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Use of Fluorescence Probes for Characterization of Solvation Properties of Micelles: A Linear Solvation Energy Relationship Study

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Analysis involving the linear solvation energy relationship (LSER) of the energy of maximum fluorescence of seven structurally related probes in a micellar medium has been made to obtain solvation properties of the aqueous micellar phase. Solvation interactions as expressed by the empirical Kamlet−Taft solvatochromic parameters representing dipolarity/polarizability (π^*), hydrogen bond donor acidity (α), and hydrogen bond acceptor basicity (β) have been determined for aqueous micelles formed by cetyl trimethylammonium bromide, sodium dodecyl sulfate, and Triton-X 100. The parameters agree well with those reported by other workers using absorption probes. Solvatochromic measurements also allowed the determination of partition coefficient values for the probe molecules between the micellar and the aqueous phase. The observed values have been rationalized in terms of different modes of solute−solvent interaction.

Introduction

Micellar phases provide unique environments, and as such they are used in various areas of chemistry. They are used as media for enhancing the solubility of hydrophobic drug molecules[1,2] and as catalysts[3] and detergents.[4] They are also used to alter selectivity of separation in liquid chromatography and micellar electrokinetic chromatography (MEKC).[5−8] Enhanced solubility of organic molecules in the micellar phase points to the existence of significant interaction of the molecules with the micellar environment. Several independent modes of solute−solvent interaction have been identified for a microscopic description of the interaction of a solute in a simple environment provided by a pure solvent.[9,10] In such a situation, it is customary to write an observed parameter of a solute−solvent system in terms of the linear solvation energy relationship (LSER).[11−15] It has been observed that a solvent interacts with a solute by three independent modes, namely, dipolarity/polarizability, hydrogen bond donation (HBD), and hydrogen bond acceptance (HBA). These three modes are conveniently represented by the three parameters π^*, α, and β, respectively, as developed by Kamlet, Taft and co-workers.[16] Linear dependence through LSER on three solvent parameters is used to correlate and predict a wide variety of solvent effects on equilibrium, kinetic, and spectroscopic parameters.[11] Successful attempts have been made by Vitha et al.[17,18] and Fuguet et al.[19,20] in recent times to characterize solvation interaction in a micellar phase by the three parameters π^*, α, and β. These workers have used different absorption probes for determination of different solvatochromic parameters. While Vitha et al. used the solvatochromic comparison method developed by Kamlet−Taft and co-workers, Fuguet et al. used the multiparameter equation method developed by Marcus.[21−23] Moreover, their data treatment methodologies were also different. The difficulty with the use of absorption probes is that a higher probe concentration as required for some of the probes for the determination of maximum absorption can lead to a change in micellar structure. Moreover, the use of different indicator solutes for determining different parameters rests on the assumption that all indicator molecules probe the same region of the micelle. It is instructive to determine the parameters using fluorescence probes and to examine whether convergent results are obtained. In this paper, we have determined values of π^*, α, and β of the micellar phase provided by cationic cetyl trimethylammonium bromide (CTAB), anionic sodium dodecyl sulfate (SDS), and neutral poly(ethylene glycol) tertoctyl phenyl ether (Triton-X 100, TX100) surfactants using the LSER approach. Seven structurally related dyes (Figure 1) have been used. The results have been compared with the values reported in the literature. Values of the partition coefficient of some of the dyes between micellar phase and aqueous phase have also been determined by studying solvatochromic fluorescence of the dyes as a function of surfactant composition.

Background

In general terms, LSER is expressed by the following equation.[24,25]

$$\mathrm{XYZ} = \mathrm{XYZ}_0 + \text{cavity formation energy} + \sum \text{solute} - \text{solvent interaction energy} \quad (1)$$

In the above equation, XYZ is a property linearly related to the free energy of the system. The term XYZ_0 denotes a constant and depends solely on the solute. Summation in the above equation extends over all the possible modes of solute−solvent interaction.[26,27] There are two similar forms of the equation used for LSER analysis, viz., the one developed by Kamlet and co-

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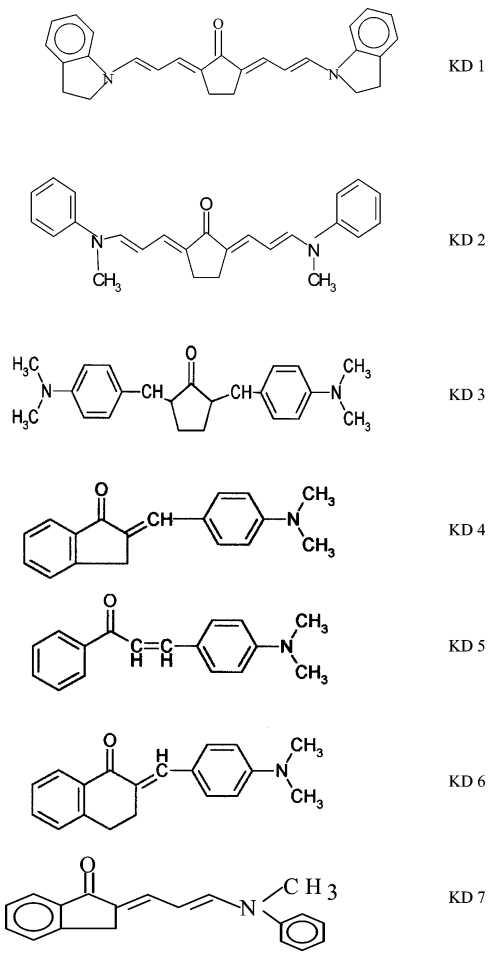

Figure 1. Fluorescence probes used in the present study.

workers and the other proposed by Abraham and co-workers. The two approaches differ in the use of descriptors of solute−solvent interaction. We shall use the Kamlet version of LSER as expressed by the following equation:

$$\mathrm{XYZ} = \mathrm{XYZ}_0 + m\delta_H^2 + p\pi^* + a\alpha + b\beta \qquad (2)$$

In this equation, the cavity term is written as product of the coefficient *m* (depending on the molar volume of the solute) and the Hildebrand solubility parameter, δ_H^2, of the solvent,[28] and the solute−solvent interaction is written in terms of nonspecific (π^*) and specific (α and β) interaction parameters. Since entropy does not change during a spectroscopic transition,[29] the transition energy can be regarded as related to a change in free energy. Again, during a spectroscopic transition the volume of the solute remains constant and as a result the cavity term drops out.[12] Thus one can write the maximum energy of transition (*E*) of the solute (s)−solvent (i) system as follows:

$$E(\mathrm{s,i}) = E_0(\mathrm{s}) + p(\mathrm{s})\pi^*(\mathrm{i}) + a(\mathrm{s})\alpha(\mathrm{i}) + b(\mathrm{s})\beta(\mathrm{i}) \qquad (3)$$

The coefficients *p*(s), *a*(s), and *b*(s) depend on the solute and are related respectively to dipolarity/polarizability and HBA and HBD ability of the solute.[12] Equation 3 can be used to treat the solvatochromic transition energy for a fixed solute for a series of solvents whose π^*, α, and β values are known. Multiple linear regression analysis (MLRA) of *E* with π^*, α, and β will then provide the *p*, *a*, and *b* terms. This procedure is used to get the LSER equation for a particular solute.[24] Conversely the equation can be used to analyze the transition energy of a series of solutes in a fixed solvent (medium). The use of the LSER approach for a particular aqueous micellar system using various solutes is very common in explaining the chromatographic retention factor of solutes and the partition of solutes in the aqueous and micellar phase.[8,30] In the present study, MLRA of the energy of maximum fluorescence (*E*) has been sought with the known solute parameters *p*, *a*, and *b* to get the values of π^*, α, and β for the solvent. Ketocyanine dyes provide an interesting series of solutes, which are characterized by solvatochromic fluorescence.[31] The spectroscopic transition leading to the fluorescence in these molecules has been established as due to intramolecular charge transfer (ICT) involving the carbonyl oxygen and nitrogen atom of the amino group.[31,32] We have studied the solvatochromic fluorescence energy of the ketocyanine dyes (KD1 and KD2, Figure 1) and other structurally related solutes (KD3−KD7, Figure 1) extensively in various pure solvents.[30−33] MLRA of maximum fluorescence energy in pure solvents has been done with solvent parameters π^*, α, and β to get *p*, *a*, and *b* coefficients for the solutes. The relevant parameters are given in Table 1. As stated earlier, *p* is related to the dipolarity parameter of a solute. The dipole moment of the solute in the ground state is a good descriptor of this property.[25] Table 1 lists the values of the dipole moment of the solutes in the ground state (μ_0) as obtained for AM1 calculation.[32−35] The reasonable correlation of *p* with μ_0 as shown in Figure 2a supports this. Similarly *a*-coefficients are related to the HBA ability of solutes. It is reasonable to suppose that the charge density on the oxygen atom of the carbonyl group in these compounds would favor the HBA ability of the solute molecules under study. These quantities, as calculated by AM1 calculation, have been listed in Table 1. Figure 2b shows the correlation between *a*-coefficients and the charge density on the carbonyl oxygen atom.

TABLE 1: Solute Properties

indicator solutes	E_0(s)	*a*(s)	*b*(s)	*p*(s)	*R*, *n*[a]	(μ_0)/D	negative charge density on carbonyl oxygen
KD1	57.20	7.31	2.61	4.04	0.97, 22	4.02	0.315
KD2	57.80	7.28	1.71	2.46	0.97, 22	3.65	0.310
KD3	63.99	5.29	5.00	11.25	0.98, 24	4.75	0.296
KD4	64.50	3.24	4.57	9.19	0.97, 22	4.87	0.287
KD5	64.30	3.05	3.71	9.36	0.96, 24	4.29	0.304
KD6	64.30	3.60	5.50	8.50	0.98, 22	4.31	0.303
KD7	63.81	2.62	2.08	4.30	0.98, 22	4.17	0.296

[a] *R*, correlation coefficients; *n*, number of solvents.

Experimental Section

Chemicals. The solutes were synthesized by methods described in the literature.[29−33] The surfactants CTAB (Lancaster) and SDS (Sigma) were purified by repeated crystallization from ethanol. The nonionic TX100 [Sigma] was used as received. The $E_T(30)$ probe [2,6-di-phenyl-4(2,4,6-triphenyl-1-pyridino)-phenolate] was obtained from Prof. Ch. Reichardt, Merburg, Germany, as a generous gift.

Solution Preparations. Solutions for spectroscopic measurements were prepared by the following method. First a stock solution of the dye was prepared in dry ethanol ($\sim 10^{-4}$ M). A 0.05 mL portion of the above stock solution was introduced in a volumetric flask and spread over the flask, and the solvent was evaporated under gentle heating. Then 5 mL of the surfactant solution was added to the flask, and the solution was sonicated for about 1 h. The resulting clear solution was then directly taken into the spectrophotometer cuvette.[36] The concentration of the dye in solutions was in the range 10^{-5}−10^{-6} M. All water used for solution preparation was triply distilled.

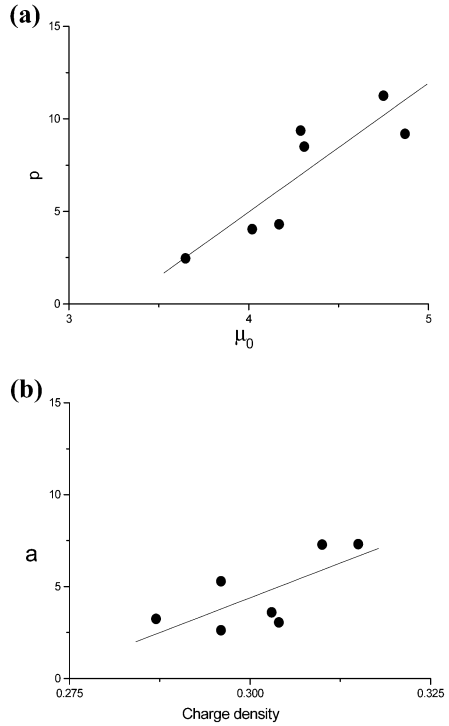

Figure 2. Plot of *p*-coefficient vs μ_0 (a) and *a*-coefficient vs negative charge density on oxygen (b).

Spectroscopic Measurements. Fluorimetric measurements were done on a Hitachi F-4500 spectrofluorimeter fitted with a thermostated sample compartment. A temperature of 298 ± 0.1 K was maintained by circulating water from a constant-temperature bath (Heto-Holten). The sample was allowed to equilibrate at that temperature by keeping it in the thermostated sample compartment for 10 min before collection of the spectra. Several replicate measurements were done for a particular solution, and the mean of the maximum wavelength values was taken. $E_T(30)$ values for the micellar environment were obtained from the wavelength of maximum absorbance (measured on a Shimadzu UV 2101 PC UV−vis spectrophotometer fitted with a temperature-controlled unit) for the indicator solute using the relation[24]

$$E_T(30)/\text{kcal mol}^{-1} = 28590/(\lambda/\text{nm}) \quad (4)$$

Data Analysis. The electronic transition energy of a solvatochromic indicator depends on the nature of the environment around the solute. We have determined the values of the energy of maximum transition in the micellar phase by a procedure proposed by Fuguet et al.[19,20] The transition energy in a solution containing both the micellar and the aqueous phase is assumed to be given by the following relation:

$$\sigma = (n_m\sigma_m + n_{aq}\sigma_{aq})/(n_m + n_{aq}) \quad (5)$$

$$E/\text{kcal mol}^{-1} = 2.859\sigma/kK \quad (6)$$

In eq 5, σ and n are the wavenumbers of maximum fluorescence and the number of moles of an indicator, respectively. The suffixes "m" and "aq" represent the micellar and aqueous phase, respectively. Values of n_m and n_{aq} are related to the molar based partition coefficient (P) of the solute between the micellar and the aqueous phase and are given by the relation[19,20]

$$n_m/n_{aq} = P\upsilon(C_T - \text{cmc})/[1 - \upsilon(C_T - \text{cmc})] \quad (7)$$

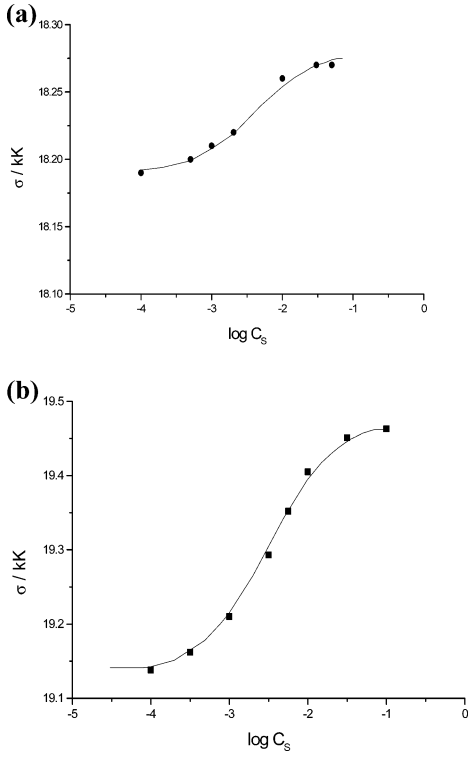

Figure 3. Representative plots of σ vs log C_S for KD6 (a) and KD7 (b) in SDS. The continuous line represents the best-fit curve using σ_{aq}, σ_m, and P as given in Table 2.

In the above equation, υ is the molar volume of surfactant; C_T and cmc are the total concentration and critical micellar concentration (cmc) of the surfactant, respectively.

Using equations 5 and 7, we get eq 8:

$$\sigma = [P\upsilon C_S\sigma_m + (1 - \upsilon C_S)\sigma_{aq}]/[P\upsilon C_S + (1 - \upsilon C_S)] \quad (8)$$

$$C_S = C_T - \text{cmc} \quad (9)$$

Measurement of the wavenumber of maximum fluorescence as a function of C_S, the concentration of the surfactant in the aggregated phase, allows estimation of P, σ_m, and σ_{aq} if the molar volume of surfactant is known. A plot of σ values versus log C_S gives a sigmoid curve. We have fitted the experimental σ versus log C_S curve by varying the values of P, σ_m, and σ_{aq}. Values of υ for SDS and CTAB have been taken as 0.246 and 0.324 L mol^{-1}.[37,38] The value for TX100 has been estimated from molecular dimensions as 0.294 L mol^{-1}. Of the seven dyes, KD1, KD2, and KD3 are practically insoluble in water and an appreciable solubility is attained only when the total surfactant concentration exceeds the cmc. The above procedure was adopted for the probes KD4−KD7 only. Figure 3 shows representative best-fit curves. The best-fit parameters for the solutes are listed in Table 2A, and the fitting statistics are presented in Table 2B. It appeared that σ_m is practically equal to the value of σ when C_T is high (>50 mM). Similarly the value of σ_{aq} is equal to the value reported for water. For the dyes KD1−KD3, the value of σ for a high concentration of surfactant (>50 mM) was taken as the value of σ_m. Values of σ_{aq} for these dyes were calculated by extrapolation. Values of σ for the dyes in aqueous ethanol were plotted against the mole fraction of water (x_w) in the mixture. A nonlinear variation of σ with x_w was observed in all cases (Figure 4). It has been found that σ versus x_w could be best fitted with an equation

TABLE 2: (A) Emission Maxima for the Dyes in Water and Micellar Media and Their Respective Micelle−Water Partition Coefficients; (B) Statistics Related to the Fitting of Experimental σ to Equation 8

Section A

	σ/kK				log $P_{m/aq}$		
indicator solutes	water	SDS	CTAB	TX100	SDS	CTAB	TX100
KD1	15.39 ± 0.01	15.57 ± 0.02	16.23 ± 0.02	15.87 ± 0.02			
KD2	16.40 ± 0.01	16.61 ± 0.02	17.24 ± 0.02	16.95 ± 0.02			
KD3	16.95 ± 0.02	17.33 ± 0.01	17.24 ± 0.02	17.27 ± 0.02			
KD4	18.18 ± 0.03	18.35 ± 0.03	18.52 ± 0.03	19.05 ± 0.02	2.81 ± 0.03	3.17 ± 0.02	4.10 ± 0.01
KD5	18.02 ± 0.02	18.52 ± 0.02	18.54 ± 0.01	19.05 ± 0.02	2.40 ± 0.03	3.46 ± 0.02	4.22 ± 0.01
KD6	18.19 ± 0.02	18.30 ± 0.02	18.52 ± 0.02	18.87 ± 0.02	3.00 ± 0.02	3.41 ± 0.02	4.12 ± 0.01
KD7	19.13 ± 0.01	19.48 ± 0.01	19.80 ± 0.01	19.62 ± 0.02	3.11 ± 0.02	4.34 ± 0.02	4.42 ± 0.01

Section B[a]

	SDS		CTAB		TX100	
indicator solutes	*R*	sd	*R*	sd	*R*	sd
KD4	0.94	0.02	0.95	0.01	0.94	0.02
KD5	0.95	0.02	0.95	0.02	0.95	0.02
KD6	0.92	0.03	0.94	0.02	0.94	0.03
KD7	0.97	0.01	0.98	0.02	0.97	0.01

[a] *R* and sd denote the correlation coefficient and standard deviation, respectively.

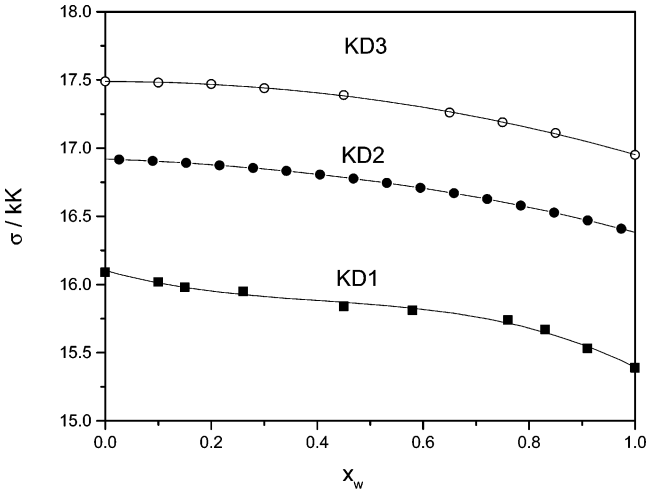

Figure 4. Variation of σ for the dyes KD1 (■), KD2 (●), and KD3 (○) in aqueous ethanol as a function of the mole fraction of water (x_w) in the mixture.

cubic in x_w. The best-fit equations for the dyes KD1−KD3 are

$$\sigma = 16.10 - 1.08x_w + 1.98x_w^2 - 1.64x_w^3 \quad \text{(KD1)} \quad (10a)$$

$$\sigma = 16.94 - 0.16x_w - 0.26x_w^2 - 0.12x_w^3 \quad \text{(KD2)} \quad (10b)$$

$$\sigma = 17.49 - 0.002x_w - 0.51x_w^2 - 0.03x_w^3 \quad \text{(KD3)} \quad (10c)$$

The values of σ_{aq} were calculated from the above equations by putting $x_w = 1$.

Results and Discussions

Solvatochromic Parameters. For a particular micelle, the energy of maximum transition (E_m) for a particular solute, as calculated from σ_m by using eq 6, is given by the following equation:

$$[E_m(s) - E_0(s)] = a(s)\alpha_m + b(s)\beta_m + p(s)\pi^*_m \quad (3a)$$

The values of α_m, β_m, and π^*_m that give the best correlation in the least-squares sense of $[E_m(s) - E_0(s)]$ with $a(s)$, $b(s)$, and $p(s)$ for the seven solutes were then determined. Alternatively, we have for the micellar and aqueous phase

$$[E_m(s) - E_{aq}(s)] = a(s)[\alpha_m - \alpha_{aq}] + b(s)[\beta_m - \beta_{aq}] + p(s)[\pi^*_m - \pi^*_{aq}] \quad (11)$$

TABLE 3: Solvatochromic Properties for Different Micellar Media

							$E_T(30)$/kcal mol^{-1}	
micelles	α	Δα	β	Δβ	π*	Δπ*	calcd[a]	reported
SDS	1.14	−0.071	0.70	0.329	0.52	−0.231	54.5	58.2[b], 57.5[c]
CTAB	0.87	−0.359	0.53	0.129	0.68	−0.027	52.2	53.4[b], 53.1[c]
TX100	1.06	−0.098	0.71	−0.076	0.56	−0.139	53.8	52.8[b], 53.0[c]

[a] Calculated value using eq 11. [b] Present work. [c] Reference 39.

A correlation analysis involving $[E_m(s) - E_{aq}(s)]$ in place of $[E_m(s) - E_0(s)]$ provides $\Delta\alpha = [\alpha_m - \alpha_{aq}]$, $\Delta\beta = [\beta_m - \beta_{aq}]$, and $\Delta\pi^* = [\pi^*_m - \pi^*_{aq}]$. The results are summarized in Table 3. It appears from the sign of Δα that the HBD strength of the micellar region is, in general, less than that of the aqueous phase. The change from the aqueous phase follows the order CTAB > SDS ≅ TX100. Note that the anionic micelle formed by SDS has better HBD strength than the other micelles. Earlier workers have also reported a similar trend in the variation of α values as the micelle is changed from cationic to anionic. Thus the values of α for the micellar phase of SDS and DTAB as reported by Vitha et al. are 0.873 and 0.700, respectively.[17,18] Similarly Fuguet et al. reported α = 0.82 and 0.62 for SDS and CTAB, respectively.[19,20] The sign of Δβ indicates that ionic micelles have relatively more HBA basic than the aqueous phase. The neutral TX100 micelle on the other hand has HBA ability comparable to that of the aqueous phase. The results are in qualitative agreement with those obtained by others. Thus for the SDS micellar phase values of 0.401 and 0.62 have been reported by Vitha et al.[17] and Fuguet et al.,[19] respectively. π* values for the micellar phase of the surfactant are less than that of the aqueous phase for all the micelles as reflected by the negative values of Δπ*. These findings have also been made by others by solvatochromic comparison studies and LSER analysis of solute partitioning between the two phases.[19] The change from the aqueous phase follows the order SDS > TX100 > CTAB. However, the magnitude of π* for the micellar phase

is rather low compared to those obtained by using π^*-probes. Thus the average value of π^*, as reported by earlier workers, is of the order of 1.0 for all the micellar phase, while a value of ~0.6 has been obtained in the present work.

The micellar phase consists of a hydrocarbon core and a polar region. The polar headgroups, the bound counterions (in the case of ionic micelles), and water molecules bound to the headgroups mainly constitute the polar region. Our previous work has established that the dye molecules are located in the polar region near the micelle−water interface. As such the polarity monitored by the dye molecules used in the present study corresponds to this region of the micelles. These properties in the micellar phase arise partly due to the presence of bound water molecules and counterions. The headgroup in a SDS micelle ($-O-SO_3^-$) can bind more water molecules than a headgroup in CTAB ($-N(CH_3)_3^+$). In the former case, the negative charge is distributed over the oxygen atoms, while in the case of ($-N(CH_3)_3^+$) the intervening methyl groups restrict the water molecules from coming closer to the headgroup. Moreover, the counterion (Na^+) in the case of SDS can bind more water molecules by solvation than the corresponding counterion (Br^-) in CTAB. The greater HBD ability of the anionic SDS micelle relative to the cationic CTAB micelle can be rationalized due to the presence of a larger number of bound water molecules in the Stern layer of the micelle. On the other hand, the TX100 monomer surfactant molecule possesses some HBD strength due to the presence of −OH groups. Thus a higher value of α is expected for TX100 micelles. The higher HBA ability of SDS relative to CTAB micelles can also be rationalized in terms of the presence of water molecules as explained above. Moreover, in the case of SDS, the presence of ($-O-SO_3^-$) headgroups adds to the HBA basicity of the micelle formed. The headgroup of the neutral TX100 surfactant contains a phenyl group followed by a polyoxyethylene chain terminating in a hydroxyl group. Thus the polar region is expected to resemble an alcohol environment. Thus the determined solvatochromic parameters are close to that of ethanol[13] ($\alpha = 0.86$, $\beta = 0.75$, $\pi^* = 0.54$), which closely resembles the chain end of the surfactant.

The overall polarity of a medium as conveniently expressed by the $E_T(30)$ parameter depends on the solvatochromic parameters as follows:[24]

$$E_T(30) = 31.2 + 15.2\alpha + 11.5\pi^* \quad (12)$$

The calculated values of $E_T(30)$ for the micelles are given in Table 3. The values are in good agreement with the values obtained by direct experiment (also given in Table 3).

Partition Coefficient. Values of the molar based partition coefficent (P) of the solute between the micellar and the aqueous phase as given in Table 2A indicate the order SDS < CTAB < TX100 for log P values for all the solutes. Thus the dyes are more soluble in CTAB and TX100 than in SDS micelles. The order of P values agrees qualitatively with that of the binding constant of the dye with micelles.[32,33] Using LSER formalism, the P values can be written as follows:

$$\log P_{m/aq} = \log P_0 + \beta_S[\alpha_m - \alpha_{aq}] + \alpha_S[\beta_m - \beta_{aq}] + \pi_S[\pi^*_m - \pi^*_{aq}] + V_S[\delta_{Hm}{}^2 - \delta_{Haq}{}^2] \quad (13)$$

The second, third, and fourth terms of the right-hand side of eq 12 indicate contribution due to HBD acidity, HBA basicity, and dipolarity/polarizability interaction. The fifth term represents the cavity term. For SDS and TX100 micelles for a given solute, we write from eq 13

$$\log P_{SDS/aq} - \log P_{TX100/aq} = \beta_S[\alpha_{SDS} - \alpha_{TX100}] + \alpha_S[\beta_{SDS} - \beta_{TX100}] + \pi_S[\pi^*_{SDS} - \pi^*_{TX100}] + V_S[\delta_{HSDS}{}^2 - \delta_{HTX100}{}^2] \quad (14)$$

Small differences between the solvatochromic parameters for the two micellar phases indicate that the difference in log P values cannot be solely due to a difference in these parameters. LSER analysis of partition coefficients indicated that the relative contributions of different interactions toward partitioning of a solute between the two phases are as follows: dipolarity ~ ca. 2−3%, HBD/HBA ~ 25−30%, and cavity ~ 40−45%.[30] Thus the difference of energy for the creation of a cavity in different micelles also plays a significant role in determining log $P_{m/aq}$ values.

Conclusions

The solvation properties of the micellar phase can be rationalized in terms of LSER using the Kamlet−Taft solvatochromic parameters. The parameters have been determined by a LSER analysis of the fluorescence maximum of seven structurally similar dyes. Due to their structural similarity, all the dyes are located in the same region of a micelle. This eliminates the problem of using structurally different probes for different solvatochromic parameters. However, convergent results regarding the relative value of solvatochromic parameters are obtained whether one uses absorption or fluorescence probes.

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