

Use of Fluorescence Probes for Studying Kamlet–Taft Solvatochromic Parameters of Micellar System Formed by Binary Mixture of Sodium Dodecyl Sulfate and Triton-X 100

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Fluorescence probes have been used to estimate Kamlet–Taft solvatochromic parameters α and π^* representing hydrogen-bond donation ability and dipolarity/polarizability, respectively, of sodium dodecyl sulfate (SDS)–Triton X 100 (TX100) mixed aggregates with varying compositions. The hydrogen-bond donation ability of the mixed aggregate has been found to increase with SDS composition, whereas the dipolarity/polarizability parameter decreases. The relative contribution of electrostatic and steric effect toward the total free energy of micellization have been calculated for the mixture. The solvatochromic parameters α and π^* depend linearly on the total free energy of micellization, indicating a correlation between aggregational and solvatochromic properties.

Introduction

Mixed surfactants provide interesting systems, and as such they are widely studied both by rigorous experimentation^{1–10} and theoretical approaches.^{11–18} Most of the studies are devoted to either estimation or prediction of the aggregational properties like critical micellization constant (cmc), composition at cmc, interaction parameter, aggregation number, or stability of the mixed micellar system. However, some studies involving photoluminescence techniques have been done to explore the polarity, as given by an effective dielectric constant (ϵ), and the viscosity of mixed micellar surfaces.^{19–22} This technique mainly makes use of a suitable photoactive solute molecule, popularly known as a probe, which have different luminescence properties in different environments. Micelles are well known for their capacity of solubilizing solute molecules (mainly of hydrophobic in nature) in an aqueous medium. The enhanced solubility of organic molecules in the micellar phase points to the existence of significant interaction of the molecules with the micellar environment. The use of a single polarity parameter, as given for example by dielectric constant (ϵ), to characterize the strength of solute–solvent interaction has often been criticized.²³ In the multiparametric approach, three independent modes, namely, dipolarity/polarizability, hydrogen-bond donation (HBD), and hydrogen-bond acceptance (HBA) ability, have been characterized to describe solute–solvent interaction. Kamlet, Taft, and co-workers introduced the solvatochromic parameters π^* , α , and β for homogeneous media, respectively, and these are supposed to act as faithful descriptors of the three basic modes of interaction in homogeneous media.²⁴ It is instructive to study whether the interaction of a solute with a micellar phase can be partitioned into contribution due to the

three basic modes of solvation. Recently, Vitha et al.^{25,26} and Fuguet et al.^{27,28} proposed methodologies for the estimation of π^* , α , and β for pure micellar media using absorption probes. Solvatochromic parameters for heterogeneous media have also been estimated by our group using fluorescence probes.^{29,30} No study has been done as yet on the solvation characteristics on mixed micellar systems. But a prior knowledge of solvatochromic properties of mixed micellar media is helpful for understanding the selectivity of separation in micellar electrokinetic chromatography.^{31,32} In the present work, we have extended our study to the mixed micellar system formed by anionic sodium dodecyl sulfate SDS and nonionic Triton X 100 (TX100). Although this system is widely studied in the context of aggregation behavior and polarity (as determined by ϵ), no work has been devoted as yet for the estimation of solvatochromic properties of this system. In this work, we have investigated the variation of solvatochromic properties, namely, dipolarity/polarizability and hydrogen-bond donation (HBD ability) as given by π^* and α , respectively, of the mixed surfactant system with composition by monitoring the fluorescence parameters of two probe molecules, namely, pyrene and a ketocyanine dye, as shown in Figure 1. The results have been explained in the light of presently available theories. Furthermore, the free energy contribution (both steric and electrostatic) toward micellization has been calculated for the system as a function of surfactant composition and its correlation with the solvatochromic parameters has been explored.

Materials and Methods

Chemicals. SDS [Sigma] was purified by recrystallization from ethanol. TX-100 [Sigma] is used without further purification. The dye was prepared by the methods described earlier.³³ Pyrene was obtained from Aldrich at 99% purity and was used

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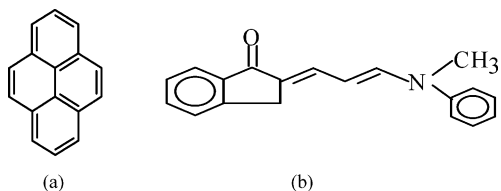


Figure 1. Fluorescence Probes used in the present study: (a) pyrene, (b) ketocyanine dye.

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.

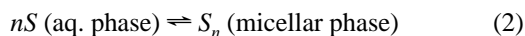
Solution Preparations. Solutions for spectroscopic measurements were prepared by the following method. At first, a stock solution of the dye ($\sim 10^{-4}$ M) was prepared in dry ethanol. The above stock solution (0.05 mL) was introduced in a volumetric flask, spread over the flask, and the solvent 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.³⁰ The concentration of the dye in solutions was in the range of 10^{-5} to 10^{-6} M. In the case of pyrene, a similar procedure has been adopted and the final concentration of pyrene in solution was maintained at 10^{-7} M so that the band due to excimer emission does not occur. Water used for solution preparation was triply distilled.

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, Denmark). Samples were allowed to equilibrate at that temperature by keeping it in the thermostated sample compartment for 10 min before collection of the spectra. For the ketocyanine dye and pyrene, excitation wavelengths of 450 and 338 nm, respectively, have been used. Several replicate measurements were done for a particular solution, and the mean of the maximum wavelength values was taken. The energy of maximum fluorescence was calculated from the wavelength of maximum fluorescence using the relation

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

$E_T(30)$ values were obtained from the wavelength of maximum absorption of the $E_T(30)$ solute using eq 1. Absorption measurements have been done on a SHIMADZU UV 2101 PC UV-vis spectrophotometer fitted with a temperature-controlled unit.

Estimation of the Micellar Phase Property Free from Aqueous-Phase Contribution. Micellization is essentially a dynamic process involving equilibrium between the surfactant molecules (S) in the aqueous phase and those in the micelles, as represented by



An indicator solute molecule is distributed between the two phases. Any spectroscopic parameter (P) of the indicator molecule for such systems will be determined by the time average location of the probe in the system.³⁴ Thus, the observed property P can be assumed to be represented by a mole fraction average of the aqueous phase property (P_{aq}) and micellar phase property (P_m), as given by the following equation.

$$P = \frac{n_{aq}P_{aq} + n_mP_m}{n_{aq} + n_m} \quad (3)$$

where n refers to the number of moles of the solute and the subscripts aq and m denote the aqueous phase and the micellar phase, respectively. Calculation of values P_m and P_{aq} requires knowledge of n_m and n_{aq} , which in turn are related to the partition coefficient (K) of the solute between the two phases. Fuguet et al. has shown that the parameters are related by the following equation.²⁷

$$P = [KvC_S P_m + (1 - vC_S)P_{aq}]/[KvC_S + (1 - vC_S)] \quad (4)$$

The equation can be rearranged as²⁹

$$P = P_{aq} + (KP_m - P_{aq})vC_S + (1 - K)vC_S P \quad (4a)$$

where, $C_S = (C_T - cmc)$ is the concentration of the surfactant in the aggregated phase and v is the molar volume of the surfactant. A multiple linear regression analysis (MLRA) of the measured property P with vC_S and $vC_S P$ can thus provide parameters P_m , P_{aq} , and K . Any property (P) of the indicator solute that has dependence on its local environment can be used. In present study, we have used the ratio of intensity of the first and the third vibronic band (I_1/I_3) in the emission spectra for pyrene as relevant parameter. For the ketocyanine dye, the maximum energy of fluorescence, $E(F)$, has been used as the parameter. The above procedure has been used in our earlier studies for determining the values of the partition coefficient and the energy of maximum fluorescence of ketocyanine dyes in the micellar phase for homomicelles²⁹ and heteromicelles.²² It is important to mention that for surfactant concentration well above the critical micellar concentration (cmc) the observed $E(F)$ values approached that for the micellar phase. This fact has been utilized for the estimation of the I_1/I_3 ratio for pyrene and the $E_T(30)$ value in the mixed micellar phase formed by SDS + TX 100.

Estimation of π^* and α Parameters. Dong and Winnik³⁵ have found that the I_1/I_3 ratio of pyrene fluorescence for homogeneous media is correlated with the π^* values of a series of protic solvents as

$$(I_1/I_3) = 1.304\pi^* + 0.46 \quad (5)$$

We have shown in an earlier communication that this equation can be used to estimate π^* for heterogeneous media and the values agree well with those obtained by using other fluorescence probes.³⁰ In the present work, the above empirical relation has been used to calculate π^* employing the micellar-phase value of I_1/I_3 for mixed micelle of varying composition. The average error in the estimation of π^* is $\pm 5\%$. To estimate α , we have adopted the following procedure. It is known that the position of the maximum of fluorescence of ketocyanine dyes in a solution is highly solvent-sensitive and the energy of maximum fluorescence is linearly dependent on the solvatochromic parameters. The dyes are solubilized in the micelle-water interface.³⁶ It is believed that the polarity characteristics of the micelle-water interfacial region resemble those of aqueous alkanols.³⁷ In the present work, the values of $E(F)$ of the ketocyanine dye have been determined in various pure n -alkanols and mixed binary aqueous alkanol systems for which the values of solvatochromic parameters are known.³⁸ Table 1 shows the $E(F)$ values for different systems. A MLRA of $E(F)$ with the solvatochromic parameters has been performed. It has

TABLE 1: Energy of Maximum Fluorescence, $E(F)$ of the Ketocyanine Dye in Pure and Mixed Aqueous Solvents at 298 K

composition	volume fraction of water	$E(F)$ (kcal mol ⁻¹)	α^a	π^*^a
water	1.0	54.7	1.17	1.09
water + methanol	0.4	55.6	0.98	0.97
	0.2	55.8	1.04	1.08
	0.0	56.0	0.93	0.60
water + ethanol	0.9	55.0	1.09	1.17
	0.8	55.5	1.00	1.10
	0.7	55.8	0.96	0.99
water + propanol	0.6	56.1	0.96	0.88
	0.9	55.3	1.01	1.03
	0.8	55.7	0.93	0.91
	0.7	56.0	0.91	0.82
	0.6	56.1	0.91	0.76
	0.5	56.2	0.91	0.71
	0.4	56.2	0.88	0.69
	0.3	56.3	0.83	0.67
	0.2	56.4	0.79	0.64
	0.1	56.5	0.76	0.59
	0.0	56.8	0.77	0.50

^a Reference 38.**TABLE 2: Aggregational Properties of SDS + TX100 Mixture as a Function of Composition**

x_{SDS}	cmc ^a (mM)	$x_{\text{SDS}}^{\text{m}}$		
		using KCD ^b	using pyrene ^c	present work
0.0	0.25	0.00	0.00	0.00
0.1	0.25	0.08	0.08	0.08
0.2	0.26	0.19		0.13
0.3	0.30	0.21	0.15	0.18
0.4	0.33	0.25		0.22
0.5	0.37	0.28	0.21	0.25
0.6	0.43	0.32		0.27
0.7	0.65	0.33	0.29	0.30
0.8	0.75	0.36	0.32	0.34
0.9	0.80	0.39	0.37	0.38
1.0	7.60	1.00	1.00	1.00

^a Present work. ^b Reference 22. ^c Reference 9.

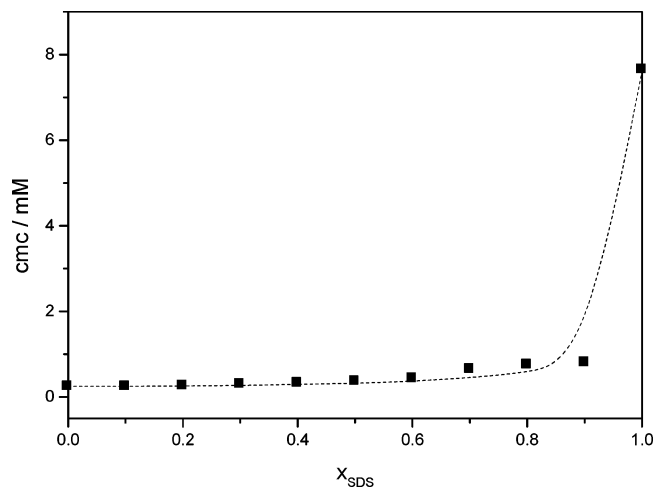
been found that the $E(F)$ of the ketocyanine dye correlates well with the α and π^* parameters for a series of pure alkanols and water–alkanol mixtures. Thus

$$E(F) = (59.8 \pm 0.5) - (3.60 \pm 0.15)\alpha - (0.6 \pm 0.05)\pi^*; \\ n = 18, r = 0.95, \text{ standard deviation} = 0.186 \quad (6)$$

We can assume that this relationship is also valid for heterogeneous media. The value of α for the micellar phase was obtained using eq 6 from the known values of $E(F)$ and π^* for the micellar phase.

Results and Discussion

Aggregation Properties of Mixed Micelles. Values of cmc for different surfactant composition have been determined by the pyrene I_1/I_3 ratio in the present work. Table 2 lists the values. The estimated cmc varies slowly in the composition range $0 \leq x_{\text{SDS}} \leq 0.9$, where x_{SDS} denotes the mole fraction of SDS in the surfactant mixture. Beyond this range, however, the values of cmc increases abruptly. The results agree well with those obtained by Ruiz et al.⁹ A similar variation of cmc with surfactant composition has been reported by us in our previous publication where we determined the values using the ketocyanine dye.²² Values of $x_{\text{SDS}}^{\text{m}}$, representing the mole fraction of

**Figure 2.** Variation of cmc as a function of x_{SDS} . The line shows the variation of cmc with x_{SDS} as calculated by regular solution theory using $\beta' = -3.7$.

SDS in mixed micelle as calculated according to Rubingh's approach using the present data for the micellar system have been listed in Table 2. Note that the mole fraction of SDS in the mixed aggregate is always smaller than that in the bulk. This indicates that the aggregated form is richer in TX100. The difference between the micellar and the bulk mole fraction is more prominent for $x_{\text{SDS}} > 0.4$. Table 2 also shows values of $x_{\text{SDS}}^{\text{m}}$ as reported in the literature. The estimated value of the interaction parameter (β') of the regular solution theory using present data comes as -3.7 . The value is close to that obtained by Ruiz et al. ($\beta' = -3.3$) and our group ($\beta' = -3.9$). Figure 2 shows the plot of cmc (present work) as a function, the bulk composition of SDS (x_{SDS}). The line showing the variation of cmc with x_{SDS} as calculated by regular solution theory using $\beta' = -3.7$ has also been shown in Figure 2.

Maeda¹⁵ proposed that for nonionic (1) and ionic (2) mixed micelles the free energy of micellization (G_{mic}) can be written in terms of the micellar composition (x^{m}) as given by

$$G_{\text{mic}}/RT = \ln C_{12} = B_0 + B_1 x_2^{\text{m}} + B_2 (x_2^{\text{m}})^2 \quad (7)$$

where C_{12} is the cmc for the mixed surfactant and x_2 is the mole fraction of the ionic component in the mixed micelle. The three constants B_0 , B_1 , and B_2 are related to the cmc of the component surfactants and the interaction parameter (β') of the regular solution theory as follows:

$$B_0 = \ln C_1 \quad (8)$$

$$B_1 + B_2 = \ln(C_1/C_2) \quad (9)$$

and

$$B_2 = -\beta' \quad (10)$$

In the above equations, C_1 and C_2 denote the cmc values for the nonionic and ionic micelle, respectively. It has been observed that the value of the cmc for a particular surfactant composition as obtained in the present work is correlated with the mole fraction of SDS in micelle, x_2^{m} , as follows.

$$\ln(C_{12}/M) = -(8.31 \pm 0.14) + (2.24 \pm 0.18)x_2^{\text{m}} + (1.24 \pm 0.06)(x_2^{\text{m}})^2; \quad r = 0.99, \text{ standard deviation} = 0.18 \quad (11)$$

TABLE 3: Parameters of the Probes in the Micellar Phase as a Function of Surfactant Composition

x_{SDS}	$E(F)^a$	I_1/I_3
0.0	56.0	1.40
0.1	56.0	1.38
0.2	55.9	1.36
0.3	55.9	1.35
0.4	55.9	1.34
0.5	55.8	1.32
0.6	55.8	1.29
0.7	55.7	1.27
0.8	55.6	1.23
0.9	55.5	1.19
1.0	55.2	1.14

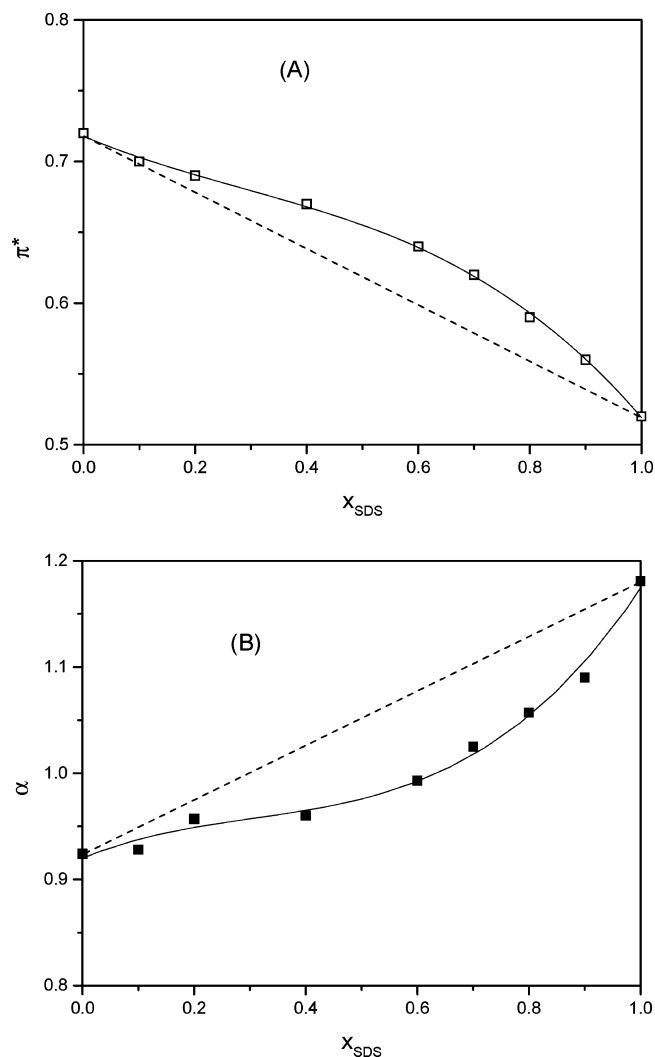
^a Reference 22.**TABLE 4: Polarity Parameters of the Micellar Phase for SDS + TX100 Micelles as a Function of Surfactant Composition**

x_{SDS}^a	α	π^*	$E_T(30)$	
			calcd	expt ^b
0.0	0.92	0.72	53.5	52.8
0.1	0.93	0.70	53.4	53.3
0.2	0.96	0.69	53.6	53.8
0.3	0.96	0.68	53.6	54.4
0.4	0.96	0.67	53.5	54.9
0.5	0.99	0.66	53.8	55.4
0.6	0.99	0.64	53.6	55.9
0.7	1.03	0.62	53.9	56.4
0.8	1.06	0.59	53.1	57.1
0.9	1.09	0.56	54.2	57.6
1.0	1.18	0.52	55.5	57.8

^a Total concentration of surfactant in the mixture is 10 mM for mixed surfactants. ^b Reference 22.

Note that the value of constant term (B_0) closely approximates $\ln C_1$ and ($B_1 + B_2$) is close to $\ln(C_1/C_2)$, where C_1 and C_2 are the cmc values for TX-100 and SDS, respectively. From eq 10, we infer that $\beta' = -1.24$, which is close to that obtained by Park et al.¹⁰ The value of β' as obtained by the present analysis, however, differs from the value obtained by Ruiz et. al ($\beta' = -3.3$) and our group ($\beta' = -3.9$). It appears that the B_2 parameters of the Maeda approach and β' of the regular solution theory are not exactly the same. The positive value of B_1 indicates that for the SDS-TX100 system the head group interaction is more important than the hydrocarbon chain interaction. It is supposed that the high charge density of the $-\text{O}-\text{SO}_3^-$ head group of SDS exerts a strong ion-dipole interaction with the polyoxyethylene (POE) moiety of TX100. The effect is more pronounced in the higher mole fraction region of SDS.

Kamlet-Taft Solvatochromic Parameters: Dipolarity/Polarizability (π^*) and Hydrogen-Bond-Donation Ability (α) of the Aggregates. The micellar phase values of (I_1/I_3) for pyrene emission and $E(F)$ for the ketocyanine dye for the SDS + TX-100 system have been listed in Table 3. The total concentration of the surfactants was kept at 10 mM. Values of α and π^* , as calculated by eqs 5 and 6, have been listed in Table 4. The π^* values obtained using pyrene are 0.52 and 0.72, respectively for SDS and TX100 homo-micelle (Table 4). However, the average values of π^* for SDS as reported by other workers using absorption probes is on the order of 1.0.^{25–28} It has been mentioned in our earlier communication that the difference in the value of π^* obtained using absorption probes may be due to the different locus of solubilization of absorption

**Figure 3.** Plots of (A) π^* and (B) α as a function of composition of SDS + TX100 mixture. The dotted line denotes the ideal line.

and fluorescence probes.²⁹ Our study indicates that convergent values of π^* are obtained by the fluorescence probe technique using pyrene and a series of structurally similar ketocyanine dyes.³⁰ The relatively high π^* value of TX-100 compared to that of SDS as obtained in the present case indicates that the dipolarity/polarizability of the TX-100 micellar phase is higher than in the case of the SDS micellar phase. The hydrogen-bond-donation parameter α has been found to be 1.18 for SDS in the present work. Again this value is in accordance with the results obtained in our previous study but differs from the values obtained by the other groups using absorption probes.^{25–28} The α value for TX100 (= 0.88) is close to that of the ethanol ($\alpha = 0.86$). The head group of TX-100 contains a phenyl group followed by a polyoxyethylene (POE) chain terminating to a hydroxyl group. Thus, the polar region is expected to resemble an alcohol environment. The increased HBD ability of the SDS micellar phase compared to that formed by TX-100 has been rationalized in terms of the presence of bound water molecules to a greater extent in the former case.²⁹

The values of α and π^* for the mixed SDS + TX-100 micellar phase as a function of composition of the mixture have been shown in Figure 3. The π^* value of mixed micellar aggregates decreases as the mole fraction of SDS in the surfactant mixture (x_{SDS}) increases. A reverse trend is obtained for the hydrogen-bond-donation (HBD) parameter (α). The decrease of the π^* value with an increase in the percentage of

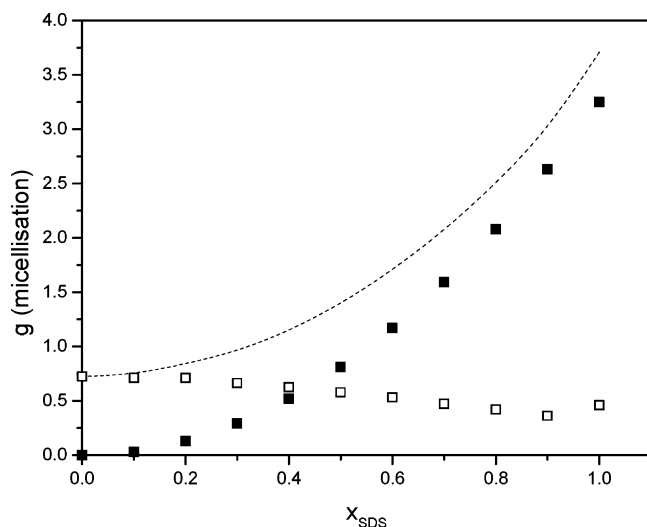


Figure 4. Plots of free energy of micellization as a function of composition of SDS/TX100 mixture. The steric (\square) and electrostatic (\blacksquare) contributions and the total value (—) have been shown.

SDS in the mixture is rational in the view of relatively smaller dipolarity/polarizability of SDS. Increase of the value of α with the addition of SDS can be explained as due to an increased percentage of the $-\text{O}-\text{SO}_3^-$ group and the counterion, Na^+ in the Gouy–Chapman layer of the mixed micelle. These in turn can bind more water molecules in the micellar region, and as such the HBD ability increases and higher α results. The rate of change of the solvatochromic parameters, however, is not uniform. The rate is relatively slow in the low-mole-fraction region of SDS (particularly up to $x_{\text{SDS}} \approx 0.5$) and is appreciable after $x_{\text{SDS}} \geq 0.5$. Thus, due to the addition of SDS in smaller proportions the nature of the micelle changes only very slowly. This characteristic has also been reported by Ruiz et al.²⁰ The enhanced rate of change of solvatochromic parameters (α and π^*) in the higher mole-fraction of SDS, however, indicates that on addition of TX-100 to SDS micelles the nature of the micelles changes rapidly. This behavior is also consistent with the observation that the aggregation properties, as revealed by cmc and x^{m} values, also change rapidly at the SDS richer range. Probably, the repulsive interaction between the ionic head groups in SDS plays a significant role. The nonlinear variation of solvatochromic parameters with surfactant concentration is indicative of the nonideal mixing behavior of the component surfactants in the micelles. In the event of ideal mixing of the components, the observed property at a particular composition would be given by the average of the properties in the two components weighted by the mole fraction of the components. The ideal lines showing a linear variation of the property over the entire mole-fraction range have been shown in Figure 4. In the present study, the deviation from the ideal behavior for both parameters (α and π^*) is maximum when $x_{\text{SDS}} \sim 0.6$. In a recent publication,²² we have determined the total aggregation number (N_{T}) and the individual number of surfactant monomers (N_i) in the mixed micelles formed by SDS + TX-100 using the steady-state fluorescence quenching (SSFQ) method. It has been found that for a total surfactant concentration much greater than the cmc the mole fraction of the i th surfactant in the micelle, as given by N_i/N_{T} , is almost equal to the average mole fraction. Thus, the deviation from ideal behavior arises due to interaction between the component surfactants. In fact, the negative value of the interaction parameter β for this mixed surfactant system points to the synergistic interaction between the components. The maximum deviation from ideality at $x_{\text{SDS}} \sim 0.6$ thus

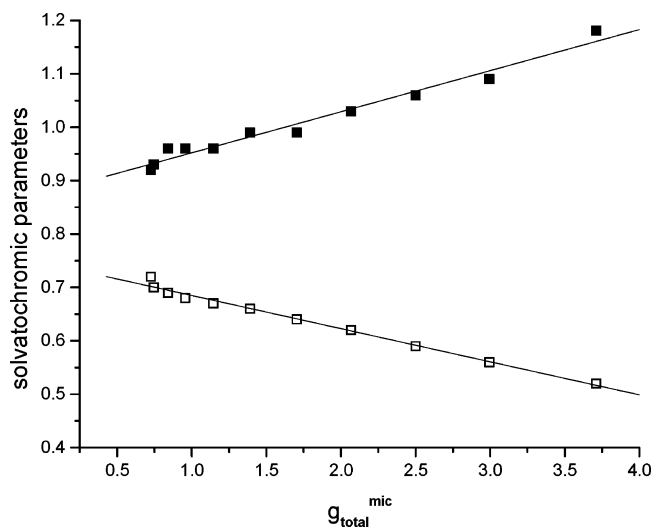


Figure 5. Plots showing variation of α (\blacksquare) and π^* (\square) values with $g_{\text{total}}^{\text{mic}}$ (total free energy of micellization) for mixed SDS + TX-100 surfactant system.

indicates that the interaction between the cosurfactants is maximum at this composition.

We have calculated the $E_{\text{T}}(30)$ parameter using the value of the obtained solvatochromic parameters. It is known that the $E_{\text{T}}(30)$ parameter is related to the hydrogen-bond donation ability (α) and dipolarity/polarizability (π^*) of a medium by the following empirical relation:²³

$$E_{\text{T}}(30) = 31.2 + 15.2\alpha + 11.5\pi^* \quad (12)$$

The calculated values of $E_{\text{T}}(30)$ can be compared with the experimentally determined value as obtained earlier.²² Table 3 lists the calculated and experimental values. Note that at the low mole-fraction range of SDS the calculated and experimental values are quite close. However, the agreement is not very good at higher SDS mole fractions. It may be pointed out in this context that the value of a solvent-sensitive parameter in a heterogeneous medium depends on the locus of solubilization of the probe. At TX-100 rich compositions, the locus of solubilization of the fluorescence probe (as used in the present study) and the absorption probe ($E_{\text{T}}(30)$ solute) is almost the same, whereas at higher SDS mole fractions the $E_{\text{T}}(30)$ probe is located at a somewhat more polar region.

Our results indicate that the variation of the polarity parameters is similar to that of the aggregation properties. To investigate this, we have calculated the contribution of the steric and electrostatic effects toward the free energy of micellization for the SDS + TX-100 system. According to the molecular thermodynamic approach of Blankshtein, the steric contribution to the free energy change per monomer, $g_{\text{steric}}^{\text{mic}}$, is given by¹⁸

$$g_{\text{steric}}^{\text{mic}} = -kT \left[x_1 \ln \left(1 - \frac{a_{\text{h1}}}{a} \right) + (1 - x_1) \ln \left(1 - \frac{a_{\text{h2}}}{a} \right) \right] \quad (13)$$

where x_1 is the mole fraction of surfactant 1 in the binary mixture, a_{h1} and a_{h2} are the average cross sectional area of head 1 and head 2, respectively, and a is the average area per surfactant molecule at the interface.

Estimation of the steric contribution has been done using a_{h1} (for SDS) = 25 \AA^2 and a_{h2} (for TX-100) = 60 \AA^2 .³⁹ Values of a , the average surface area per head group for mixed micelles,

were computed from the knowledge of that for the pure surfactants assuming the relation

$$a = a_1x_1 + a_2x_2 \quad (14)$$

For a pure homomicelle containing i th surfactant, the value a_i was calculated assuming the following relation for a spherical micelle of radius R containing N_i number of surfactant monomers.

$$a_i = \frac{4\pi R_i^2}{N_i} \quad (15)$$

The value of R for SDS and the TX-100 micelle was calculated using the relation given by Blankshtein.¹⁶ The electrostatic contribution to the free energy $g_{\text{el}}^{\text{mix}}$ for the SDS/TX-100 mixture was calculated for anionic + non-ionic surfactant mixture using the equation³⁹

$$g_{\text{el}}^{\text{mic}} = \alpha_i^2 \left[\frac{2\pi e^2 d}{4\pi\epsilon a_e} (1/(1 + \kappa l_c)) \right] \quad (16)$$

where l_c is the extended alkyl chain length, d is the capacitor thickness in the double layer model, a_e is the equilibrium area per molecule, and κ is the inverse Debye screening length. Calculations have been done using the value of the parameters used by Penfold et al.³⁹ Contributions of $g_{\text{ster}}^{\text{mix}}$ and $g_{\text{elec}}^{\text{mix}}$ toward the total free energy of micellization have been shown in Figure 4. Note that the variation of $g_{\text{total}}^{\text{mic}}$ is small in the range $0 \leq x_{\text{SDS}} \leq 0.4$. Beyond this range, however, the value increases rapidly with x_{SDS} . A similar variation has also been observed for the solvatochromic parameters. We have plotted the polarity parameters π^* and α versus the overall free energy of micellization (steric + electrostatic) as calculated above. Figure 5 shows the correlation. Note that the polarity parameters show excellent correlation with the free energy of micellization values. This indicates that the solvatochromic parameters describing micropolarity of the SDS + TX100 system is significantly dependent on the aggregational properties of the surfactant mixtures.

Conclusions

Polarity characteristics as determined by Kamlet–Taft solvatochromic parameters have been determined for the micellar system formed by mixed binary surfactants SDS + TX-100. The observed value of the parameters at a particular surfactant composition deviates from the mole fraction average of the property in the component surfactants. The aggregation and the polarity characteristics of the system run parallel. In the composition range $0 \leq x_{\text{SDS}} \leq 0.4$, these properties change slowly while a faster rate of change is observed for systems having composition beyond this range.

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