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Interaction of charge transfer fluorescence probe with non-ionic surfactants: Estimation of physico-chemical properties and association constant

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ABSTRACT

Fluorescence behavior of intramolecular charge transfer probe *trans*-ethyl-*p*-(dimethylamino) cinnamate (EDAC) is extremely sensitive to the local environment. This study explores the interaction of EDAC with several Igepal, Brij and Tween series of non-ionic surfactants by steady state and picoseconds time-resolved fluorescence spectroscopy. The physico-chemical properties, like critical micelle concentration and micropolarity of the micellar media surrounding the probe were determined. In most of the cases, the observed values were in good agreement with the data reported in the literature. Results obtained from time-resolved fluorescence experiments show a substantial reduction in total non-radiative decay rate of the probe in micellar medium compared to that in aqueous phase. This indicates preferential association of the probe inside the micellar core. The association constant of the probe-micelle interaction was also evaluated in different cases.

1. Introduction

Recently, surfactants have become the subject of intense investigation by researchers in the fields of chemical kinetics and biochemistry due to the unusual properties of the polymeric forms of these materials. There has been a growing interest in elucidating micellar characteristics primarily due to the fact that they are among one of the simpler membrane mimetic systems [1-3]. The application of non-ionic surfactants is rapidly increasing in many fields such as cosmetics, pharmaceuticals, paints and so on [4]. Also, the development of non-ionic, safe, biodegradable microemulsions with specific properties like high solubilization power and temperature insensitivity has been the focus of current interest [5]. Micelles are aggregated structures formed by the interaction of several surfactant molecules. Generally, surfactant molecules are characterized by possessing both hydrophobic and hydrophilic moieties and above a certain concentration (called critical micelle concentration, cmc), the surfactant molecules group together to form a micelle with fairly discrete structure. Effective use of the surfactants in different biological or industrial applications mentioned above requires a knowledge of several micellar properties like critical micelle concentration (cmc), effective solution polarity etc.

Formation of micelles from the monomer surfactant molecules is generally followed by sharp changes in several solution properties like conductivity, viscosity, osmotic pressure, density, polarity, specific heat, refractive index and solubilization power etc. Fluorescence spectroscopy can also serve as a fantastic tool to study the micellization of surfactants due to its excellent sensitivity towards the environment surrounding the fluorophore [6,7]. However, this technique may be more suited to study the aggregation of surfactants in the low concentration region, as additional complication due to scattering may appear in higher surfactant concentration. By comparing the fluorescence spectral data obtained in the micellar medium with the calibration curve constructed using various homogeneous systems, mean micellar properties like effective polarity, apparent viscosity, aggregation numbers and electrostatic mean field potentials at interfaces have been successfully determined [8,9]. However, most of the fluorescence based studies involve the use of a specific probe molecule to investigate the micellization behavior of the most common non-ionic surfactant, tritonX-100, along with the representative ionic surfactants like sodium dodecyl sulfate (SDS) and cetyl trimethyl amonium bromide (CTAB). The applicability of the particular probe to study several other important classes of non-ionic surfactants like polyoxyethylene based Igepal, Brij and/or Tween series surfactants are scantly monitored. Some of the relatively recent literatures are available for monitoring the micellization process of these surfactant systems with fluorescence, as well as other related techniques, using probes like safranine-T, 1-anthracene sulphonate, pyrene-1-carboxaldehyde, benzimidazole derivatives etc. to report their cmc [10-14] and also the local polarity parameters [15-19]. Ideally, when using a fluorescent probe molecule, one assumes that it should not perturb the system significantly in spite of being extremely sensitive to the environment where it is located within the aggregate. However, the most widely studied system safranine-T is itself a cationic species and known to form 1:1 intermolecular charge transfer complex with Tween and Igepal series surfactants [15]. As the micellar structure often critically depends on the interfacial potential, characterization of the non-ionic micelles with diffusive charged species like safranine-T might be erroneous. On the other hand, non-ionic pyrene has always been a popular choice as a fluorescent probe to study the micellar aggregation for different kind of surfactants [20,21]. It was found that the

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ratio of first to third vibrational fluorescence band intensity is an efficient reporter for different physico-chemical properties during micelle formation. However, the main disadvantage of using pyrene as fluorescent probe is its low solubility in aqueous media. Furthermore, fine structure in the fluorescence spectrum, strong concentration dependence of fluorescence intensity etc. are other additional complications which demand the search for new fluorescent probes. Intramolecular charge transfer (ICT) process in covalently linked donor-acceptor system seems to have an added advantage in this respect; since it does not need to diffuse to show the characteristic charge-transfer fluorescence band like in intermolecular case. Furthermore, the extreme sensitivity of the ICT probes to local polarity prompted a large number of studies of this process in a variety of micro-heterogeneous medium [22-24].

It was found that non-ionic, water soluble ICT probe *trans*-ethyl *p*-(dimethylamino) cinnamate, EDAC (structure given in Figure 1, inset) is extremely sensitive to solvent polarity and that the fluorescence properties show very good correlation with solvent polarity parameter. The characteristic property of a locally excited (LE) and ICT state was determined [25]. Also, the change in dipole moment in the ground and excited states was calculated from steady state spectral measurements in the series of solvents with varying polarity using Lippert-Mataga relationship. Furthermore, the clean and clear largely Stokes-shifted ICT fluorescence as well as noticeable change in fluorescence spectral position with polarity of the medium prompted us to use EDAC as a probe to study the micellization behavior of various non-ionic surfactants by steady state and picoseconds time-resolved fluorescence spectroscopy. The aim of the present work was to investigate, using EDAC as a fluorescence polarity probe, to study the micellization behavior of several non-ionic surfactants, interfacial polarity of the local environment around the probe as well as the nature of bindingtheir interaction.

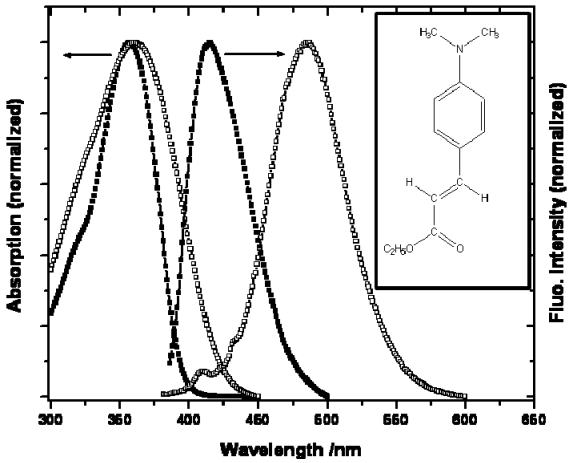

Figure 1. Absorption and emission spectra of ~1.0 × 10^{-5} M solution of EDAC in 1,4-dioxane (filled squares) and water (empty squares). Structure of the probe (*trans*)-ethyl *p*-(dimethylamino) cinnamate (EDAC) is also shown.

2. Experimental

2.1. Chemicals

Trans-ethyl-*p*-(dimethylamino)cinnamate was synthesized using standard procedure based on Reformatsky reaction [25]. A total of nine polyoxyethylene series of non-ionic surfactants viz. polyoxyethylene-5-nonyl phenyl ether (Igepal CO-520), polyoxyethylene-9-nonyl phenyl ether (Igepal CO-630), polyoxyethylene-12-nonyl phenyl ether (Igepal CO-720), polyoxyethylene-10-cetyl ether (Brij-56), polyoxyethylene-20-cetyl ether (Brij-58), polyoxyethylene-10-oleyl ether (Brij-97), polyoxyethylenesorbitan monolaurate (Tween-20), polyoxy ethylenesorbitan monopalmitate (Tween-40) and polyoxy ethylene sorbitan monooleate (Tween-80) were used in this study. The highest grade of purity available (>99.9%) of all these surfactants were obtained from Sigma-Aldrich Chemicals Pvt. Ltd. (India) and used as received. The water used as solvent in all the measurements was obtained from Elix 10 water purification system (Millipore India Private Ltd). The concentration of the probe (~1.0 × 10^{-5} mol dm^{-3}) was low enough to avoid any aggregation and/or inner filter effect (maximum absorbance was kept below 0.2 at excitation wavelength) and kept constant during variation of surfactant concentration. All experiments were carried out at ambient temperature (297 K).

2.2. Instrumentation

Steady-state absorption spectra were recorded on a Perkin-Elmer model Lambda 25 absorption spectrophotometer. Fluorescence spectra were taken in a Hitachi model F-4500 spectrofluorimeter. Fluorescence quantum yields (ϕ_f) were calculated by comparing the total fluorescence intensity (F) under the whole fluorescence spectral range with standard reference using quinine sulfate in 1M H_2SO_4 (ϕ_f^S =0.54) using the following equation [25].

$$\phi_f^i = \phi_f^s \cdot \frac{F^i}{F^s} \cdot \frac{1-10^{-A^s}}{1-10^{-A^i}} \cdot \left(\frac{n^i}{n^s}\right)^2 \quad (1)$$

where, A^i and A^s are the optical density of the sample and standard, respectively, and n is the refractive index of solvent. The relative experimental error of the measured quantum yield was estimated within ±5%.

The fluorescence decay curves in homogeneous buffer solution as well as in the presence of different surfactant concentration were obtained using time correlated single photon counting (TCSPC) technique. Details of time resolved fluorescence measurement are essentially the same as described elsewhere [26]. The excitation was done at 380 nm obtained by frequency doubling (GWU, Spectra Physics) of the tunable, picosecond version of a Ti:Sapphire laser (Tsunami 3950 Standard, Spectra Physics, Mountain View, CA) output in the range of 720~830 nm pumped by 5W Nd-YLF laser (Millenia X, Spectra Physics). Fluorescence decay curves were obtained at the laser repetition rate of 4 MHz by a micro-channel plate photomultiplier (Model R2809U, Hamamatsu) coupled to a TCSPC set-up. The Instrument response function (IRF, ~40 ps FWHM) at 380 nm was obtained by using a dilute colloidal suspension of dried non-dairy coffee whitener. The experimentally obtained fluorescence decay traces I(t), collected at the magic angle (54.7°) to eliminate any contribution from the anisotropy decay, were expressed as a sum of exponentials (Equation 2) and analyzed by non – linear least–square iterative convolution method based on Lavenberg-Marquardt [27] chi-square (χ^2) minimization algorithm (Equation 3).

$$I(t) = \sum_i \alpha_i \exp(-t/\tau_i) \quad (2)$$

where, α_i is the amplitude of the i^{th} component associated with fluorescence lifetime τ_i such that $\sum\alpha_i = 1$.

$$\chi^2 = \frac{\sum_{i=1}^{N}[y_i - f(x_i)]^2}{N-P} \quad (3)$$

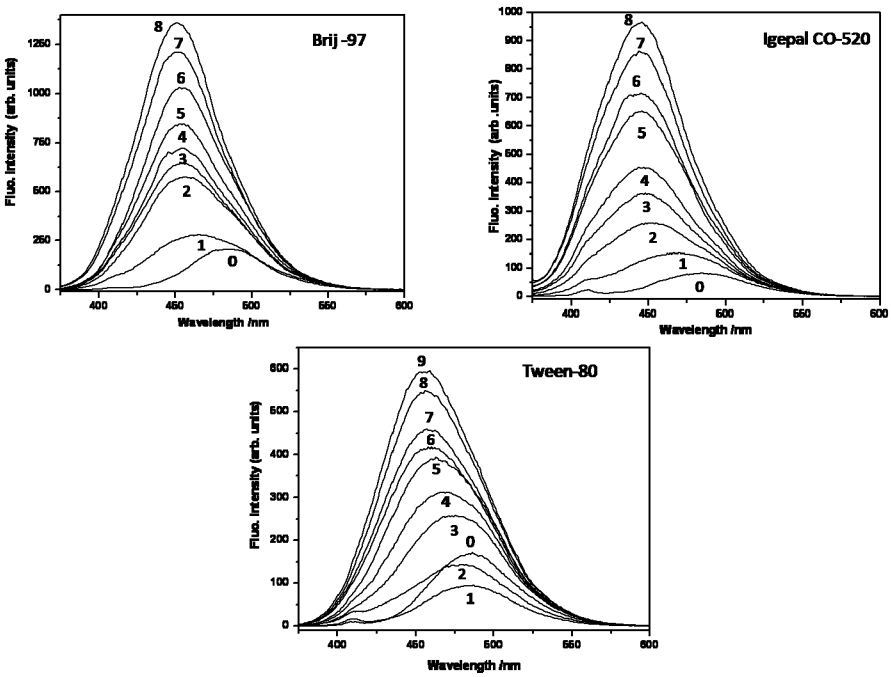

Figure 2. Variation of EDAC fluorescence intensity with increasing concentration of surfactants. [Brij-97] /mM = 0.0 (0), 0.05 (1), 0.1 (2), 0.15 (3), 0.2 (4), 0.25 (5), 0.4 (6), 0.6 (7) and 0.8 (8); [Igepal CO-520] /mM = 0.0 (0), 0.5 (1), 1.0 (2), 1.5 (3), 2.0 (4), 2.5 (5), 3.0 (6), 6.0 (7) and 8.0 (8); [Tween-80] /mM = 0.0 (0), 0.002 (1), 0.01 (2), 0.015 (3), 0.02 (4), 0.03 (5), 0.04 (6), 0.05 (7), 0.06 (8) and 0.07 (9).

N is the number of data points and P is the number of free parameters in the fitting function. The reliability of fitting was also checked by Durbin-Watson (DW) parameter and visual inspection of residual distribution in the whole fitting range [28].

3. Results and discussion

3.1. Steady state spectral properties

The absorption spectrum of the aqueous solution of EDAC shows a broad, unstructured band with the maximum centered at around 360 nm, whereas, the fluorescence spectra originated at 485 nm is due to the emission from the charge transfer state [25]. Figure 1 shows the representative absorption and emission spectra of aqueous solution of EDAC, along with those in 1,4-dioxane, which is widely accepted as the homogeneous mimics of micellar core [29]. Table 1 contains the fluorescence maximum (ν_{fl}^{max}), fluorescence spectral full width at half maxima (ν_{fwhm}), energy of intersection of absorption spectra and normalized fluorescence emission spectra ($\nu_{0,0}$) as well as Stokes-shift ($\Delta\nu_{ss}$) for EDAC in homogeneous as well as different non-ionic surfactant systems. From Figure 1, it is seen that the absorption spectral position of EDAC is independent on solvent polarity indicating relatively non-polar nature of the ground state; in sharp contrast to the fluorescence spectra that shows appreciable red shift (~70 nm) while moving from 1,4-dioxane to water. This large spectral shift in polar solvent clearly indicates the charge transfer nature of the fluorescing species. Again, the absorption spectral position remains practically unaffected by the addition of all the surfactants. However, the fluorescence spectral peak position is strongly dependent on the amount of the surfactant in the solution. In general, gradual addition of surfactants is associated with a blue shift in the emission maximum along with an increase in fluorescence intensity in all the cases (Figure 2) suggesting that the environment around the probe gets perturbed as we move from pure solvents to aqueous micellar solutions. In analogy with the results discussed earlier for homogeneous solvent systems [25], a blue shift of fluorescence maximum suggests that the polarity of the micellar environments is less than the polarity of the bulk water. The fluorescence spectral blue shift for EDAC is about ~35 nm in Igepal series compared to its position in aqueous solution. On the other hand, in Brij and Tween series of non-ionic surfactants the shifts are ~30 nm.

Apart from the shift in spectral position, fluorescence intensity of the EDAC increases remarkably in the micellar medium (Figure 2), till it reaches a plateau at high concentrations. This observation is true for all non-ionic surfactants studied here and can be rationalized on the basis of the association of the probe in a less polar site within the micellar aggregates as compared to pure aqueous phase. As discussed in our previous studies [30-32], the increase in fluorescence yield of EDAC in micro-heterogeneous environment of non-ionic surfactants is related to the decrease in non-radiative relaxation in the confined cavity of the host. This decrease in non-radiative relaxation might be due to the following. The ICT state of EDAC is believed to be originated due to the twisting motion of the dimethylamino group [25]. The increase in ICT fluorescence yield may be due to locking-in of this low frequency twisting motion. Furthermore, in the micellar environment, the reduced polarity destabilizes the ICT state and consequently, increases the energy gap between this state and the triplet and/or ground state. The resulting decrease in non-radiative decay process leads to the enhancement of ICT emission yield. However, the nature of the non-polar interior of the micellar core does not change once the surfactant monomers assemble to form the micellar aggregates. Therefore, the ICT fluorescence intensity reaches a plateau, as shown in Figure 2. Interestingly, initial addition (till 4~5 mM) of all the Tween series surfactants studied here results a small decrease in ICT fluorescence intensity (see Figure 2, as example for Tween-80) unlike the other micellar systems, where a regular increase in intensity is observed.

Table 1. Fluorescence properties of EDAC in water, 1,4-dioxane and different micellar media.

Medium	ν_{fl}^{max} /cm^{-1}	ν_{fwhm} /cm^{-1}	$\nu_{0,0}$ /cm^{-1}	$\Delta\nu_{ss}$ /cm^{-1}
Water	20,620	2,750	23,190	6,190
1,4-dioxane	24,213	2,940	25,695	3,642
Igepal CO-520	22,420	3,580	24,715	5,356
Igepal CO-630	22,075	3,310	24,625	5,710
Igepal CO-720	22,100	3,203	24,530	5,700
Brij-56	21,880	3,690	24,520	5,895
Brij-58	21,975	3,409	24,371	5,795
Brij-97	22,170	3,250	24,680	5,604
Tween-20	21,980	3631	24,496	5,800
Tween-40	22,025	3,622	24,544	5,750
Tween-80	21,975	3,603	24,446	5,800

Table 2. Fluorescence quantum yield (ϕ_f), decay time (τ), mean fluorescence decay time ($<\tau>$), radiative (κ^r) and total nonradiative ($\sum\kappa^{nr}$) decay constants of EDAC in aqueous solution as well as in the presence of different non-ionic surfactants.[a]

Medium	$\phi_f/10^{-3}$	Fluorescence decay time (τ)			χ^2	$<\tau>$ ns	κ^r /10^8s^{-1}	$\sum\kappa^{nr}$ /10^{10} s^{-1}
		τ_1/ns(α_1)	τ_2/ns(α_2)	τ_3/ns(α_3)				
Water	3.2	0.09(1.0)	-	-	0.98	0.09	0.4	1.1
Igepal CO-520	20.4	0.087(0.513)	0.255(0.439)	0.578(0.048)	1.06	0.188	1.09	0.52
Igepal CO-630	25.1	0.084(0.457)	0.263(0.495)	0.554(0.048)	1.03	0.199	1.26	0.49
Igepal CO-720	28.3	0.064(0.506)	0.249(0.445)	0.501(0.049)	0.92	0.172	1.65	0.56
Brij-56	7.6	0.050(0.574)	0.212(0.422)	0.772(0.004)	1.01	0.121	0.63	0.82
Brij-58	11.3	0.035(0.733)	0.210(0.265)	0.999(0.002)	0.97	0.083	1.36	1.19
Brij-97	28.8	0.020(0.593)	0.170(0.366)	0.355(0.041)	0.86	0.089	3.23	1.09
Tween-20	13.4	0.042(0.643)	0.233(0.350)	0.660(0.007)	0.91	0.113	1.19	0.87
Tween-40	13.3	0.061(0.514)	0.232(0.462)	0.539(0.024)	1.25	0.153	0.87	0.64
Tween-80	13.8	0.073(0.551)	0.254(0.446)	1.238(0.003)	0.91	0.157	0.88	0.63

[a] The pre-exponential factors (α_i) associated with each decay component (τ_i) as obtained fitting the experimental points using Equation (2) are given in parentheses; chi-square (χ^2) values obtained from data fitting algorithm are also given in each case.

Similar observation was reported earlier for fluorescence studies in pyrene-1-carboxaldehyde in mixed non-ionic micellar system [11]. Although the reason for this observation is not clear yet, it might be due to the difference in the onset of micellization in these three series of surfactants.

3.2. Picosecond time-resolved fluorescence of EDAC in micellar medium

Excited state lifetime of a fluorophore in a micellar solution serves as a sensitive parameter for exploring the local environment around the fluorophore. Furthermore, this also contributes to the understanding of different interactions between the probe and the micelle [33]. On the basis of this, time-resolved fluorescence studies were performed on EDAC under fully micellized condition of surfactants. The aqueous buffer solution of EDAC undergoes single exponential decay with a fluorescence lifetime of 90 ps [25]. However, the decay curves show significant contributions from more than one component in micellar solutions, as evidenced by the inspection of distribution of weighted residuals as well as the reduced χ^2 values. All the fitting parameters are displayed in Table 2. Multi-exponential decay of fluorescence in micellar systems is quite common and believed to be originated due to the inhomogeneous distribution of fluorescent probes in different micellar sub-domain. However, it is often difficult to mechanistically assign the various components of the decay. If we assume that the diffusion of the probe molecule is rather slow in micellar medium, there is always a probability that the probe molecule in different micro-domains of micellar systems are excited simultaneously to give multi-exponential fluorescence decay. Instead of emphasizing too much to the individual decay components, we define the average decay time of the fluorophore in the micellar environment using Equation 4 to discuss the fluorescence decay behavior.

$$<\tau>=\sum_i \alpha_i \times \tau_i \qquad (4)$$

The calculated values are listed in Table 2. It is interesting to note that the mean fluorescence decay time of EDAC in micellar media is always larger than the corresponding values in homogeneous medium; however, the difference is more in case of Igepal surfactants in comparison with both Tween and Brij series surfactants. Fluorescence quantum yield (ϕ_f) calculated from the area of the total fluorescence emission over the whole spectral range, the radiative (κ^r) and total nonradiative ($\sum\kappa^{nr}$) decay rate constants calculated from Equation 5 are also listed in the same table. The increase in ϕ_f and substantial decrease in $\sum\kappa^{nr}$ in micellar environment points to the restricted low-frequency motion of the fluorophore inside the micellar sub-domains as discussed in Section 3.1 above.

$$\kappa^r = \phi_f / <\tau>; \kappa^{nr} = (1-\phi_f)/<\tau> \qquad (5)$$

3.3. Interaction of the probe with non-ionic surfactants: Association constant and physico-chemical properties of the local environment

It is important to note that in order to be able to use as a fluorescence probe to determine the physico-chemical properties of the micellar system; care must be taken about the solvent relaxation [34]. Generally, solvent relaxation around the excited fluorophore should be complete prior to fluorescence emission. Steady state technique for checking the solvent relaxation behavior is to verify the so called "red edge relaxation" effect [35]. Excitation at the long wavelength absorption tail for EDAC in aqueous and non-ionic surfactant media does not affect the fluorescence band maxima, which indicates excellent solvent relaxation in these heterogeneous media and confirms applicability of EDAC to estimate several physico-chemical properties in the micellar environment. Indeed, we have shown earlier [30] that the calculated values of critical micelle concentration (cmc) as well as polarity parameters based on EDAC fluorescence behavior in several well known surfactants such as SDS, CTAB and tritonX-100 are in excellent agreement with the literature values. In the following subsections, we describe the determination of several physico-chemical properties of non-ionic micellar systems from EDAC fluorimetric titration data.

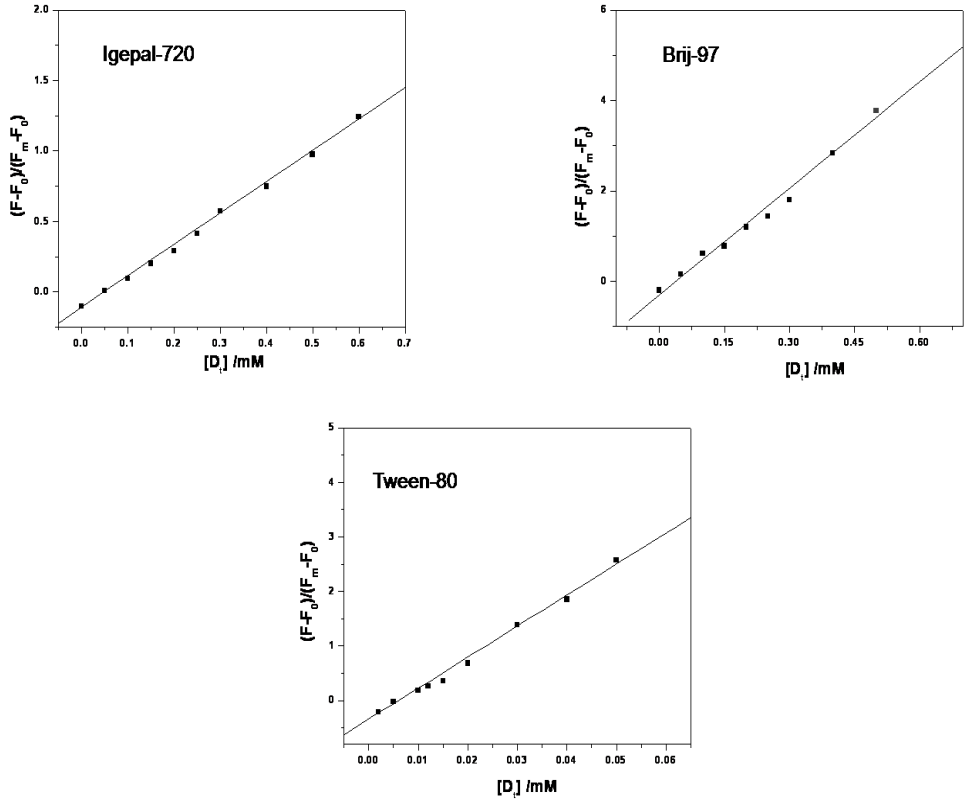

Figure 3. Variation of $(F-F_0)/(F_m-F_0)$ with total surfactant concentration $[D_t]$ for some representative non-ionic surfactant system. The constant of dye-micelle interaction can be calculated from the slope of the straight line.

3.3.1. Association Constant

The association of the fluorescent probe to the miceller sub-domain can be described by the following equilibrium [36].

$$S_a + D_m \xleftrightarrow{K_S} S_m \tag{6}$$

where, S_a and S_m denote the substrate concentrations expressed as molarities in terms of total volume of solution in the aqueous phase and in the micellar pseudo-phase, respectively. D_m is the molar concentration of surfactant is micellar form.

The equilibrium constant for the process, often termed as association constant, is given by

$$K_S = \frac{[S_m]}{[S_a][D_m]} \tag{7}$$

Considering, the aggregation number of the micelle formation to be constant, the total substrate concentration (S_t) and the total detergent concentration (D_t) can be written as $[S_a]+[S_m]$ and $[S_m]+[D_m]+cmc$, respectively. cmc indicates the critical micellar concentration.

The fraction of micelle associated substrate is defined as

$$f = \frac{[S_m]}{[S_t]} \tag{8}$$

then, one obtain

$$\frac{f}{1-f} = K_S\{[D_t]-[S_t]\times f\} - K_S \times cmc \tag{9}$$

Under the experimental condition of $[S_m]<<[D_t]$ and $[D_t]>>cmc$, the above equation can be approximated as

$$\frac{f}{1-f} = K_S \times [D_t] \tag{10}$$

Experimentally, f can be calculated by steady state fluorescence experiments in presence and absence of micellar systems as follows.

$$f = \frac{F-F_0}{F_m-F_0} \tag{11}$$

where, F, F_o, and F_m are the intensity of fluorescence emission at a particular wavelength under the whole fluorescence emission spectra of the probe in the surfactant, water and in fully micellized conditions, respectively. Substituting the value of f one can write:

$$\frac{F-F_0}{F_m-F_0} = K_S \times [D_t] \tag{12}$$

A plot of $(F-F_o)/(F_m-F_o)$ vs $[D_t]$ gives a straight line, the slope of which gives the value of the association constant, K_s. Some representative plots are shown in Figure 3 and the corresponding values of the binding constant of EDAC with different non-ionic surfactant systems are tabulated in Table 3.

Table 3. Physico-chemical properties and association constant (K) of different micellar systems obtained by using EDAC as fluorescence probe.[a]

System	Physico-chemical properties			K /10⁴, M⁻¹
	cmc /mM	ε	$E_T(30)$ /kcal mol⁻¹	
Igepal CO-520	0.43 (0.47 [10])	24.2 (42 [15])	45 (44 [15])	3.6
Igepal CO-630	0.36 (0.48 [11])	41.2	47 (52 [11])	3.3
Igepal CO-720	0.30 (0.49 [10])	40.4 (10 [15])	47 (48 [11])	2.4
Brij-56	0.03 (0.023 [12])	50.2 (57 [16])	48 (51 [16])	4.6
Brij-58	0.03 (0.03 [13])	45.7 (40 [16])	47 (46 [16])	6.8
Brij-97	0.28 (0.34 [12])	36.3	46	1.1
Tween-20	0.09 (0.08 [14])	45.5 (12 [18])	47 (43 [17])	5.6
Tween-40	0.03 (0.027 [14])	43.4 (12 [18])	47 (42 [17])	7.6
Tween-80	0.018(0.012 [14])	45.8 (5 [18])	47	5.7

[a] The literature values of the physico-chemical properties are mentioned in the parentheses along with the reference numbers.

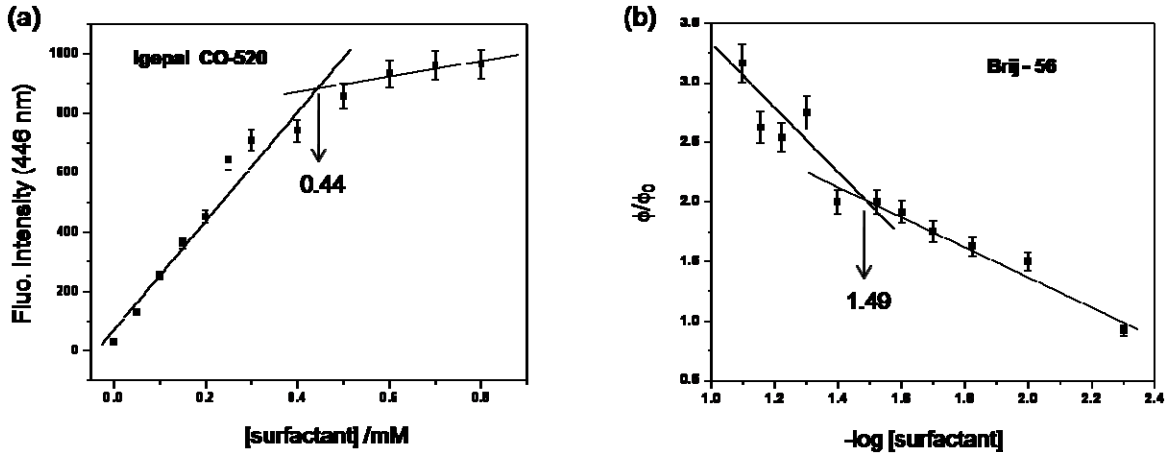

Figure 4. Determination of critical micelle concentration from the break points of variation of fluorescence intensity with surfactant concentration (a) and ratio of fluorescence yield of EDAC in presence and absence of surfactant with negative logarithm of surfactant concentration (b).

3.3.2. Critical micellar concentration (cmc)

The formation of micelle from the monomer surfactant molecules occurs within a narrow range of concentration, usually known as cmc. The cmc is an extremely useful quantity as it describes the surfaces and interfacial activity of the surfactant molecules in solution. A sudden break from the linear variation of any observable parameter of the probe with increase in surfactant concentration often indicates the approach to cmc. Literature reports show that the cmc of surfactant systems can be obtained from the fluorescence data in two ways: firstly, the intensity is plotted directly against surfactant concentration [30] and secondly, a plot of ratio of quantum yields of the fluorescence probe in the presence of surfactant to that in pure homogeneous medium (ϕ/ϕ_0) against negative logarithm of surfactant concentration is also used [11] to find the break points. We have used both the methods and some of the representative plots are given in Figure 4. Both these measurements lead to the cmc value which is very close to each other; an average of these two measurements is given in Table 3 along with the available literature data for different non-ionic surfactants. It is seen that the measured cmc values in this report are in excellent agreement with the literature data. This further confirms the applicability of EDAC as an ICT fluorescence probe to study the micellization behavior of different surfactants.

3.3.3. Polarity parameters

The variation of fluorescence properties like emission maxima (ν_{fl}^{max}), Stokes-shift ($\Delta\nu_{ss}$) etc. for EDAC in pure solvents and/or in different homogeneous solvent mixtures, with different polarity, viscosity and hydrogen bonding ability was studied in detail [25]. These parameters reveal excellent correlation with static dielectric constant (ε) of the medium and given by the following set of equations. The corresponding plots are shown in Figure 5.

$$\nu_{fl}^{\max}(cm^{-1}) = (22673.02 \pm 100.07) + (-24.38 \pm 2.02) \times \varepsilon \quad (13)$$

$$\Delta\nu_{SS}(cm^{-1}) = (4675.32 \pm 77.23) + (17.85 \pm 1.47) \times \varepsilon \quad (14)$$

These correlation equations can be used to estimate the static dielectric constant of the micellar environment from the known values of the steady state spectral parameters given in Table 1. The average values obtained from the measurements, using Equations (13) and (14), respectively, are given in Table 3 along with the available literature data. Although, the obtained values are in close agreement with that in literature in the case of Brij series surfactants; the surprisingly small values for Tween series surfactants reported in reference [18] are very far from the values obtained in our experiment. Similar trend was observed in case of Igepal CO-720 also. On the other hand, the calculated value of Igepal CO-520 is less than the literature report. Although the reason for these differences is not clear at this point, it may be due to the fact that the different probe molecules used in different studies may be located preferentially at varied environment of a micellar cavity. Furthermore, the presence of a fluorescent probe may perturb the intrinsic structure of the micellar cavity. Depending on the location of the probe and also the degree of perturbation, the reported values are only indicative of the local environment for different probe molecules in the micellar cavity. Essentially, the difference between the measured data and the reported values may be due to different local environment of the probe binding site as well as

microscopic heterogeneity of the micelle due to the difference in surfactant structure.

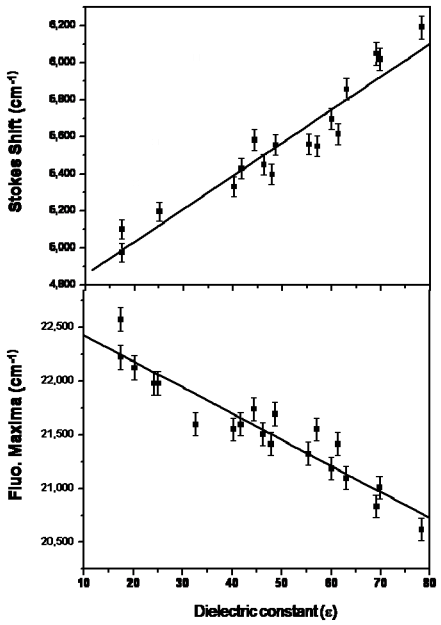

Figure 5. Systematic variation of EDAC fluorescence properties with static dielectric constant of the medium. The effective dielectric constants of the mixed solvent systems were calculated in the same procedure as mentioned in reference [25]. The correlation equations are given in the text.

The empirical polarity scale, $E_T(30)$ for micellar media can also be estimated from the correlation equations of ν_{fl}^{max}, and $\Delta\nu_{ss}$ described earlier [37]. This uni-parametric scale depends on both the medium dielectric properties and hydrogen bonding acidity, but it does not take care of the hydrogen bonding acceptor basicity of the surrounding environment [38]. The specificity of Lewis acid-base interactions in $E_T(30)$ parameter arise from the negative charge localized on the phenolic oxygen of betaine molecule. Quantitative estimation of the effect of several solvent parameters on the different steady state fluorescence properties of EDAC was reported recently using multi-parametric approach based on Kamlet-Taft equation [39]. The results indicate that the basicity of the medium has indeed negligible influence (< 8 %) on ν_{fl}^{max} and $\Delta\nu_{ss}$ of EDAC. Consequently, EDAC can also be used as a very efficient reporter of $E_T(30)$ value of the medium. The calculated values are shown in Table 3 along with the available literature data for different surfactant systems. It is indeed observed that the calculated values are in very good agreement with the literature values.

4. Conclusion

The fluorescence properties of polarity sensitive probe EDAC is found to be dramatically altered in micellar medium when compared to the aqueous bulk phase. The blue shift in the fluorescence spectral position, considerable increase in ICT fluorescence intensity indicates the presence of the probe inside the micellar domain. Despite potential complexity of micro-aggregates containing intrinsically heterogeneous non-ionic surfactants systems, several mean microscopic properties, such as association constant, polarity parameters etc. were obtained using fluorimetric titration of EDAC in the different micellar structure. Effective polarity of different micellar media and critical micellar concentration determined by using EDAC as a probe are in good agreement with the literature reported values.

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