sodium dodecyl sulphate (SDS) and triton X-100 (TX-100). Modification of microenvironmental properties of SDS micelles by addition of water-soluble polymer polyvinyl pyrrolidone (PVP) has also been studied.

2. Experimental section

2.1. Materials and methods

The dye was prepared by the methods described earlier [1]. SDS (Sigma) was purified by recrystallisation from ethanol. TX-100 (Sigma) of purity >99% and the neutral polymer PVP (Aldrich) of purity >99% with average molecular weight ca. 29,000 were used as received. For preparing solutions of surfactant mixtures and surfactant–polymer mixtures, the required amount of surfactant–polymer were

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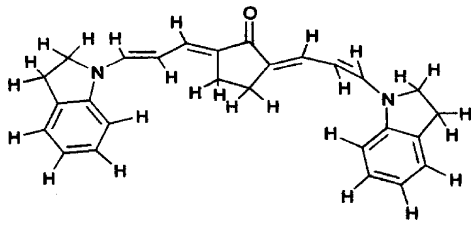

Fig. 1. Optimised geometries of ketocyanine dye by MOPAC version-6 with axial ratio 16.48:10.64.

added to triply distilled water, and the contents were sonicated in an ultrasound sonicator (JENCOS, UK, Model T80) for a considerable period. Solutions for spectroscopic measurements were prepared by the following method. At first a stock solution of the dye was prepared in dry ethanol ($\sim 10^{-4}$ M). A 0.05 ml of the above stock solution was introduced in a volumetric flask, spread over the flask and the solvent evaporated under gentle heating. Then 5 ml of the heterogeneous medium has been added to the flask and the solution was sonicated for about 1 h. The resulting clear solution was then directly taken into spectrophotometer cuvette [15]. Concentration of the dye in solutions was in the range 10^{-5} to 10^{-6} M.

2.1.1. Steady state spectral measurements

Absorption spectral measurements were performed on a Shimadzu UV 2101 PC UV-Vis spectrophotometer fitted with a temperature controlled unit (Model TB-85 Thermobath, Shimadzu). The steady-state fluorescence emission and excitation spectra were recorded on a Hitachi F-4500 spectrofluorimeter equipped with polarisation accessory and a temperature controlled cell holder. Temperature was controlled within ±0.1 K by circulating water from a constant temperature bath (HETO HOLTEN). Measurements of steady-state fluorescence anisotropy (r) were calculated using the following equation [18]:

$$r(\lambda) = \frac{I_{VV}(\lambda) - G(\lambda) I_{VH}(\lambda)}{I_{VV}(\lambda) + 2G(\lambda) I_{VH}(\lambda)} \quad (1)$$

where $I(\lambda)$ denotes the fluorescence intensity at the wavelength λ and the first and second subscripts, respectively, refer to the settings of the polarisers on excitation and emission side. Subscripts H and V refer to the horizontal and vertical setting of the polarisers, respectively, and $G(\lambda) = I_{HV}(\lambda)/I_{HH}(\lambda)$, is an instrumental factor representing the polarisation characteristics of the photometric system. Value of r for a particular system remained constant over the emission band. To check the reproducibility, anisotropy values were taken for several replicate measurements. The errors were within ±0.005. Values of quantum yield have been measured using fluorescein in 0.1N NaOH as a standard [19]. Excitation has been done at 450 nm. To avoid reabsorption of the emitted light, absorbances for all solutions were kept below 0.08. Measurements were done at 298 K assuming 0.90 as the quantum yield value for the standard.

2.1.2. Time-resolved fluorescence measurement

The experimental setup for picosecond time correlated single photon counting (TCSPC) is as follows. A picosecond diode laser at 408 nm (IBH, UK, NanoLED-07, s/n 03931) is used as a light source (instrument response ~70 ps). The fluorescence signal was detected in magic angle (54.70) polarisation using Hamamatsu MCP PMT (3809U). The decays were analysed using IBH DAS-6 decay analysis software. Intensity decay curves so obtained were fitted as a sum of exponential terms

$$F(t) = \sum a_i \exp\left(\frac{-t}{\tau_i}\right) \quad (2)$$

where $F(t)$ is the fluorescence intensity at time t, a_i the pre-exponential factor representing the fractional contribution to the time-resolved decay of the component with a lifetime τ_i. All the decay curves showed bi-exponential nature. The decay parameters were recovered using a non-linear least squares iterative fitting procedure. Fitting with χ^2 values not more than 1.5 was taken as acceptable. Mean (average) lifetimes $\langle\tau\rangle$ for bi-exponential decays of fluorescence were calculated from the decay times and pre-exponential factors using the following equation:

$$\langle\tau\rangle = \frac{a_1\tau_1 + a_2\tau_2}{a_1 + a_2} \quad (3)$$

The radiative (k_r) and non-radiative (k_{nr}) rate constants were calculated using the equations given below

$$k_r = \frac{\phi_F}{\tau} \quad (4)$$

$$k_{nr} = \tau^{-1} - k_r \quad (5)$$

where ϕ_F is the fluorescence quantum yield and τ the experimentally observed excited state lifetime.

3. Results and discussions

The dye is practically insoluble in water due to the presence of two hydrophobic wings and becomes soluble (solubility $\sim 10^{-6}$ M [20]) only when the total surfactant concentration exceeds the critical micellisation concentration (CMC). Steady-state and time-resolved fluorescence studies of the dye have been done using surfactant concentration beyond the CMC for SDS + TX-100 mixed micelles [21] or critical aggregation concentration (CAC) of SDS in aqueous PVP solution [16].

4. Mixed micellar system

4.1. Absorption and steady-state fluorescence studies

Fig. 2 shows the representative absorption spectrum of the dye in a homo-micelle. Two bands clearly appear in the

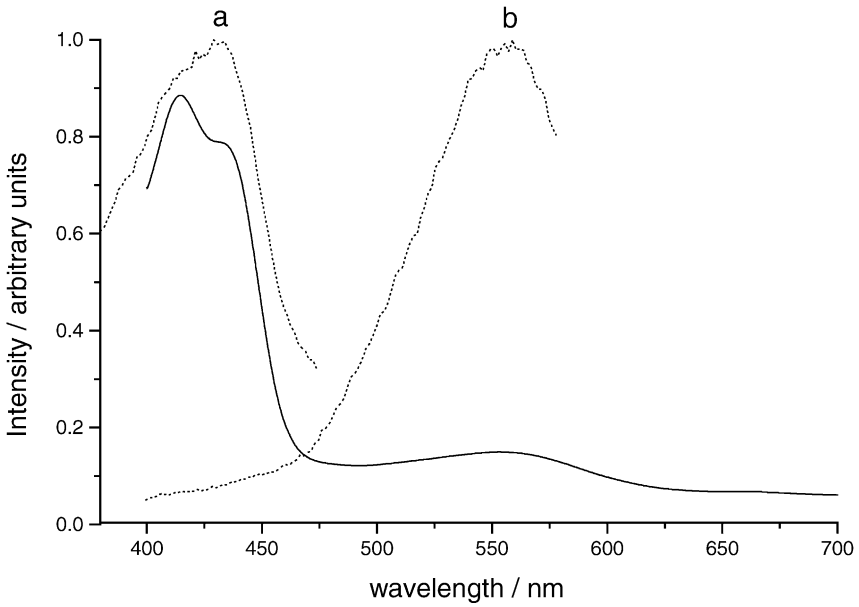

Fig. 2. Absorption (—) and excitation spectra (···) of the dye in SDS homo-micelles at 303 K. (a) Emission collected at 500 nm; (b) emission collected at 620 nm.

spectrum, but their relative intensities depend on the nature of surfactant. It has been shown in our earlier studies in homogeneous solvent that the absorption band of the dye shows solvatochromism [3], the wavelength of maximum absorption shifting to the blue as the polarity decreases. For a solvent with no solvation interaction with the dye, the position of maximum absorption can be estimated as 425 nm and the band shifts to longer wavelength as the polarity of the medium increases. In a protic solvent, however, a H-bonded species exists, which shows maximum absorbance around 550 nm. Our present results thus indicate that in a heterogeneous medium the dye molecules exist as different species in two different environments. The band around 550 nm corresponds to a protic environment, while that around 420 nm is due to a non-polar environment. It is likely that the dye molecules are distributed between the core and the interfacial region, the former is mostly hydrocarbon-like while the latter provides an environment where the hydrogen-bonded complex of the dye can exist. The extent to which the hydrogen-bonded complex exists in the system can be calculated from the ratio of intensity of the two bands. It depends, however, on the nature of surfactant (ca. 10 and 5% for SDS and TX-100, respectively). Moreover, the process of H-bonded complex formation has been found to be exothermic. The estimated ΔH values, as obtained from studies at different temperatures (283–313 K), are 0.3 and 1.5 kcal mol^{-1} for SDS and TX-100, respectively. Moreover, the band due to H-bonded species shows a blue shift as temperature increases. This is intelligible in terms of lesser H-bond interaction at elevated temperatures.

Fig. 3 shows the fluorescence spectrum of the dye in heterogeneous media. For excitation wavelength of 430 nm two fluorescence bands, one around 500 nm and the other around 600–620 nm can clearly be identified. Excitation at 550 nm gives only the 600–620 nm fluorescence. The excitation spectrum when the emission is collected at 500 nm is similar to the absorption spectrum in the non-polar environment as shown in Fig. 2. On the other hand, when the emission is collected at 620 nm one gets an excitation spectrum, identical to the absorption spectrum of the H-bonded complex. Thus the two bands in the fluorescence spectrum of the dye originate from two different emitting states of the dye present in two different environments in a heterogeneous medium. Earlier works with the dye indicated that the emitting state of the dye in a protic solvent is different from that as in the case of an aprotic solvent. In an aprotic solvent the fluorescence band, which is supposed to originate due to $S_1 \rightarrow S_0$ transition (with intramolecular charge transfer, ICT, involving carbonyl oxygen and the nitrogen atom), shifts to the blue as the polarity of the medium is decreased [1–3]. In a protic solvent the initially prepared excited state goes over to a twisted intramolecular charge transfer, TICT, state and the fluorescence takes place from that state [22]. The band around 500 nm observed in the present case (henceforth called N-band) corresponds to a non-polar hydrocarbon environment present in the core region of the micelle. On the other hand the band around 600–620 nm (P-band) is characteristic of a protic environment. Studies in homogeneous solvent indicate that the band around 600–620 nm is characteristic of alkanols (e.g. ethanol 624 nm, octanol 600 nm). It is known that the interfacial region of an aqueous micelle with water–hydrocarbon interface is mimicked by alkanols [23–25]. Thus the P-band presumably corresponds to the interfacial region of the micelle. The fraction of dye molecules in the aqueous bulk phase is negligible as can be inferred from the insolubility of the dye in aqueous surfactant solu-

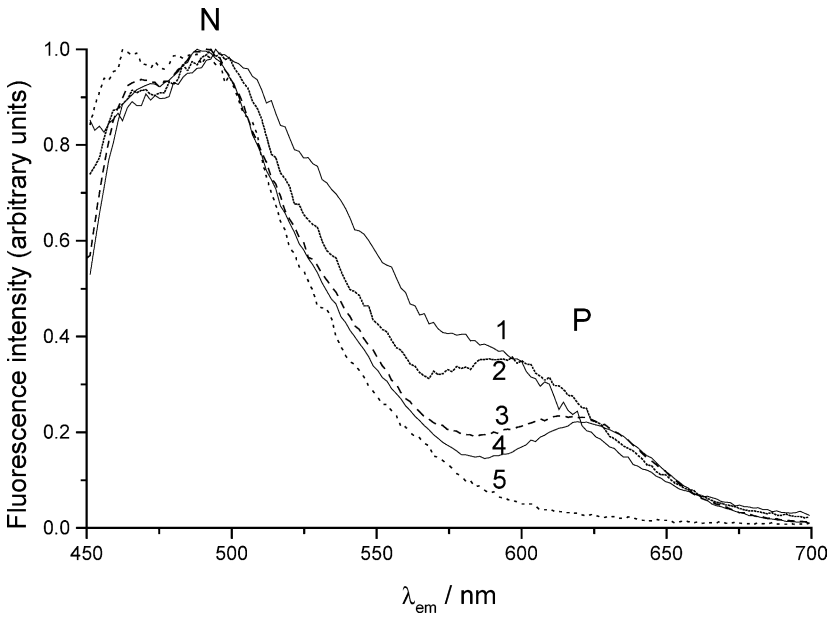

Fig. 3. Fluorescence bands of the dye in different media. SDS + TX-100 mixed micelles, mole fraction of SDS are 0.0 (1), 0.5 (2), 0.8 (3) and 1.0 (4); aqueous polymer solution (5).

tion of concentration less than CMC. The maximum fluorescence of the dye in water has been estimated to be at 650 nm by extrapolating the data in aqueous ethanol. We have not observed appreciable fluorescence in the region of 650 nm, which is characteristic of the dye in aqueous medium. Steady state spectroscopic results can thus be rationalised by using a two-state model where dye molecules are distributed between the core and interfacial region of a micelle. Relevant parameters for the fluorescence bands as a function of surfactant composition are given in Table 1. The effective polarity as indicated by the wavelength of maximum fluorescence (λ_{em}) is rather insensitive towards a variation of surfactant composition in mixed micellar core. The value of λ_{em} decreases gradually as one goes from pure TX-100 to pure SDS. On the other hand, polarity of the interfacial region changes significantly, decreasing as the percentage of TX-100 in the surfactant mixture increases. The N-band is characterised by higher value of steady-state fluorescence anisotropy (r). The position of the maximum emission for the N-band depends on the excitation wavelength showing red edge excitation shift (REES) as indicated in Table 1. On the other hand the position of the P-band is independent of the excitation wavelength. Existence of REES has often been explained in the light of motional restriction of a probe molecule in a confined environment [26,27]. In the present case the observed REES can be rationalised in terms of hindrance to relaxation of the S_1 state of the dye confined in the core of the micelle. The high value of fluorescence anisotropy, as observed for the N-band (Table 1) also supports this view. As expected, the value of r slightly decreases

Table 1
Steady-state fluorescence parameters for the dye in SDS + TX-100 media

Mole fraction of SDS (α_{SDS})	Fluorescence emission maxima for N-band (nm)[a]			Fluorescence maxima for P-band (nm) (excitation at 540 nm)[a]
	Excitation at 430 nm	Excitation at 480 nm	Extent of REES (nm)	
0.0	498 (0.30)	516 (0.28)	18	595 (0.08)
0.1	497 (0.30)	514 (0.28)	17	596 (0.09)
0.2	497 (0.36)	512 (0.34)	15	597 (0.09)
0.3	497 (0.35)	511 (0.32)	14	599 (0.10)
0.4	496 (0.32)	509 (0.30)	13	601 (0.11)
0.5	495 (0.30)	507 (0.29)	12	603 (0.12)
0.6	495 (0.35)	506 (0.32)	11	607 (0.13)
0.7	494 (0.34)	505 (0.31)	11	610 (0.14)
0.8	493 (0.33)	503 (0.30)	10	615 (0.16)
0.9	492 (0.32)	502 (0.29)	10	620 (0.17)
1.0	490 (0.30)	500 (0.28)	10	626 (0.20)

[a] Inaccuracy ±1 nm, value within bracket indicates fluorescence anisotropy.

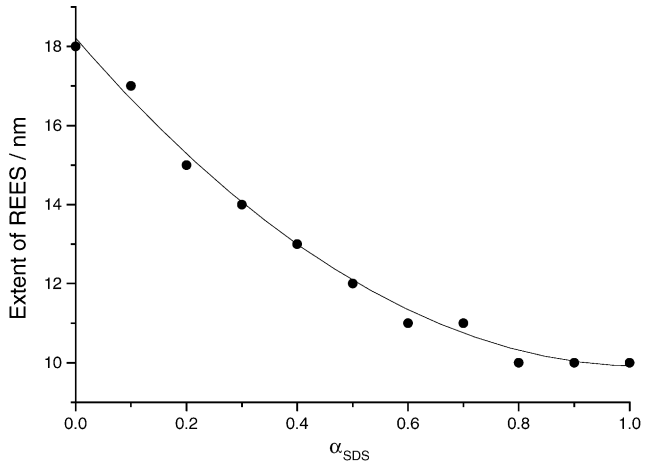

Fig. 4. Red edge excitation shift (REES) of N-band of the dye as a function of surfactant composition.

as the excitation wavelength is at the red edge of the absorption band (Table 1). The extent of REES depends on the nature of the hydrocarbon core. Thus it is greater in TX-100 micelle than in SDS homo-micelle indicating greater motional restriction in the core of TX-100 micelles. In the case of hetero-micelles the REES depend on the composition as can be seen from Fig. 4. The nature of variation in the TX-100 rich region is different from that in the SDS rich region, the former showing a steeper change. Absence of REES in the interfacial region may be explained as due to longer lifetime and greater mobility of the fluorophore in this region.

4.1.1. Lifetime and photophysical parameters

Fluorescence decays have been analysed for both the N and P-bands. For all the solutions the decay curves were best fitted by a bi-exponential fit. N-band is characterised by a faster decay with lifetime (τ) ~50 ps (>94%) and a relatively slower decay component (<6%). P-band on the other hand is characterised by two lifetime values ~300 ps (≥25%) and ~1500 ps (≤75%). Table 2 lists the lifetime values (τ_1 and τ_2) and the fractional contribution to the time-resolved decay of the component with lifetimes τ_1 and τ_2 as a function of surfactant composition. Values of average lifetime ($\langle\tau\rangle$) as calculated using Eq. (3), have also given in Table 2. Our previous work indicated that the fluorescence decay of the dye in a homogeneous media is best fitted by a single exponential term and the value of τ depends on solvent polarity [8]. It is characterised by a longer lifetime in protic solvents where the dye exists as H-bonded species (e.g. 1750 ps in methanol, 1680 ps in ethanol, compared to a value of 766 ps for benzene). Results in heterogeneous media indicate that different species exist in the system. Thus the observed τ-value ~1500 ps can be associated with the emitting state for the H-bonded species. On the other hand the τ-value ~300 ps is characteristic of the emitting state for the bare form of the dye molecule. The existence of lifetime <50 ps is not clearly understood.

As discussed earlier, absorption spectral studies have indicated the existence of two forms of the dye, viz the bare and the H-bonded species (in S_0 state), present in equilibrium in a heterogeneous medium. On excitation the emission takes from the S_1 state in a non-polar environment. On the other hand the emitting state in the case of a H-bonded complex is a TICT state. Bi-exponential fluorescence decay of both N-band and P-band of the dye in a heterogeneous medium indicates that two species are present in each of the two different microenvironments, viz, non-polar hydrocarbon core of the micelle and the interfacial region. Both the H-bonded form ($\tau \sim 1500$ ps) and the bare form ($\tau \sim 300$ ps) exist in the interfacial region. In the core, however, the H-bonded form does not exist, but a species characterised by a shorter decay time ($\tau \sim 50$ ps) and the bare form of the dye are present. It appears that N-band is, on the average, faster decaying than the P-band. To study the photophysical parameters in the excited state, we have calculated the rate of deactivation of the excited state by radiative (k_r) and non-radiative (k_{nr}) paths using the $\langle\tau\rangle$ value and the measured value of quantum yield, ϕ_F as given in Table 2. The calculated values of k_r and k_{nr} have also been listed in Table 2. The k_r value for the N-band is practically constant, averag-

Table 2
Photophysical parameters for the dye in SDS/TX-100 mixed micelle

α_{SDS}	N-band								P-band					
	a_1	a_2	τ_1^m (ps)	τ_2 (ps)	$\langle\tau\rangle^m$ (ps)	ϕ^n	k_r^m ($\times10^{-8}$ s^{-1})	k_{nr} ($\times10^{-9}$ s^{-1})	a_1	a_2	τ_1 (ps)	τ_2 (ps)	$\langle\tau\rangle$	k_{nr} ($\times10^{-8}$ s^{-1})
0.0	0.94	0.06	44	359	63	0.018	2.9	15.6	0.42	0.58	300	1540	1020	5.8
0.1	0.95	0.05	37	298	50	0.018	3.6	19.5	0.39	0.61	318	1550	1070	5.3
0.2	0.96	0.04	32	270	41	0.018	4.4	23.7	0.37	0.63	332	1560	1100	5.1
0.3	0.97	0.03	28	274	35	0.019	5.4	27.8	0.34	0.66	342	1550	1140	4.8
0.4	0.97	0.03	25	312	34	0.019	5.6	28.8	0.32	0.68	347	1550	1170	4.6
0.5	0.98	0.02	24	383	32	0.019	6.0	31.1	0.30	0.70	348	1540	1180	4.5
0.6	0.98	0.02	25	487	34	0.020	5.8	26.7	0.29	0.71	345	1520	1180	4.5
0.7	0.99	0.01	26	623	32	0.025	7.8	27.5	0.27	0.73	338	1500	1190	4.4
0.8	0.99	0.01	30	793	38	0.031	8.2	22.7	0.26	0.74	327	1480	1180	4.5
0.9	0.98	0.02	34	996	53	0.040	7.6	13.8	0.26	0.74	310	1450	1150	4.7
1.0	0.96	0.04	40	1230	88	0.050	5.7	7.2	0.25	0.75	290	1410	1130	4.8

m: error ± 15%, n: error ± 0.002.

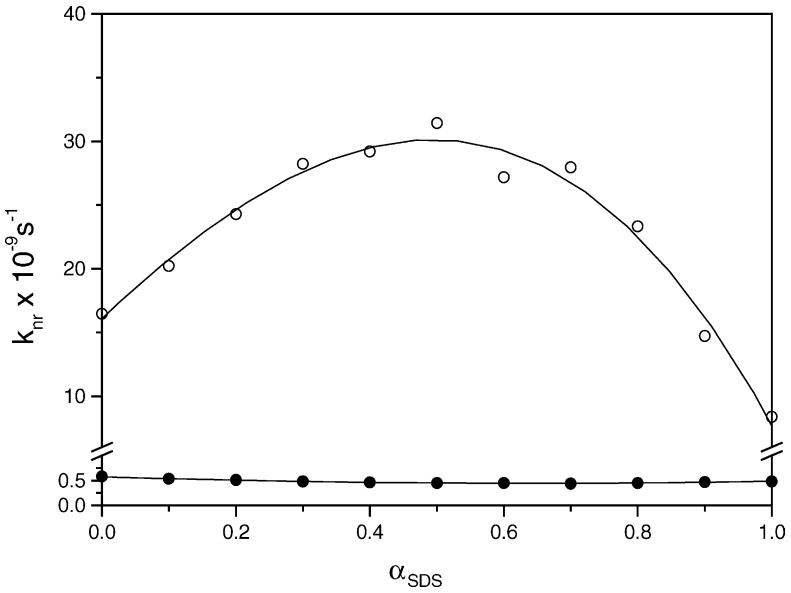

Fig. 5. Variation of k_{nr} as a function of bulk surfactant composition in the core (○) and interfacial (●) region of the micelle.

ing to a value of $5.3 \times 10^8\ s^{-1}$. We have shown in a previous communication that the value of k_r for the dye does not depend much on the nature of the environment around the dye. The reported value for homogeneous media is $\sim 4 \times 10^8\ s^{-1}$ [8]. The experimentally determined value for heterogeneous media is close to this value within experimental inaccuracy. We have calculated the k_{nr} values for the P-band assuming a value of $k_r = 4 \times 10^8\ s^{-1}$. The calculated values are listed in Table 2. Note that the dynamics is slower (by a factor of 15 or more) in the interfacial region relative to the core region. The slower rate of de-excitation in a protic environment can be explained in terms of stronger dye–solvent interaction through hydrogen bonding between the carbonyl group of the dye and protic solvent molecules [8]. Variation of k_{nr} values with the composition of surfactants is interesting enough. Fig. 5 shows the variation as a function of α_{SDS}, the average mole fraction of SDS in the binary surfactant mixture. While the decay rate does not vary much with α_{SDS} in the interfacial region, the decay rate at the core first increases up to $\alpha_{SDS} = 0.5$ and then decreases. This can be rationalised in terms of variation of surfactant–surfactant interaction with surfactant composition in the two regions.

4.1.2. Micro-viscosity

It is known that the measured steady state anisotropy (r) gives information about the rotational reorientation time (τ_R) of the absorption dipole moment. In the case of isotropic rotations the measured value of r is given by Perrin's equation [28,29]:

$$\frac{1}{r} = \frac{1}{r_0} + \frac{\tau}{r_0 \tau_R} \tag{6}$$

where τ is the lifetime of the excited state, r_0 refers to the value of fluorescence aniosotropy in the limiting condition characterised by the absence of rotational diffusion. For this dye r_0 has been found to be 0.4 [30]. Theoretically, τ_R is given by the Stokes–Einstein–Debye (SED) equation [31–33]:

$$\tau_R = \frac{v \eta f C}{k_B T} \tag{7}$$

where v is the molar volume of the solute, k_B the Boltzman constant, η the coefficient of viscosity of the medium at a temperature T. The parameter f is dependent on the molecular shape and for an oblate ellipsoid is given by [34]:

$$f = \frac{2(p^4 - 1)}{3\{(p^2 - 2)p^2(p^2 - 1)^{-1/2} \arctan(p^2 - 1)^{1/2} + p^2\}} \tag{8}$$

where p is the axial ratio of the ellipsoid. Different solvents give different slip and stickiness with the solute molecule that is accounted for through C in Eq. (7). It appears from Table 1 that the r_P values are relatively lower than r_N values ($r_N \geq 0.3$). This is tantamount to saying that the rotational restriction on the absorption dipole is greater in the core than in the interfacial region. We have calculated microviscosity of the interfacial region using the r_P values. To calculate the value of η by using Eq. (7), knowledge of v, f and C are required. The value of v and f can be calculated from the molecular dimension as obtained from semiempirical molecular orbital calculation at the AM1 level. Thus one obtains $v = 588\ cm^3\ mol^{-1}$ and $f = 1.02$ for the dye [30]. Assuming stick boundary condition is valid in a protic media for the dye, we get $C = 1$. Since r_P refers to the interfacial region of micelles, the emitting species is the H-bonded complex and as such, the lifetime values for this species (τ_2 for P-band in Table 2) has been used in the present calculation. The calculated values of η are given in Table 3. Alternatively an estimate of η can be obtained by

Table 3
Steady-state fluorescence and micro-environmental parameters in SDS/TX-100 mixed micellar system

α_{SDS}	r_P	η (cP)			δ
		a	*b*	*c*	
0.0	0.08	1.40	1.60	1.50	0.00
0.1	0.09	1.64	1.87	1.76	−0.04
0.2	0.09	1.66	1.88	1.77	−0.03
0.3	0.10	1.88	2.15	2.01	−0.17
0.4	0.11	2.15	2.45	2.30	−0.20
0.5	0.12	2.41	2.75	2.58	−0.23
0.6	0.13	2.67	3.04	2.85	−0.26
0.7	0.14	2.95	3.36	3.15	−0.29
0.8	0.16	3.61	4.10	3.85	−0.22
0.9	0.17	3.93	4.46	4.19	−0.23
1.0	0.20	5.18	5.86	5.52	0.00

a: calculated from Eq. (9), *b*: calculated from Eq. (6), *c*: average error = ±5%.

a comparison method. As discussed earlier, P-band refers to micelle–water interface and this region is characterised by water–hydrocarbon interface and can be mimicked by a mixture of ethanol and a long chain alcohol. In a previous communication [30] we have shown that microviscositiy of a micellar medium can be measured by comparing the value of r in the medium with that in ethanol–octan-1-ol mixture. For that, plots of $1/r$ versus τ/η were made at the required temperature for ethanol–octan-1-ol mixture. A linear relation, as given by Eq. (9) was obtained:

$$\frac{1}{r} = 2.53 + 9.08\frac{\tau}{\eta} \tag{9}$$

The value of τ/η was then obtained from Eq. (9) using the value of r for the micellar medium. Value of η was then calculated using known values of τ (vide supra). The calculated values are also given in Table 3. Interestingly, the values of η calculated by the two procedures are very close. Average of the values calculated by two procedures are also given in Table 3. Fig. 6(A) shows η as a function of surfactant composition. In an ideal case the value of η in a binary mixture of surfactant (η_{12}) can be written as an average of η-values for pure surfactant components (η_1 and η_2) weighted by their mole fractions (α).

$$\eta_{12} = \alpha_1\eta_1 + (1-\alpha_1)\eta_2 \tag{10}$$

Thus a plot of η_{12} versus α_1 would give a straight line in an ideal case. A non-linear variation of η_{12} with α_1 as observed in the present case thus points to non-ideal behaviour of the surfactant mixture. The dimensionless quantity (δ) defined as

$$\delta = \frac{\eta_{12} - \alpha_1\eta_1 - (1-\alpha_1)\eta_2}{\eta_1 - \eta_2} \tag{11}$$

can be used as a measure of deviation from ideality. Values of δ (using SDS as the component 1) are listed in Table 3. Note that a negative deviation from ideality (δ negative) has always been observed. Fig. 6(B) shows the variation of δ with α_1. Maximum variation from ideality is observed at a value of $\alpha_1 = 0.70$. Deviation from ideality of physical quantities of a two-component system has often been rationalised in terms of non-zero enthalpy of mixing. In mixed binary surfactant systems synergistic or antagonistic interactions between the component surfactant molecules are well documented in the literature [35–39]. In SDS + TX-100 mixed binary system a synergistic interaction between the surfactant components have been found to exist [21]. The negative deviation from ideality observed in the present case can thus be rationalised in terms of synergistic surfactant–surfactant interaction.

4.1.3. PVP + SDS system

The emission spectrum of the dye A in an aqueous solution of PVP (0.8×10^{-4} M), in absence of any surfactant is

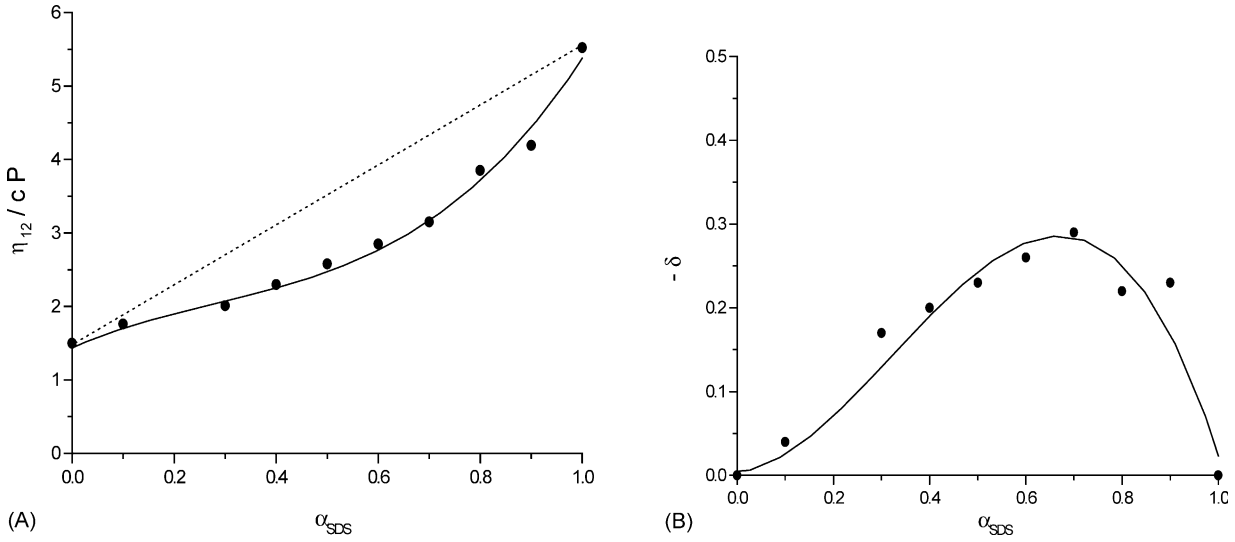

Fig. 6. (A) Plot of η_{12} (average values in Table 3) vs. average mole fraction of SDS in SDS + TX-100 binary mixture. (B) Variation of the parameter δ with surfactant composition.

Table 4
Photophysical parameters of the dye in polymer–surfactant system

Media	a_1	a_2	τ_1 (ps)	τ_2 (ps)	$\langle\tau\rangle$ (ps)	ϕ	k_r ($\times 10^{-8}\,s^{-1}$)	k_{nr} ($\times 10^{-9}\,s^{-1}$)
Aqueous PVP	0.99	0.01	20	625	26	0.013	5.0	38
Aqueous PVP + SDS	0.98	0.02	38	2400	85	0.032	3.8	11.4
	(0.45)	(0.55)	(220)	(1500)	(911)	–	(4.0)	(10.7)

The entries within bracket indicate parameters for P-band.

shown in Fig. 3. Note that the P-band (around 620 nm), corresponding to the H-bonded solute, is absent in the spectrum. Thus the results indicate that the dye is located almost exclusively in a hydrophobic region in aqueous PVP solution. It is known that a polymer in an aqueous solution remains as self-entangled chain when its concentration is below the crossover value (C^*) [40,41]. Value of C^* has been calculated for PVP and has found to be 0.83 M [17], which is well above the concentration of PVP used in the present study. Our results indicate that the dye is solubilised in the self-entangled polymer chain. However, on addition of SDS at a concentration greater than its critical aggregation constant (2×10^{-3} M) the P-band appears. But it is shifted to the blue compared to the P-band in pure aqueous SDS micelle. The position of the N-band remains unaltered. Thus we may infer that the micro-polarity of the hydrophobic region is similar to that in pure SDS micelle, whereas the interfacial region is characterised by a lower micro-polarity compared to that of the pure micelle. Other workers have been made similar observations from steady state and time-resolved fluorescence studies using 2,6-*p*-toluidinonaphthalene sulphonate (TNS) as the probe [17]. Our results can be explained in terms of the "necklace and bead" model for polymer–micelle system [15]. In absence of surfactant molecules, PVP remains in the aqueous solution as a folded structure and the probe molecule is solubilised inside a hydrophobic region. Gradual addition of SDS brings unfolding of polymer, which induces micellisation and formation of "necklace and bead" structure. It is known that two possible structures may be distinguished, viz, one in which aggregate of surfactant molecules wraps around the hydrophobic sites of polymer and the other where the polymer wraps around the surfactant head groups. In the former case, there is no significant modification of micelle–water interface whereas in the latter case the micelle–water interface is significantly reduced. Shifting of the P-band of the dye to the blue points to an enhanced hydrophobicity of the interface in presence of PVP indicating that the latter structure where the polymer wraps around the head groups is most likely to be present in the solution.

Lifetime and other relevant parameters for the dye in aqueous PVP and PVP + SDS solution are given in Table 4. It appears that addition of PVP to SDS brings about an enhancement of non-radiative decay process (as compared to pure SDS solution). The micro-viscosity (η) at the water–SDS micelle interface in presence of PVP has been calculated by similar procedures as described earlier. Thus in an aqueous solution of PVP containing 4×10^{-3} M SDS, a value of 0.28 for r_P has been obtained. This gives an average value of $\eta_{micro} = 8.54$ cP for the system which is higher than that of the SDS micelle–water interface 5.52 cP. This also point to a significant modification of SDS micelle–water interface due to addition of the neutral polymer PVP.

5. Conclusions

1. The ketocyanine dye serves as a good indicator solute for studying heterogeneous media. The dye molecules distribute in the core and interfacial region of the micelle. The concentration of the dye in the bulk aqueous phase is negligibly small.
2. While the bare form of the dye is present in the core, a hydrogen-bonded species exists in the interfacial region. The latter is characterised by a longer lifetime.
3. Photophysical parameters for the two forms of the dye are different. The radiative rate is almost independent on the nature of the environment, but the non-radiative rate is faster for the species in the core.
4. Microviscosity of micelle–water interface, as determined from fluorescence anisotropy and lifetime, differs from the ideal values. A parameter describing the extent of deviation from ideality has been proposed.
5. The interfacial region of SDS micelle in presence of PVP is characterised by a lower polarity and higher viscosity compared to pure SDS micelles. This is in consistent with a "necklace and bead" model of SDS + PVP system where the polymer wraps the micelle.

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