Influence of a Neutral Polymer (PVP) on the Solvatochromic Properties of SDS Micelles

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In the present work, we have studied the influence of a water-soluble neutral polymer (poly-*N*-vinyl pyrrolidin-2-one, PVP) on the Kamlet−Taft polarity parameters of sodium *n*-dodecyl sulfate (SDS) micelles. We have used pyrene as an independent dipolarity/polarizability (π^* parameter) descriptor molecule. It has been found that the addition of polymer (0.1 wt % PVP) increases the π^* value of SDS micelles, suggesting that PVP−SDS aggregates have a larger dipolarity/polarizability than that of SDS micelles. Linear solvation energy relationships involving the fluorescence transition energy of four structurally similar ketocyanine dyes have also been used to evaluate the polarity parameters. It is interesting to observe that the addition of polymer leads to a decrease in both the hydrogen-bond donation (α-parameter) and hydrogen-bond acceptance ability (β-parameter) of the micellar aggregate formed by PVP−SDS, whereas the dipolarity/polarizability value shows an increasing trend. Moreover, convergent results have been obtained for the π^* value for PVP−SDS aggregates, using pyrene as a π^* descriptor and ketocyanine dyes as molecular probes.

Introduction

Mixtures of water-soluble polymers and surfactants find numerous industrial applications. The interaction between single-tailed anionic surfactants and that of water-soluble uncharged polymers has been studied extensively over the years, and the field has been reviewed recently.[1,2] Particularly, the interaction between sodium *n*-dodecyl sulfate (SDS) and neutral polymer poly-*N*-vinyl pyrrolidin-2-one (PVP) has been studied widely.[3−6] The polymer PVP is used primarily, because of its efficiency in forming complexes with anionic surfactants, and, in that sense, it is the most efficient one. The extensive research on that field has been devoted primarily to explore the physiochemical aspects, about the probable microstructure of such complexes and the microenvironmental parameters of the aggregates. Mainly two types of experimental techniques have been used; one involves measurement of macroscopic properties (e.g., viscosity, conductivity, surface tension, etc.) and the other uses spectroscopic techniques that measure changes in the local environment surrounding an indicator molecule, often called a probe. Fluorescence spectroscopy has already been emerged as a sensitive tool for various heterogeneous media for obtaining information regarding the microenvironmental parameters (micropolarity, microviscosity, etc.).[2,6,7] The interaction of the probe molecule with its immediate environment ultimately modulates an observed parameter of such solute−solvent systems. It has been observed that the solvent influence on equilibrium, kinetic, and spectroscopic parameters[8] can be explained by postulating three independent modes of solute−solvent interaction—namely, dipolarity/polarizability, hydrogen-bond donation (HBD), and hydrogen-bond acceptance (HBA). They are conveniently represented, respectively, by the three parameters π^*, α, and β, as developed by Kamlet, Taft, and co-workers.[9] Successful attempts have been made recently by Vitha and co-workers[10,11] and Fuguet and co-workers,[12,13] to characterize solvation interaction in a micellar phase by the three parameters π^*, α, and β. Kim et al.[14] obtained the solvation parameters of aqueous poly(ethylene glycol) solutions. These workers have used different absorption probes to determine different solvatochromic parameters. A difficulty with the use of absorption probes is that a higher probe concentration, higher than that 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 to determine different parameters rests on the assumption that all indicator molecules probe the same region of the micelle. In a previous communication,[15] we have discussed a method for determining the π^*, α, and β values of the micellar phase provided by cationic, anionic, and neutral surfactants using the linear solvation energy relationships (LSER) approach. This method involves the use of a set of structurally similar fluorescence probes. Fluorescence probes are preferred over an absorption probe, because they are sensitive at low concentrations and they do not perturb the micellar structure. In the present communication, we have extended our previous study to a polymer−surfactant system to reveal the influence of polymer on the solvation properties of micelles. Although the PVP−SDS system is widely studied, no work has been done as yet to explore the polarity of the system as expressed by the solvatochromic Kamlet−Taft parameters. The solvent-sensitive transition energy of four ketocyanine dyes (Figure 1) has been analyzed to get information regarding the polarity of the system. Besides these fluorescence probes, we have used the I_1/I_3 intensity ratio of the fluorescence band of pyrene as an independent descriptor of the π^* value of the microheterogeneous system, as proposed by Dong and Winnik.[16]

Theoretical Background

Linear Solvation Energy Relationship. It is customary to write any property linearly related to the free energy of a system

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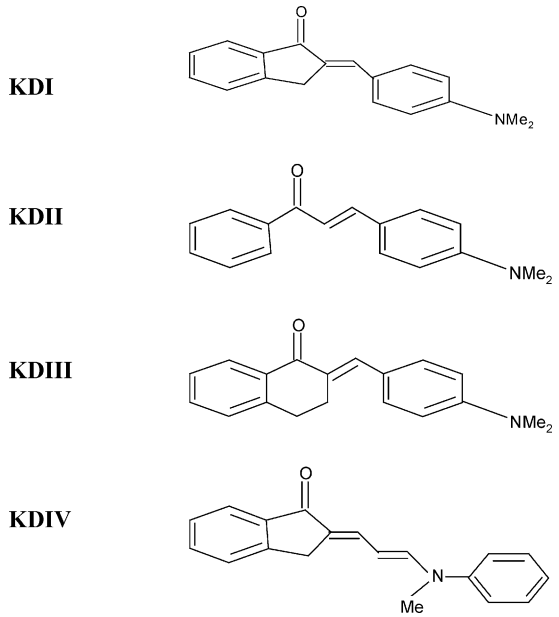

Figure 1. Ketocyanine dyes used in this work.

(*XYZ*) in terms of LSER, using the following equation:[9,17,18]

$$XYZ = XYZ_0 + \text{cavity term} + \sum(\text{solute} - \text{solvent interaction energy}) \quad (1)$$

The term XYZ_0 denotes a constant and is dependent solely on the solute. The cavity term includes the cavity formation energy and solvent−solvent interaction energy and is related to the tightness or structuredness of solvents. Summation in the solute−solvent interaction energy term in the above equation extends over all the possible modes of solute−solvent interaction.[19,20] Using the Kamlet−Taft version of LSER, we can write

$$XYZ = XYZ_0 + m\delta_H^2 + p\pi^* + a\alpha + b\beta \quad (2)$$

In this equation, the cavity term is written in terms of the Hildebrand solubility parameter (δ_H^2) of the solvent.[21] The solute−solvent interaction is written in terms of nonspecific (π^*) and specific (α and β) interaction parameters. The coefficients *m*, *p*, *a*, and *b* represent the relative contributions of δ_H^2, π^*, α, and β toward the *XYZ* property. Because entropy does not change during a spectroscopic transition,[22] the transition energy can be regarded as being 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 disappears.[23] Thus, one can write the maximum energy of transition (*E*) of the solute−solvent (s−i) system, as follows:

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

The coefficients *p*(s), *a*(s), and *b*(s) are dependent on the solute and are related to the dipolarity/polarizability, HBA, and HBD ability of the solute, respectively.[23] It has been observed that the energy of maximum fluorescence of the ketocyanine dyes conform to eq 3. Ketocyanine dyes provide interesting series of solutes, which are characterized by solvatochromic fluorescence.[24,25] The spectroscopic transition leading to the fluorescence in these molecules has been established as being due to an intramolecular charge transfer (ICT) involving the carbonyl O and N atoms of the amino group.[24,25] We have studied the solvatochromic fluorescence energy of the ketocyanine dyes extensively in various pure solvents.[26,27] Multiple linear regression analysis (MLRA) of the maximum fluorescence energy in pure solvents have been performed with the solvent parameters π^*, α, and β to obtain the *p*, *a*, and *b* coefficients for the solutes. One can use the equation to analyze the solvent-sensitive transition energy of a series of structurally similar solutes, namely the ketocyanine dyes, in a fixed solvent (medium). The LSER approach in this form has been applied for a particular aqueous micellar system, using various solutes to explain the chromatographic retention factor of solutes and the partition of solutes between aqueous and micellar phases.[28,29] Thus, with the known solute parameters *p*, *a*, and *b*, as obtained from studies in pure solvents, values of π^*, α, and β for another medium can be obtained by a MLRA.

Two-Phase Equilibrium and Separation of Properties. Beyond a certain concentration, called the critical micellization concentration (CMC), the surfactant monomer molecules start to form aggregates (micelles). Micellization is essentially a dynamic process involving an equilibrium between the aqueous phase (composed of surfactant monomers) and the micellar pseudo phases, represented as

$$\text{aqueous phase} \rightleftharpoons \text{micellar phase} \quad (4)$$

Any property of an indicator solute that has dependence on its local environment can be used to reveal the equilibrium process. Polarity-dependent spectroscopic parameters of suitable probe molecules are widely used for this purpose. The ratio of emission intensity of the first to third vibronic bands of pyrene (I_1/I_3) has extreme sensitivity to its local polarity,[30] and this property is now widely used to explore different microheterogeneous media.[7] Similarly, the transition energy (*E*) of some solvatochromic probes can also be used. Under the conditions that the two phases exist in equilibrium, the indicator molecules will be distributed between the aqueous and micellar phases. Any spectroscopic parameter of the probe for such a system will be determined by the time-average location of the probe in the system.[6] Thus, an observed parameter (*X*) is assumed be given by an average of the properties in the two phases, weighted by the concentration of the solute in the two phases:

$$X = \frac{n_m X_m + n_{aq} X_{aq}}{n_m + n_{aq}} \quad (5)$$

where *n* refers to the number of moles and the subscripts "m" and "aq" denote the micellar and aqueous phase, respectively. To obtain the value of X_m and X_{aq} from eq 5, one requires knowledge of n_m and n_{aq}, which, in turn, are related to the partition coefficient of the solute between the two phases. Very recently, Fuguet and co-workers[12,13] proposed a method for separating the observed parameters into the properties of corresponding two pure phases using a partition-coefficient-based analysis. We have also used the method to obtain the parameters for the two pure phases.[15] Values of n_m and n_{aq} are related to the molar-based partition coefficient (*P*) of the solute distributed between the micellar and aqueous phases, via the following relation:

$$\frac{n_m}{n_{aq}} = \frac{PV_m}{V_{aq}} = \frac{P\upsilon C_S}{1 - \upsilon C_S} \quad (6)$$

where V_m and V_{aq} are the volumes of micellar and aqueous phases, respectively, υ is the molar volume of surfactant, and $C_S = C_{Total} - CMC$.

Using eqs 5 and 6 and then rearranging, one can obtain the following relation:

$$X = X_{aq} + [P\upsilon X_m - \upsilon X_{aq}]C_S - [P\upsilon - \upsilon]XC_S \qquad (7)$$

MLRA involving X, C_S, and XC_S will allow one to obtain X_{aq}, X_m, and P for the system, using a value of $\upsilon = 0.246$ l mol^{-1} for SDS.[31] Thus, using the above method, one can separate the spectroscopic parameters for the two phases.

Experimental Section

Chemicals. The ketocyanine dyes were synthesized by methods described in the literature.[26,27]

Pyrene was obtained from Aldrich at 99% purity and was used as received. The surfactant SDS (SIGMA) was purified by repeated crystallization from ethanol. The neutral polymer PVP (Aldrich) of >99% purity with an average molecular mass of ca. 29 000 was used as received.

Solution Preparations. Solutions for UV/Vis 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 of this stock solution was introduced in a volumetric flask and spread over the flask, and then the solvent was evaporated under gentle heating. Five milliliters of the surfactant solution then was added to the flask, and the solution was sonicated for ~1 h. The resulting clear solution was then directly taken into the spectrophotometer cuvette.[2] Concentrations of the ketocyanine dye solutions were in the range of $10^{-5}-10^{-6}$ M. The water used for the solution preparation was triply distilled. In case of pyrene, a similar procedure has been adopted and the final concentration of pyrene in solution was maintained at $\sim 10^{-7}$ M. The concentration of PVP in all solutions was kept fixed at 0.1 wt % for the PVP−SDS system.

UV/Vis Spectroscopic Measurements. Fluorimetric measurements were performed on a Hitachi model F-4500 spectrofluorimeter that had been 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). Samples were allowed to equilibrate at that temperature by keeping it in the thermostated sample compartment for 10 min before collection of the spectra. Excitations were performed at the wavelengths of maximum absorption for the ketocyanine dyes. For pyrene, an excitation wavelength of $\lambda = 338$ nm has been used. Several replicate measurements were performed for a particular solution, and the mean of the maximum wavelength values or I_1/I_3 ratios (in the case of pyrene) were taken.

Results and Discussions

Pure SDS System. Figure 2 shows the variation of the I_1/I_3 ratio of pyrene, as function of the SDS concentration. Two different regions are evident from the plot. At very low SDS concentration, the I_1/I_3 ratio is high (~1.7), which then decreases sharply as the SDS concentration increases, which indicates the formation of micelles. The I_1/I_3 ratio then becomes low (~1.18), and it practically remains constant with further additions of surfactant. A low I_1/I_3 value indicates that pyrene molecules are solubilized within the hydrophobic domain of the micelles formed. The dotted line in the plot indicates the CMC for the surfactant, the value of which has been determined to be ~8.1 mM, which is very much in agreement with earlier studies.[32] Using eq 7 and applying MLRA, we have separated the I_1/I_3 values for the two phases. Values of the parameters

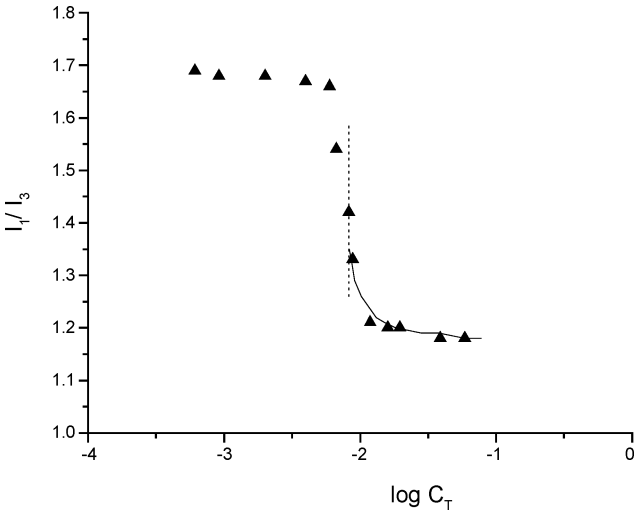

Figure 2. Plot of I_1/I_3 ratio for pyrene as a function of log C_T of SDS in the absence of polymer; the continuous line represents the best-fit curve according to eq 7 using the values given in Table 1 (entry A), and the dotted vertical line indicates the critical micellization concentration (CMC).

along the fitting statistics are given in Table 1. The calculated curve using the best-fit parameters in the c(SDS) range above CMC has been shown in Figure 2. In absence of any polymer, we obtained I_1/I_3 values of 1.37 and 1.18 for the aqueous phase and the SDS micellar phase, respectively. The molar-based partition coefficient, which represents the distribution of pyrene in the two phases, has been determined to be high (~2800). The value of I_1/I_3 for the micellar phase is in agreement with that obtained by others.[4,6] The lower value of the I_1/I_3 ratio found for the micellar phase, as compared to the corresponding aqueous phase, indicates that pyrene molecules are solubilized within the hydrophobic microdomain of the micelles. Because the I_1/I_3 ratio of pyrene has an extreme sensitivity on the local polarity of a medium, it is expected that the ratio should have some correlation with the Kamlet−Taft solvatochromic parameters (α, β, and π^*), which are the main descriptors of the polarity of the medium. For pyrene, being a nonpolar polyaromatic hydrocarbon, the favorable mode of interaction with its local medium is the dipolarity/polarizability mode. Dong and Winnik[16] have observed that the I_1/I_3 ratio of pyrene has an excellent correlation with the π^* parameter for bulk liquids. They noted that the nature of correlation is dependent on the type of liquids. For protic aliphatic solvents, the following correlation equation has been found:[16]

$$\frac{I_1}{I_3} = 0.46 + 1.304\pi^* \qquad (\text{for } n = 9,\ r = 0.982,\ \text{sd} = 0.28) \qquad (8)$$

We have chosen this correlation equation involving protic aliphatic liquids because this class of solvents closely resembles the Stern layer of aqueous micelles. Using the above equation, one obtains the π^* parameter for the micellar phase to be 0.55. Interestingly, this π^* value is in very good agreement with the value obtained from our previous study on SDS micelles involving different fluorescence probes ($\pi^* = 0.52$).[15] The larger value of the I_1/I_3 ratio found for the aqueous phase indicates a greater π^* value than that of the micellar phase. It is intelligible from the fact that, in aqueous phase, which contains water and surfactant monomers, the pyrene molecules are more exposed to water molecules, sensing a hydrophilic environment, whereas in micellar phases, it experiences an average hydrophobic environment of the micellar aggregate.

TABLE 1: Best-Fit Values of the Molar-Based Partition Coefficient (P) and the I_1/I_3 Ratio for Pyrene in Aqueous SDS and SDS−PVP Systems

system[a]	I_1/I_3 ratio: aqueous phase	I_1/I_3 ratio: PVP−SDS phase	I_1/I_3 ratio: micellar phase	log P	correlation coefficient, R^2	standard deviation, sd
(A) SDS in the absence of PVP	1.37		1.18	3.45	0.92	0.09
(B) SDS in the presence of 0.1% PVP						
A ⇌ PS	1.58	1.51		3.43	0.97	0.001
PS ⇌ M		1.51	1.24	2.85	0.92	0.032

[a] A ≡ aqueous phase, PS ≡ PVP−SDS phase, and M ≡ free SDS micelle.

PVP−SDS System. The aggregational behavior of SDS has been observed to be modified dramatically in the presence of neutral water-soluble polymers such as PVP. Earlier studies by Turro et al.[6] suggest that the PVP−SDS system is characterized by three distinct regions in solution, depending on the concentration of SDS. Below a certain concentration of SDS (region I), the system is mainly composed of polymer and SDS monomers in the aqueous phase. No measurable interaction is observed between polymer and SDS in this region. For c(SDS) $> c_1$, the polymer starts to interact with SDS cooperatively and polymer-surfactant aggregates are formed. (The concentration c_1 is the critical aggregation concentration (CAC) of SDS for that particular polymer.) The association process ceases when all the polymers become saturated. This happens when the concentration of SDS reaches a particular concentration, c_2, which is often called the polymer saturation point (PSP). The concentration range between c_1 and c_2 has been denoted as region II. This region is mainly composed of polymer-surfactant aggregates. Beyond this concentration of SDS (region III), free SDS micelles begin to form, and they are in equilibrium with polymer-surfactant aggregates. Thus, the polymer-induced surfactant aggregation can be written schematically by the following equilibrium processes:

$$\underset{\text{(region I)}}{\text{aqueous phase of PVP + SDS monomer}} \rightleftharpoons \underset{\text{(region II)}}{\text{PVP−SDS aggregates}} \rightleftharpoons \underset{\text{(region III)}}{\text{free SDS micelles}} \quad (9)$$

The experimental curve of I_1/I_3 vs c(SDS) in the presence of 0.1 wt % PVP, as given in Figure 3, also shows three such regions. Values of c_1 and c_2 have been estimated as 0.0015 and 0.0065 M, respectively. Turro and co-workers[6] observed that c_1 and c_2 hardly depend on the polymer concentration, at least in the lower concentration range of PVP. In a concentration range of c(SDS) (0−0.006 M), one can assume that only the first equilibrium in expression 9 prevails. Using eq 7 for the data set in the range of c_1 and c_2, one can obtain the spectroscopic parameters separately for region I and region II. It will also allow us to obtain the partition coefficient (P_1) value for the probe molecule between the two phases. On the other hand, for c(SDS) in the range of 0.007−0.080 M, the second equilibrium in expression 9 may be assumed to exist. Using the same methodology, one can find the spectroscopic parameters (I_1/I_3) for the probe molecule solubilized in PVP−SDS aggregates and free SDS micelles, along with the corresponding partition coefficient (P_2). Results have been given in Table 1. The calculated curves using the best-fit parameters have been shown in Figure 3. Thus we have obtained the I_1/I_3 ratio for the three regions as 1.58, 1.51, and 1.24, respectively. The best-fit values of I_1/I_3 for the aqueous region (e.g., 1.37 for a solution containing SDS monomers and 1.58 for a solution containing SDS monomers and PVP) are much different than the experimental values in pure water or water containing PVP, respectively. However, the values attributed to region II ($I_1/I_3 = 1.51$) agree when they are calculated independently from experimental points in regions II and III. Perhaps the MLRA approach as performed using eq 7 works only when the micelles are well-formed. Some workers have used a sigmoid fit to describe appropriately the entire concentration (C_T) region.[33,34] The partition coefficient value for the first equilibrium process is almost four times greater than that of the second equilibrium; however, it is of the same order of the partition coefficient value for the micellization process in the absence of polymers. From the correlation in eq 8, we have obtained a π^* value of 0.80 for the PVP−SDS aggregates. For free SDS micelles, the π^* value has been determined to be 0.60, which is slightly greater than the corresponding value in the absence of polymers. This slight modification can be expected as polymers are present in the environment. It is interesting to note that polymer-surfactant aggregates have a larger π^* value than that of pure SDS micelles. It is a known fact that polymer-surfactant aggregates have a much lower aggregation number (∼30) than that of pure SDS micelles (∼60).[35] For smaller micelles, the extent of water penetration is expected to be greater, so that the π^*-determining probe (pyrene) is exposed to the water molecules present in the stern layer of the micelles, thus sensing a more hydrophilic environment.

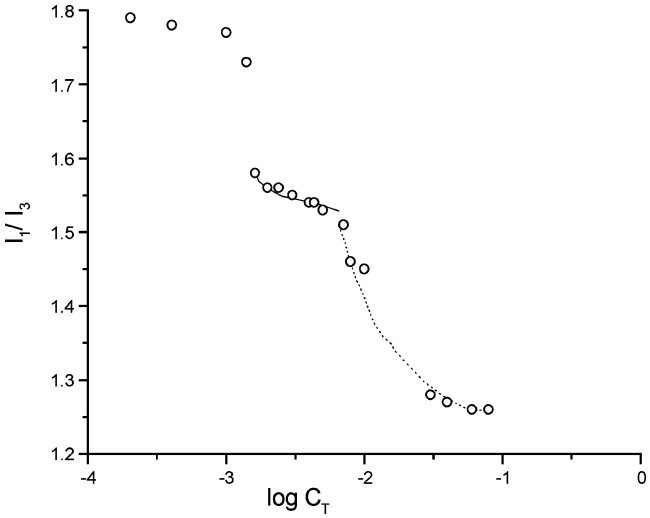

Figure 3. Plot of the I_1/I_3 ratio for pyrene as a function of log C_T of SDS in the presence of 0.1 wt % PVP polymer; the continuous and dotted lines represent, respectively, the best-fit curves of eq 7, using values for the equilibria A ⇌ PS and PS ⇌ M, as given in Table 1 (entry B).

Dipolarity (π^*), Hydrogen-Bond Donation (α), and Hydrogen-Bond Acceptance (β) for Polymer-Surfactant Aggregates. The polarity-dependent fluorescence parameter—namely, the energy of fluorescence (E)—of the four ketocyanine dyes has been used to characterize the solvation parameters for the polymer-surfactant system. Figure 4a shows a representative plot of the E value of a ketocynanine dye versus c(SDS) in the

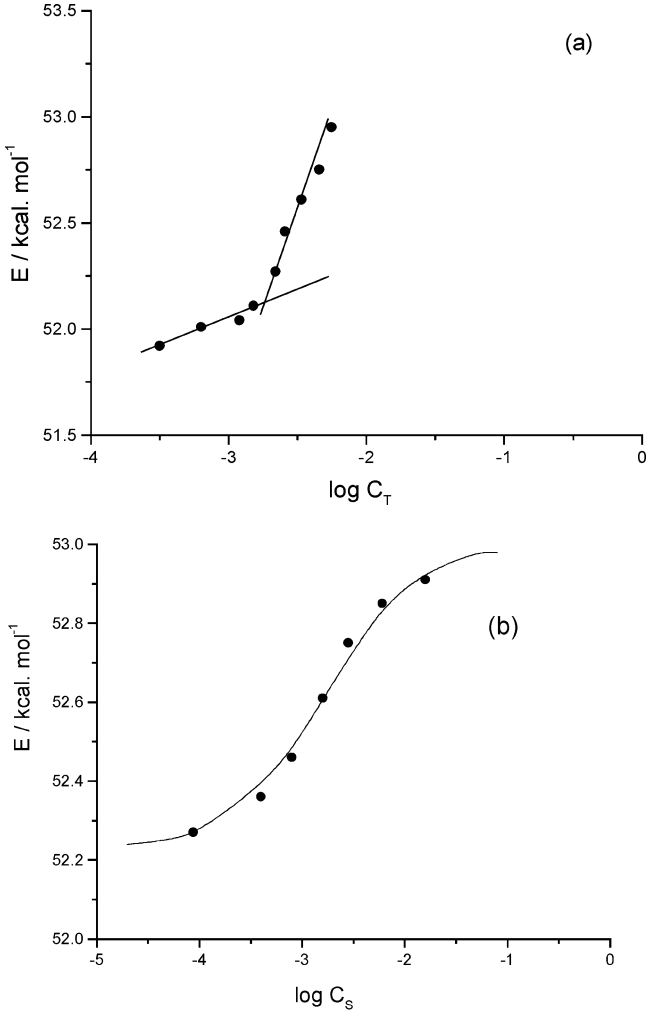

Figure 4. (a) Representative plot of E vs log C_T of SDS for indicator solute KD I in the presence of 0.1 wt % PVP. (b) Representative plot of E vs log C_S of SDS for KD I in the presence of 0.1 wt % PVP; the continuous line represents the best-fit curve using the values given in Table 2.

TABLE 2: Best-Fit Values of the Molar-Based Partition Coefficient (*P*) and Transition Energy (*E*) for the Ketocyanine Dyes in the Aqueous and PVP−SDS Aggregates for the PVP−SDS System

	E (kcal/mol)				
indicator solute	aqueous phase	PVP−SDS aggregates	log *P*	correlation coefficient, R^2	standard deviation
KD I	52.23	53.00 (52.46)	3.4	0.97	0.035
KD II	53.09	54.52 (52.95)	2.3	0.96	0.036
KD III	52.89	53.35 (52.32)	2.7	0.97	0.032
KD IV	55.12	55.81 (55.69)	2.8	0.97	0.032

[a] Entries within bracket correspond to the values in pure SDS micelles.[15]

presence of 0.1 wt % PVP. A change in slope is observed at [SDS] ≈ 1.9 mM. However, the polymer saturation point is not very much evident. Within the *c*(SDS) range of 2−6 mM, only the first equilibrium of expression 9 prevails. Using MLRA, we can obtain the E values for the two phases, namely, the aqueous and PVP−SDS aggregates and the corresponding partition coefficients. Table 2 summarizes all such parameters, including the fitting statistics. The calculated E vs log *c*(SDS) curve, using the best-fit parameters, has been shown in Figure 4b. The values within the bracket denote the corresponding values for the pure SDS micellar phase in the absence of any

TABLE 3: Solute Properties[a]

indicator solute	E_0(s)	*a*(s)	b(s)	*p*(s)	correlation coefficient, R^2	number of solvents, *n*
KD I	64.50	−3.24	−4.57	−9.19	0.97	22
KD II	64.30	−3.05	−3.71	−9.36	0.96	24
KD III	64.30	−3.60	−5.50	−8.50	0.98	22
KD IV	63.81	−2.62	−2.08	−4.30	0.98	22

polymer. For all four indicator molecules, it has been noted that the transition energy for a particular dye is higher for PVP−SDS aggregates than that for the pure SDS micellar phase. The experimental studies on PVP−SDS systems in water reveal that the interaction is hydrophobic in nature, involving the C atom closer to the polar headgroup in SDS and the C atoms of the polymer backbone.[36] Regarding the probable structure of aggregates, a "necklace and bead" model has been proposed.[2] However, two probable structures may be distinguished, viz, one in which the aggregate of surfactant molecules wrap around the hydrophobic sites of the polymer, and the other where the polymer wraps around the surfactant headgroups. For a ketocyanine dye, the E value increases as one goes to a nonpolar environment.[26,27] Thus, the increase in transition energy for the probe upon the addition of polymer supports the latter model. It may be mentioned that a similar structure for the PVP−SDS aggregates has been indicated by steady-state and time-resolved emission studies.[37] To obtain information regarding the polarity of the microenvironment of PVP−SDS aggregates, E values obtained for the PVP− SDS system have been used for LSER analysis. The difference in energy (E) of the two phases, according to LSER, can be written in the form of the following equation:

$$[E_{PVP-SDS}(s) - E_{SDS}(s)] = a(s)\,[\alpha_{PVP-SDS} - \alpha_{SDS}] + b(s)\,[\beta_{PVP-SDS} - \beta_{SDS}] + p(s)\,[\pi^*_{PVP-SDS} - \pi^*_{SDS}] = a(s)\Delta\alpha + b(s)\Delta\beta + p(s)\Delta\pi^* \quad (10)$$

Values of *a*(s), *b*(s), and *p*(s) for the four solutes, as determined from studies in pure solvents, have been listed in Table 3. Values of $\Delta\alpha$, $\Delta\beta$, and $\Delta\pi^*$ that gives the best correlation in the least-squares sense of $[E_{PVP-SDS}(s) - E_{SDS}(s)]$ with *a*(s), *b*(s), and *p*(s) for the four solutes were then determined. The values obtained are as follows: $\Delta\alpha = -0.31$, $\Delta\beta = -0.06$, and $\Delta\pi^* = 0.26$. From the negative sign of both $\Delta\alpha$ and $\Delta\beta$, it appears that the polymer-surfactant aggregated complex has a lower HBD and HBA ability than the pure SDS micellar phase. However, the polymer-surfactant complex is more dipolar in character than the SDS micellar phase. The value of $\Delta\pi^*$ obtained using ketocyanine dyes can be compared with that obtained from using another probe. As discussed earlier, pyrene acts as an independent $\Delta\pi^*$ descriptor. Note that the values of $\Delta\pi^*$, as obtained using the method described earlier using pyrene, are 0.55 and 0.80 for SDS micelles and PVP−SDS aggregates, respectively. Thus, the quantitative increase in $\Delta\pi^*$ due to the presence of PVP is almost the same, whether one uses pyrene ($\Delta\pi^* = 0.25$) or ketocyanine dyes ($\Delta\pi^* = 0.26$) as indicator molecules. Convergent results for $\Delta\pi^*$ can thus be obtained using different types of indicator molecules. We have also measured the $E_T(30)$ value of the polymer-surfactant system (region II). The probe is very slightly soluble in the appropriate concentration range of SDS; therefore, we could locate a broad band with a maximum at ∼505 nm, corresponding to a value of $E_T(30) = 56.6 \pm 0.2$ kcal/mol. The experimentally determined value for SDS micelles[15] is 58.2 ± 0.2 kcal/mol. Thus, $\Delta E_T(30) = -1.6$ kcal/mol. The $E_T(30)$ values are dependent

on the solvatochromic parameters as follows.[38]

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

Using the values of $\Delta\alpha$ and $\Delta\pi^*$, as obtained using ketocyanine probes, $\Delta E_T(30)$ becomes -1.72 kcal/mol. Thus, the values are in modest agreement.

Conclusions

(1) The I_1/I_3 ratio of pyrene has been used as a π^* descriptor for micelles and polymer-surfactant aggregates. It has been observed that the neutral polymer poly-*N*-vinyl pyrrolidin-2-one (PVP) increases the π^* value of the sodium *n*-dodecyl sulfate (SDS) micellar phase.

(2) Using four structurally similar fluorescent ketocyanine dyes as indicator solutes and developing a linear solvation energy relationships (LSER)-based technique, we have measured the variation of the Kamlet−Taft polarity parameters of SDS micelles in the presence of the polymer PVP.

(3) It has been found that PVP−SDS aggregates have higher dipolarity/polarizability values than the SDS micellar phase, but the hydrogen-bond donation (HBD) and hydrogen-bond acceptance (HBA) abilities of such aggregates have been determined to be lower than that of the SDS micellar phase.

(4) Convergent results have been obtained for the π^* value for PVP−SDS aggregates using pyrene as a π^* descriptor and ketocyanine dyes as molecular probes.

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