

Estimation of Hydrogen Bond Donating Ability and the Dipolarity-Polarizability of Associated Water Molecules at the SDS Micellar Interface Using a Fluorescence Indicator

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Abstract: A new methodology for estimation of solvatochromic properties of micelles has been proposed. Two environment sensitive emission properties of a single indicator molecule have been used for this purpose. The hydrogen bond donating ability (α) and dipolarity- polarizability (π^*) of associated water molecules at the SDS micellar interface has been estimated. The obtained result has been compared to the literature values. Effect of methodology and choice of indicator molecule has also been discussed.

Keywords: Micelles, Interfacial water, Solvatochromic properties, Fluorescence indicator

Introduction

Aqueous micellar media have widely been used in solubilising drug molecules¹⁻², catalysts for chemical reactions¹⁻², altering the selectivity of chromatographic³ and electrophoretic separation processes⁴. The interfacial region of the micelles has been used as a possible reaction site that can both accelerate and inhibit reactions compared to that in pure water^{5,6}. Choice of proper reaction medium and understanding the selectivity of separation in micellar electrokinetic chromatography rests on the general solvating ability of the medium used. Thus the knowledge of solvatochromic properties in terms of Kamlet-Taft descriptors (namely π^* , α and β) for that medium is a prerequisite⁷. Recently some group of authors including the present author have successfully tried to estimate the solvatochromic properties of micellar media, namely H-bond donating (α) and acceptance abilities (β), and the general solvating ability due to the dielectric effect *i.e.* dipolarity-polarisability (π^*)⁸⁻¹³. A common practice for estimation of these properties for micellar media is the solvatochromic comparison method using Linear Solvation Energy Relationships (LSER) employing spectroscopic probe technique. For that purposes either specific indicator molecule has been used for estimation of a particular property⁸⁻¹⁰, or a series of structurally similar indicator molecules have been used¹¹⁻¹³. However, the above procedures may be criticized for the following reasons:

- (i) Employing different types of indicator molecules for different solvatochromic properties rest on the assumption that they all probe the same region of micelle which may not be the case always in practice.
- (ii) Use of several indicators for a particular property and then averaging over the estimated values has not been recommended recently for meaningful differences in chemistry of the indicators¹⁴. To avert this problem use of a single indicator molecule is proposed in the present work.

Two different but extremely environment sensitive emission properties (specifically the energy of fluorescence maximum, $E(F)$ and the non-radiative decay constant of the excited state, k_{nr}) of an indicator molecule (a ketocyanine dye, Figure 1) has been used. Apart from high environment sensitivity, both the parameters have been found to be intensity independent *i.e.* no dependency on the dye concentration. Empirical correlations of these properties with the solvation properties of homogeneous media through LSER allow us to estimate the H-bond donating ability (α) and the dipolarity-polarizability (π^*) of sodium dodecyl sulphate micellar phase. Although there are lot of other molecular probes like ET(30), prodan, coumarin 343 *etc.* that can sense two or more solvation parameters at the same time but no comprehensive effort has been made for simultaneous estimation of more than one property of micellar media using only one indicator molecule. Moreover the present methodology will help us to check the dependency of the solvatochromic properties on the choice of indicator molecule.

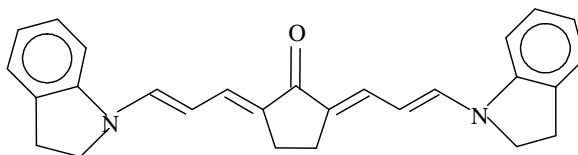


Figure 1. Solvatochromic indicator molecule

Experimental

The ketocyanine dye used in the present work has been prepared by the method described by Kessler and Wolfbeis¹⁵. All the solvents were purified by standard procedures and finally distilled over calcium hydride immediately prior to experiment to ensure the absence of moisture, peroxides and other oxidizing agents as impurities. Sodium dodecyl sulphate, SDS, was purchased from SIGMA and purified by repeated recrystallisation from ethanol. Triply distilled water was used for preparation of surfactant solutions.

Spectroscopic measurements

Steady-state fluorescence emission spectra were recorded on a HITACHI F-4500 spectrofluorimeter equipped with temperature controlled cell holder. In all the spectral measurements the concentration of the dye varied in the range 10^{-4} (surfactant solutions) to 10^{-5} (pure and mixed solvents) mol dm⁻³. The excitation / emission slit widths were set to 2.5 nm / 2.5 nm. The observed wavelength of maximum fluorescence has been converted to the energy unit by the simple relation:

$$E(F) (\text{kcal mol}^{-1}) = 28590 / \lambda (\text{nm})$$

The inaccuracy related to the measurement of $E(F)$ was found to be ± 0.1 kcal/mol. Quantum yields corrected for refractive index were based on the ratio of the areas under the emission curves to that of Rhodamine B in ethanol; the quantum yield of the latter was taken as 0.71.

For excited state lifetime measurement, fluorescence decay was studied by Time Correlated Single Photon Counting (TCSPC) using the FLUOROCUBE life-time system (IBH, s/n 04412). A nano LED of 540 nm (IBH, UK, nano LED s/n 04225) was used as excitation source with FWHM of the order of 1 ns and the pulse is passed through 5000M emission monochromator. The fluorescence signal was detected in magic angle polarization (54.70°) using cooled red sensitive photocathode (TBX 04-A) detector with a response time of 180 ps. The decays were analyzed using IBH DAS-6 decay analysis software.

Results and Discussion

Characteristics of the indicator molecule in homogeneous media

Before the estimation of solvatochromic properties for micellar interface, it is advisable to study the spectroscopic properties of the indicator in homogeneous solvent media as solvatochromic comparison method has been adopted in the present work. Polyenic bis- ω,ω' -amino ketones popularly known as ketocyanine dyes have been classified in the bichromophoric cyanine category with two ω -aminopolyenic units bound to the central carbonyl oxygen. The electronic structure of the ketocyanine dye has been found to be a resonance between neutral and the charge-separated forms¹⁵. The drift of π -electrons (upon excitation) from the donor R_2N to the acceptor $C=O$ is responsible for the charge separated form. This electronic transfer process can be controlled by suitable solvent. A polar protic environment will favour the charge separated form whereas solvent with lower polarity or no hydrogen bonding ability will favour the neutral form¹⁵⁻¹⁸. Solvatochromism thus exhibited by these dyes make them good probes for monitoring polarity and hydrogen-bonding interactions. The solvation process of the indicator molecule in polar protic solvents like alcohols can be depicted in two steps:-

- (i) Charge transfer upon electronic excitation to form the charge-separated S_1 state. Resonance stabilization of the excited state makes the carbonyl oxygen more basic than its ground state.
- (ii) In the next step, the highly basic carbonyl oxygen binds with the alcohols through H -bond formation.

The spectroscopic details of the indicator molecule have already been studied elaborately in pure solvents¹⁸, binary¹⁹⁻²¹ and ternary²² solvent mixtures, micellar media²¹⁻²⁴ and in cyclodextrin²⁵ environment. The energy of maximum fluorescence, $E(F)$ for the indicator has been found to be very much sensitive towards the solvatochromic properties of medium. For a protic solvent, the maximum energy of transition is largely determined by the hydrogen-bond donating interactions between the hydrogen atom of the solvent and the carbonyl oxygen of the dye molecule. The greater the hydrogen-bonding ability of the medium, the lower is the energy of transition. The relationship between energy of maximum fluorescence and the solvent parameters can be empirically accounted by Multiple Linear Regression Analysis (MLRA) for 22 solvents (those having $\alpha \neq 0$) and mixed solvents (Table 1) by the following LSER equation:

$$E(F) = (53.46 \pm 0.50) - (7.48 \pm 0.39) \alpha - (1.43 \pm 0.63) \pi^* \quad (1)$$

From the above relation it is clearly evident that α , the hydrogen-bond donating ability of the solvents plays a major contribution towards the energy of fluorescence of the dye molecule. We have already stated that resonance stabilized carbonyl oxygen of the dye molecule in the excited state forms tighter hydrogen-bonding with the protic solvents. To investigate the effect of medium on the dynamics of the excited state, the radiative (k_r) and non-radiative (k_{nr}) decay constants were calculated in a previous communication¹⁹ using the following expressions.

$$k_r = \phi_F / \tau \text{ and } k_{nr} = \tau^{-1} - k_r$$

The study revealed that the radiative decay constant of the dye is practically insensitive towards the medium ($k_r = 3.9 \times 10^8$). However, non-radiative decay constant shows large environment sensitivity (Table 1). Once again the sensitivity can be expressed by the following LSER equation:

$$\log k_{nr} = (10.11 \pm 0.15) - (0.87 \pm 0.12) \alpha - (0.78 \pm 0.19) \pi^* \quad (2)$$

Table 1. Emission properties of the indicator molecule in pure and mixed solvent systems

No.	Solvent	α^a	π^{*a}	$E(F)/\text{kcal mol}^{-1}$		I.P.D	$\log k_{nr}$		I.P.D
				Exp.	Calc.		Exp.	Calc.	
1	Methanol	0.98	0.60	45.00	45.27	0.60	8.68	8.78	1.15
2	Ethanol	0.86	0.54	45.80	46.25	0.98	8.88	8.91	0.34
3	1-Propanol	0.78	0.52	46.10	46.88	1.69	9.02	9.02	0.00
4	2-Propanol	0.76	0.48	47.70	47.09	1.28	9.13	9.07	0.66
5	1-Butanol	0.79	0.46	46.20	46.89	1.49	9.12	9.06	0.66
6	1-Pentanol	0.84	0.40	46.20	46.60	0.86	9.14	9.06	0.87
7	Hexanol	0.80	0.40	47.00	46.90	0.21	9.15	9.10	0.55
8	Octanol	0.77	0.40	47.60	47.13	0.99	9.21	9.12	0.97
9	Decanol	0.70	0.45	47.85	47.58	0.56	9.25	9.14	1.19
10	Chloroform	0.20	0.58	52.24	51.13	2.12	9.70	9.48	2.27
11	Acetone	0.08	0.71	51.30	51.85	1.07	9.02	9.48	5.09
12	Acetonitrile	0.15	0.85	50.40	51.12	1.43	9.23	9.31	0.87
13	Dichloromethane	0.13	0.82	50.80	51.31	1.00	9.52	9.35	1.78
14	2-Butanone	0.06	0.67	53.22	52.05	2.20	9.69	9.53	1.65
Water - methanol mixture (methanol % v/v)									
15	20.00	1.13	0.99	44.40	43.59	1.82	8.37	8.35	0.24
16	40.00	1.09	0.89	44.51	44.03	1.08	8.46	8.47	0.12
17	60.00	1.06	0.80	44.70	44.39	0.69	8.57	8.56	0.12
18	80.00	1.02	0.70	44.82	44.83	0.02	8.65	8.67	0.23
Water - ethanol mixture (ethanol% v/v)									
19	20.00	1.04	1.12	44.40	44.08	1.61	8.35	8.33	0.24
20	40.00	0.87	1.03	44.81	45.48	1.49	8.59	8.55	0.46
21	60.00	0.88	0.88	45.20	45.62	0.93	8.68	8.66	0.23
22	80.00	0.89	0.75	45.41	45.73	0.70	8.84	8.75	1.02

^a taken from Ref. 32

Statistics related to the MLRA and goodness of the fit has been summarized in Table 2 (a-c). Moreover, to assess the accuracy of the equations, the experimental values of the solvatochromic properties were fitted into the equation and the mean percentage deviation (MPD) between experimental and calculated values has been estimated. For a specific data point, the individual percentage deviation (IPD) has been calculated²⁶.

$$IPD = |(SP_i^{\text{exp}} - SP_i^{\text{cal}}) / SP_i^{\text{exp}}| \times 100 \quad (3)$$

$$MPD = \frac{100}{N} \sum_{i=1}^N |(SP_i^{\text{exp}} - SP_i^{\text{cal}}) / SP_i^{\text{exp}}| \quad (4)$$

Where SP is the solvatochromic property considered ($E(F)$ or $\log k_{nr}$) and N is the number of the experimental data points. More than 90% of the calculated SP values have IPD less than 2%. Mean percentage deviation (MPD) values have been found to be 1.13% for $E(F)$ and only 0.94% for $\log k_{nr}$. So, the accuracy of the equations has been found to be quite good.

Table 2(a). Statistics related to the multiple linear regression analysis

Property	Y-intercept			B			C			R ²	SD
	Value	Error	<i>t</i> -value	Value	Error	<i>t</i> -value	Value	Error	<i>t</i> -value		
<i>E</i> (<i>F</i>)	53.46	0.50	106.30	-7.48	0.39	-19.02	-1.43	0.63	-2.26	0.96	0.63
<i>log k_{nr}</i>	10.11	0.15	65.66	-0.87	0.12	-7.25	-0.78	0.19	-4.05	0.92	0.19

Table 2(b). ANOVA statistics for *E*(*F*)

Item	Degrees of Freedom	Sum of Squares	Mean Square	F-value	
Model	2	152.19	76.09		
Error	19	7.49	0.39	192.77	Prob > F
Total	21	159.69			

Table 2(c). ANOVA statistics for *log k_{nr}*

Item	Degrees of Freedom	Sum of Squares	Mean Square	F-value	
Model	2	2.87	1.44		
Error	19	0.70	0.04	38.93	Prob > F
Total	21	3.57			

In SDS micelles

For micro-heterogeneous media like micelles, a suitable probe molecule is one which readily partitioned into micelles and whose spectral characteristics changes in some way within the micelle. The dye molecule used in the present study has been found to be an excellent probe for micellar media²⁴. The absorption spectrum of the molecule shows two bands at 420 nm and 550 nm in SDS micellar phase. We have previously assigned the 420 nm band to the solubilization of the dye in some non-polar environment (near the core of the micelle) and the 550 nm band as for the dye molecule solubilized in some protic environment (namely the interfacial region of the micelle). 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. Steady-state fluorescence studies in SDS micellar phase show a band around 640-645 nm when the dye molecule has been excited to 550 nm light. This indicates that dye molecules are solubilised in an environment close to that of water- alkanol mixtures (octanol 600 nm, ethanol 624 nm, water 651 nm (extrapolated value)) *i.e.* the interfacial region of SDS micelle²³. The fluorescence band maximum shifts towards blue with increasing SDS concentration (Figure 2). This indicates gradual partitioning of the indicator into the micellar phase. But above critical micellar concentration (*cmc*), the band position hardly changes *i.e.* constancy of emission maximum after *cmc*.

In the present work, we have taken a SDS concentration of 20 mM, well above the *cmc* of SDS. The fluorescence band maximum has been found to be at 640 nm correspond to *E*(*F*) = 44.67 kcal mol⁻¹. Moreover, when the emission is fixed at 640 nm, the obtained excitation spectrum has been found to be identical to the absorption spectra of the dye in some protic environment. Time-resolved fluorescence study revealed that the 640 nm band shows double-exponential decay of the excited state with life-time (τ) components 300 ps ($\geq 25\%$) and 1500 ps ($\leq 75\%$) respectively. 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 the polarity of the solvent¹⁹. It is characterized by a longer τ in polar-protic solvents (methanol 1750 ps, ethanol 1680 ps) where the dye exists as H-bonded species. So, the observed value of 1500 ps may be assigned to the emitting state for the H-bonded species

of the dye localized at the interfacial region of the micelle. The experimental value of ϕ_F has been found to be 0.58 for the 640 nm band in 20 mM SDS medium. Using the above two parameters k_{nr} value of $2.8 \times 10^8 \text{ s}^{-1}$ has been calculated. Now one can easily obtain the α - and π^* - values for SDS micellar media by putting the respective $E(F)$ and $\log k_{nr}$ values in the above LSER equations (1) and (2).

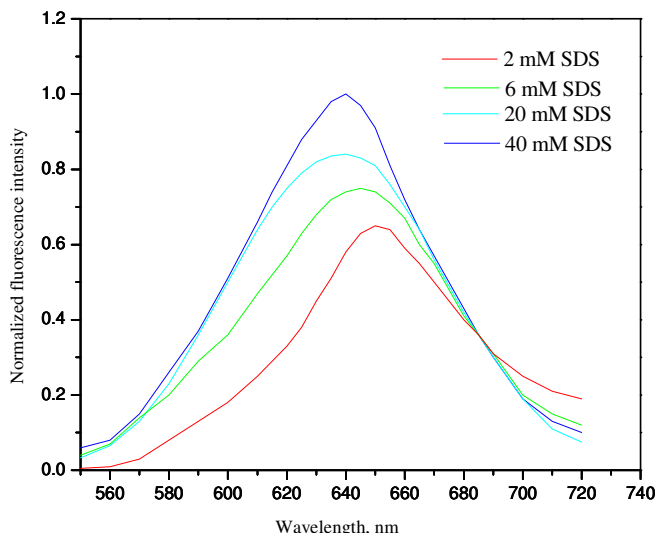


Figure 2. Fluorescence spectra of the indicator at various SDS concentrations

Estimated α and π^ of SDS micellar interface*

Using the present indicator molecule, α -value of 0.97 and π^* - value of 1.05 has been obtained for the interfacial region of SDS micelles. The obtained result needs some explanations both from qualitative and quantitative aspects. The present result of SDS system may be compared with other works on the same system also (Table 3). All the reported values are found to be smaller than that of pure water ($\alpha = 1.17$ -1.19, $\pi^* = 1.09$). SDS molecule do not possess any hydrogen-bond acidity on its own, the property originates from water molecules associated with the bound counter ions, headgroups and the first two methylene units of alkyl chain attached to the headgroups. So it can be inferred that associated water molecules at the interfacial region of micelles are less acidic and less dipolar than that of bulk water. The result is in accordance with the previous studies^{8,10-12}. Solvation dynamics²⁷⁻²⁸ and Proton NMR²⁹ studies on the structure of interfacial water of aqueous micelles has shown that they are more structured than bulk water. A water molecule at the interfacial region can take part in H-bonding with the $-\text{OSO}_3^-$ headgroup of the surfactant, with the neighbouring water molecules and to the basic (for our case C=O) part of the indicator molecule. Solvation dynamics study revealed that each headgroup is attached to water molecule through single H-bond²⁸. The other hydrogen atom of water may be either H-bonded to a nearby H_2O molecule or to the C=O part of the indicator molecule. Thus the probability of H-bond formation with the indicator molecule somewhat decreased. Thus on an average the indicator molecule senses an environment of lower acidity.

Recent molecular dynamic simulations on SDS micelle in water by Bruce *et al.* proposed a three shell water environment at the interfacial region³⁰. At the third shell, outermost region from the headgroups (where radial distance between micellar headgroup

oxygen-to-water oxygen $> 6.0\text{\AA}$), water molecules exhibit nearly identical behavior to that of bulk water; most of the water molecules have three hydrogen bonds followed by four and then two. At the intermediate region *i.e.* second shell ($3.5\text{\AA} - 6.0\text{\AA}$) relative ratio of four and two hydrogen bonds decreases. At the first shell ($< 3.5\text{\AA}$) the majority of the water molecules have only two water-to-water hydrogen bonds and a significant decrease is observed in the number of water molecules with four water-to-water hydrogen bonds. Although they have found appreciable difference in water-to-water hydrogen bonding pattern of first shell water and bulk water molecules, but average number of hydrogen bonds per water molecule (including both water-to-water and micelle-to-water hydrogen bonds) differs slightly, only the weightage shifted towards fewer number of hydrogen bonds. So, it is expected that first shell water molecules and bulk water should not differ by too large extent in their hydrogen bond donating abilities. Thus α -value of 0.97 is reasonable from that view point.

The π^* - value of 1.05 indicates that the indicator molecule is exposed to an environment of large water content, not to any non-polar region. The value supports the fact that the indicator molecule resides at the first shell of the interfacial region.

Effect of methodology and choice of indicator molecules

Table 3 summarizes all the reported values of α and π^* for SDS micellar media. α - values range from 0.8 to 1.1 whereas a larger spread (0.5-1.1) has been observed for π^* - values. Regarding the methodology used in the estimation process it is found that apart from Vitha *et al.*,³¹ that applied Kamlet-Taft solvatochromic comparison method based on the behavior of pairs of indicators, all the other workers have used the multiparametric equation as developed by Marcus^{32,33}. So, the observed spread can be assigned partly to the difference in methodology used. But even the estimated values from similar methodologies differ. Thus it is evident that choice of indicator molecule plays a role here.

Table 3. Reported α and π^* - values of SDS micellar phase

Ref.	Solvatochromic α	Properties π^*	Indicator molecule (s) used
Deb <i>et al.</i> (Ref. 13)	1.18	0.52	A ketocyanine dye and pyrene (fluorescence probes)
Shannigrahi <i>et al.</i> (Ref. 11)	1.14	0.52	A series of structurally similar ketocyanine dyes (fluorescence probes)
Fuguet <i>et al.</i> (Ref. 10)	0.79	1.02(av.)	ET(33) dye and a series of π^* -indicators (absorption probes)
Vitha <i>et al.</i> (Ref. 8)	0.73,1.01 0.87(av.)	1.06(av.)	ET(33) dye, Fe(LL) ₂ (CN) ₂ and a series of π^* -indicators (absorption probes)
De Costa <i>et al.</i> (Ref. 34)	0.82	0.52	1,5-diphenyl-3-vinyl- Δ^2 -pyrazoline (fluorescence probe)

Although the present result corroborates well to that of Vitha *et al.*⁸ and Fuguet *et al.*¹⁰ but it is better to compare the present work to that of De Costa *et al.*³⁴. for their similar methodology and as both have used single indicator molecule. They have used two environment sensitive emission properties (maximum energy of fluorescence and quantum yield) of a single indicator molecule 1,5-diphenyl-3-vinyl- Δ^2 -pyrazoline for that purposes. They have estimated α - value of 0.82 and π^* - value of 0.52. The α - value has been found to

be quite close to that of the present work, but π^* - value differ by two folds. It should be noted that the empirical relations used by them were based on fewer data points ($n = 4$ in case of quantum yield and $n = 10$ in case of maximum energy of fluorescence) compared to the present study ($n = 22$). But even then, the observed spread in the estimated properties may be assigned to the following two facts. Firstly, due to the differences in the locus of solubilization of the indicator molecule (s) within the micelle. Secondly, differences in the chemistry of the indicator (s) used. This is probably originates from the relative weightage of the dye towards the basic modes of solvation *i.e.* on the ratio (α / π^* value of the LSER equation) for a specific indicator.

Conclusion

The present work summarizes a new methodology for the estimation of solvatochromic properties of micellar interface. Two extremely environment sensitive parameters, *viz.*, energy of fluorescence maximum, $E(F)$ and the non-radiative decay constant of the excited state, k_{nr} of a single ketocyanine dye has been used for that purpose. The hydrogen bond donating ability and dipolarity-polarisability of associated water molecules at the SDS micellar interface has been found to be 0.97 and 1.05 respectively. As expected the values are to some extent lower than that of bulk water. Moreover, both the properties have some dependency on the choice of indicator molecule.

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