A Critical Assessment of Micellization of Sodium Dodecyl Benzene Sulfonate (SDBS) and Its Interaction with Poly(vinyl pyrrolidone) and Hydrophobically Modified Polymers, JR 400 and LM 200

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The self-aggregation of sodium dodecyl benzene sulfonate (SDBS) and its solution behaviors have been critically assessed by conductometric, tensiometric, spectrophotometric, flourimetric, and calorimetric methods. The interfacial adsorption behaviors of SDBS have also been assessed critically. Based on the isothermal titration calorimetric (ITC) measurements, the thermodynamics of micellization of SDBS have been examined in the light of both "mass action" and "pseudophase" principles. A method of simulation has been used to evaluate the aggregation number and the free energy of micellization according to the mass action model. The thermodynamic parameters derived indirectly from the rationale of van't Hoff and directly by microcalorimetry have been compared and discussed. The interaction of SDBS with the water-soluble polymers poly(vinyl pyrrolidone) (PVP), the chloride salt of the *N,N*-dimethyl-*N*-methyl derivative of hydroxyethyl-cellulose (JR 400), and the chloride salt of the *N,N*-dimethyl-*N*-dodecyl derivative of hydroxyethylcellulose (LM 200) have been also investigated by the conductometric and microcalorimetric methods. The critical aggregation concentration (cac) and the thermodynamics of binding of the aggregates with the polymer segments, as well as the thermodynamics of formation of free micelles in solution, in the presence of PVP, JR 400, and LM 200 have been quantitatively assessed.

Introduction

The self-aggregation of surfactants after the critical micellar concentration (cmc) is an important solution property that needs evaluation for understanding the existence of micelles in solution, as well as evaluating the thermodynamics of the process essential for characterization and comparison in terms of spontaneity and stability.[1−4] The determination of thermodynamic parameters for the nonionic surfactants through the cmc is less complex compared to the ionic surfactants owing to the binding of counterions to the charged micelles in the latter. In this connection, it may be stated that although direct determination of the enthalpy of micellization can be made in a calorimeter, such determinations are not abundant and the enthalpy estimated by the van't Hoff method often does not agree with the calorimetric enthalpy.[5,6] Further, the energetic parameters are not always evaluated on the basis of a single standard state; the results are, therefore, not comparable.

In the old literature, the counterion binding of the ionic micelles was not considered; the choice of the standard state was also not consistent.[7,8] In the current literature, the role of the counterion binding has been recognized and the mole fractional scale has been used in the evaluation of the energetics of the process.[9] But the effect of the temperature on the aggregation number and the shape of the micelle in relation to the energetics have not been reasonably addressed. The cmc's

are usually measured by tensiometric, conductometric, fluorimetric, light scattering, and calorimetric methods. In the calorimetric method, both the cmc and the enthalpy are obtained from a single run, and it is, therefore, very convenient.[10,11] In recent years, the availability of a highly sensitive microcalorimeter has made the determination accurate and authentic.[12−14] This gives a scope to compare the van't Hoff enthalpy with the calorimetric enthalpy. Such studies on the thermodynamics of micellization of ionic and nonionic surfactants have been very recently done.[9,15]

Neutral polymers are known to interact with both anionic and cationic surfactants frequently showing characteristic features of polymer-induced self-aggregation at a critical concentration called the cac (critical aggregation concentration), which is lower than the critical micellar concentration (cmc). In recent years, much attention has been given to this field for its relevance to the processing of food materials, fabric treatment, pharmaceutical preparations (particularly skin and body care products), protein extraction from cell membrane, enhanced oil recovery, transfection and gene delivery, and other surface chemistry-related applications. Basic research in this area thus has importance and is in progress.

The surfactant sodium dodecyl benzene sulfonate (SDBS) is used in chemical, biochemical, and industrial works, and it is an effective surface-active compound. It can conveniently interact with neutral and cationic polymers forming solutions of different consistencies. It has antifungal properties and has a low cost of production. So far, the solution properties of this surfactant have not been critically examined although several reports are available in the literature.[16,17] While the reports on

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the interaction of sodium dodecyl sulfate with polymers are considerable,[18,19] that with SDBS is rare. These considerations have prompted us to make elaborate and critical study of the micellization and interfacial properties of SDBS and its interaction with neutral and cationic polymers. The micellization process has been assessed by the methods of tensiometry, conductometry, fluorometry, dye solubilization, spectrophotometry, and calorimetry. The critical micellar concentration (cmc), counterion binding, micellar aggregation number, interfacial adsorption of SDBS, area occupied by the headgroup of the molecule, etc. have been also determined. The thermodynamics of micellization on the basis of both mass action and pseudophase models have been estimated by the direct calorimetric method and indirect van't Hoff procedure, and the results are critically compared. The enthalpy of micellization obtained by the above two procedures may or may not agree; a critical assessment of this fact has so far remained unattended until recently.[5,6,20,21] We have extended the analysis taking SDBS as a typical case. In addition to this, microcalorimetric and conductometric method of evaluation of the interaction of SDBS with the neutral polymer poly(vinyl pyrrolidone) (PVP, a potent substituent for albumin in blood) has been undertaken, along with the hydrophobically modified cationic polymers JR 400 and LM 200. Such studies are relevant from the stand point of preparation of cosmetics and body care products, on one hand, and enhanced oil recovery, on the other, in which flooding of surfactants and polymer solutions is required for effective solubilization and mobilization of entrapped oil in the cracks and pores in the underground rocks.

Experimental Section

Materials. The surfactant sodium dodecyl benzene sulfonate (SDBS) was a >97% pure compound of Aldrich and was used as received. The polymer PVP of viscosity-average molecular weight 40 000 was a product of Sigma. Hydrophobically modified polymers JR 400 and LM 200 of molecular weights 400 000 and 120 000 Da, respectively, were products of Amerchol Inc. (Edison, NJ). Pinacyanol chloride (1,1′-diethyl-2,2′-carbocyamine chloride) was a product of John and Baker Inc. (Phillipsburg, NJ). The pyrene and cetyl pyridinium chloride were AR grade products of Aldrich. Doubly distilled water was used in all preparations.

Methods. In the conductance method, concentrated solution of a surfactant was added in installments with a Hamilton microsyringe in water (or polymer solution) placed in a wide mouth test tube fitted with a dip-type conductivity cell of cell constant 1 cm^{-1}, the assembly being immersed in a constant temperature water bath of accuracy ±0.01 °C. After each addition, conductance of the solution was measured (after thorough mixing and temperature equilibration) with a Jenway (U.K.) conductometer. The measurements were duplicated and had accuracy of ±2%.

The surface tension of the SDBS solution was measured with a Krüss (Germany) tensiometer by the platinum ring detachment method after appropriate calibration.[22,23] Here also concentrated surfactant solution was added in installments by a Hamilton microsyringe in water taken in the working container placed in the water bath, and measurements were taken after mixing and temperature equilibration. Duplicate measurements were taken to check the reproducibility. The accuracy of measurements was within ±0.1 dyn.

The UV−visible spectrophotometric measurements were taken in a Shimadzu UV-160A (Japan) spectrophotometer using 1 cm silica cuvettes. The spectral measurements of both pyrene
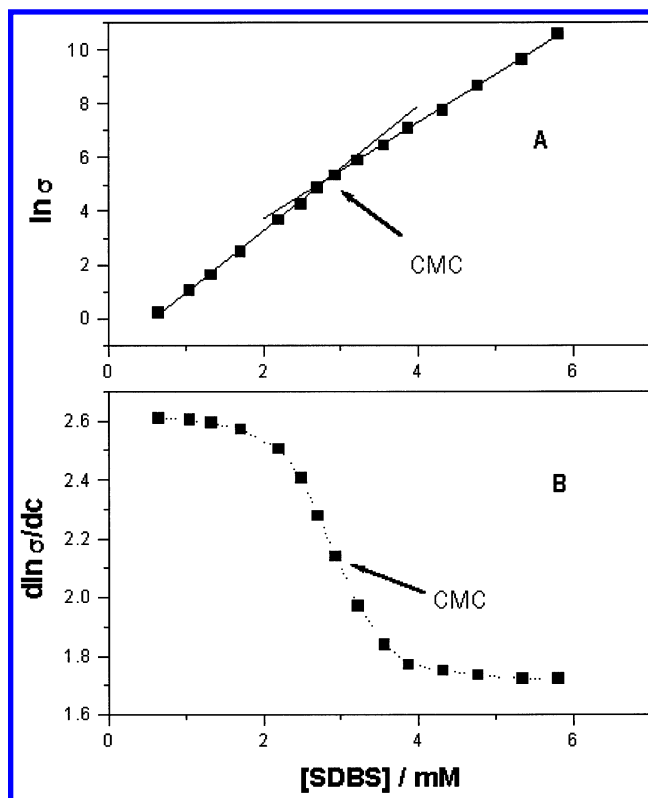

Figure 1. Conductometric evaluation of cmc of SDBS in water at 293 K: (A) conductance vs [SDBS]; (B) differential conductance vs [SDBS]. Dotted line represents the SBE fitting of differential conductance.

and pinacyanol chloride solutions in different concentrations of SDBS at controlled thermostated conditions were taken. The absorbances at the peak wavelengths were processed to determine the micellization points.

The microcalorimetric measurements were taken in an OMEGA ITC microcalorimeter of Microcal Inc. (Northampton, MA). Aliquots of a concentrated surfactant solution of volume 10 μL were added in several installments in 1.325 mL of water or polymer solution taken in the cell, and the heat flow for the dilution was measured.[9,12,18] The addition of surfactant solution and the measurements of the heat were done as programmed. The data treatment was performed with the help of Microcal Origin software. The measurements were also duplicated and taken in the temperature range of 288−323 K.

The steady-state quenching measurements of pyrene (10 μmol dm^{-3}) fluorescence (excitation at 335 nm and emission at 373 and 383 nm) by cetyl pyridinium chloride were taken in a Perkin-Elmer LS 55 fluorometer at 298 K to estimate the aggregation number of SDBS micelle at concentrations appreciably above cmc.[15,24] The probe and the quencher are considered to undergo interaction forming a complex. The ratio of the intensities of the first and the third vibronic peaks, I_1 and I_3, respectively of the fluorescence spectra of pyrene in the absence of quencher was used to detect the polarity of the micelle-forming system. The inflection point in the plot of I_1/I_3 vs [SDBS] corresponds to the cmc of the surfactant.[24,25]

Results and Discussion

Critical Micellar Concentration (CMC). The cmc of SDBS has been determined by the conductometric, tensiometric, fluorometric, spectrophotometric, and microcalorimetric methods at different temperatures. The breaks in the conductance− [SDBS] curves denote the cmc points, which are presented
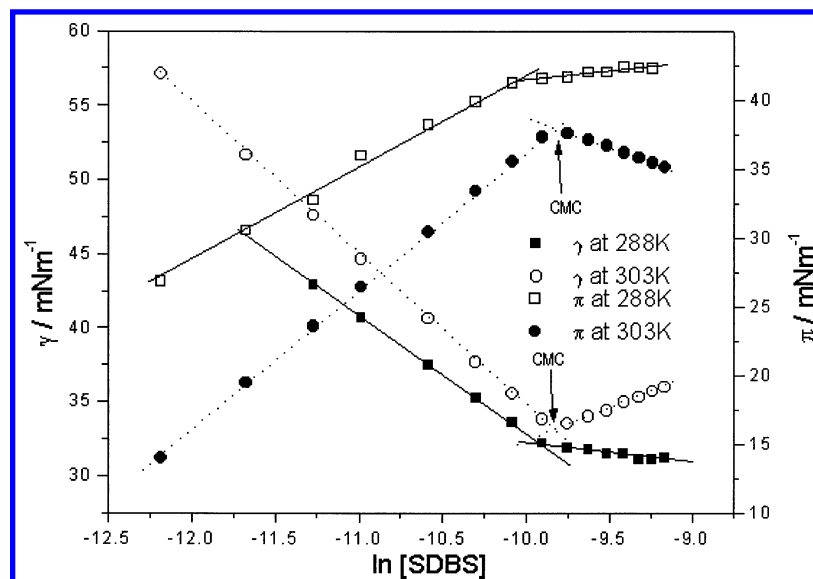
Figure 2. Tensiometric determination of the cmc of SDBS at different temperatures.
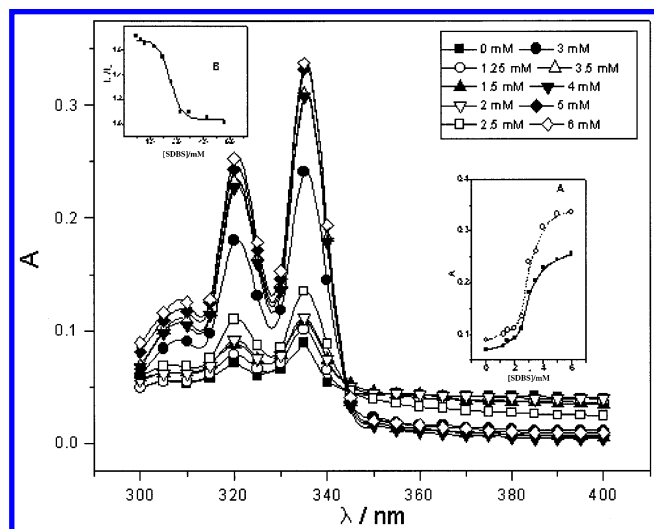

Figure 3. Spectophotometric determination of cmc of SDBS solutions using 1×10^{-5} M pyrene solution. SBE fitting curve for the absorbances at 320 nm (■) and 335 nm (○) is shown in inset A. Inset B shows the fluorometric determination of cmc in the presence of pyrene.

Figure 4. Spectophotometric determination of cmc of SDBS solutions using 4×10^{-6} M pinacyanol chloride solution. Key: (■) 0 mM; (○) 0.5 mM; (▲) 1 mM; (▽) 1.5 mM; (□) 2 mM; (●) 2.5 mM; (△) 3 mM; (▼) 4 mM; (◆) 5 mM; (◇) 6 mM. SBE fitting curve for the ratio of absorbances at 600 and 560 nm is shown in the inset.

TABLE 1: Comparison of cmc Values at Different Temperatures Obtained by Different Methods

	cmc, mM				
temp, K	cond[a]	cal	tens	pyrene abs (flu)	pCl abs
288	2.7 (2.65)	2.7	2.7		
293	2.8 (2.78)	2.8	2.8		
298	2.9 (2.93)	2.8	2.9	2.8 (2.6)	2.7
303	3.0 (2.98)	2.9	3.0	3.0	
308	3.0 (3.03)	3.0	3.1	3.1	
313	3.1 (3.08)	3.1		3.2	
318	3.2 (3.23)	3.2		3.2	
323	3.3 (3.32)	3.3			

[a] The parenthetical values are the cmc's determined by the procedure of Ruiz et al. [27]

(Figure 1) as differential conductance−[SDBS] and evaluated according to the sigmoidal Boltzmann equation (SBE) given by Hait et al.[26] and analyzed according to the procedure of Ruiz et al.[27] The cmc values are presented in Table 1. The surface tension vs ln [SDBS] plots also indicate distinct breaks indicating the formation of cmc (Figure 2). The plots of surface pressure, π, against ln [SDBS] therein also indicate the
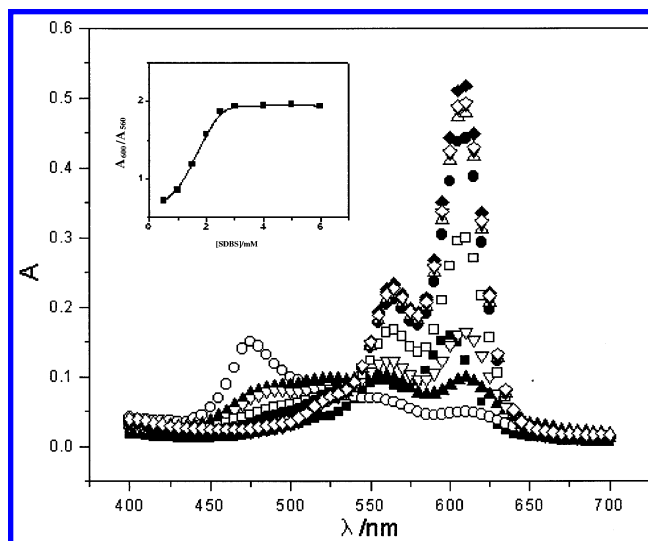
cmc point. The UV spectra of pyrene (taken in the range of 300−400 nm) in SDBS medium have shown three peaks at 310, 320, and 335 nm that enhanced with increasing [SDBS] (Figure 3). The absorbance (A)−[SDBS] profiles at 320 and 335 nm shown in the inset of Figure 3 have also conclusively evidenced the cmc point evaluated in terms of SBE equation.[26] The results at different temperatures are presented in Table 1. Such a spectral procedure using pyrene for the evaluation of cmc was not done in the past. A different but established spectral procedure followed for the determination of cmc of the anionic surfactant was the measurement of visible spectra of pinacyanol chloride in SDBS solution of increasing concentration. This cationic dye undergoes a spectral transition (pink to blue) in anionic micellar solution.[28] The spectra are illustrated in Figure 4. While the peak at 475 nm (γ band) decreased, both of the peaks at 560 and 600 nm (β and α bands) increased with increasing [SDBS]. The plot of A_{600}/A_{560} vs [SDBS] is again sigmoidal the treatment of which according to SBE[26] resulted in the estimation of cmc. The determination was done only at
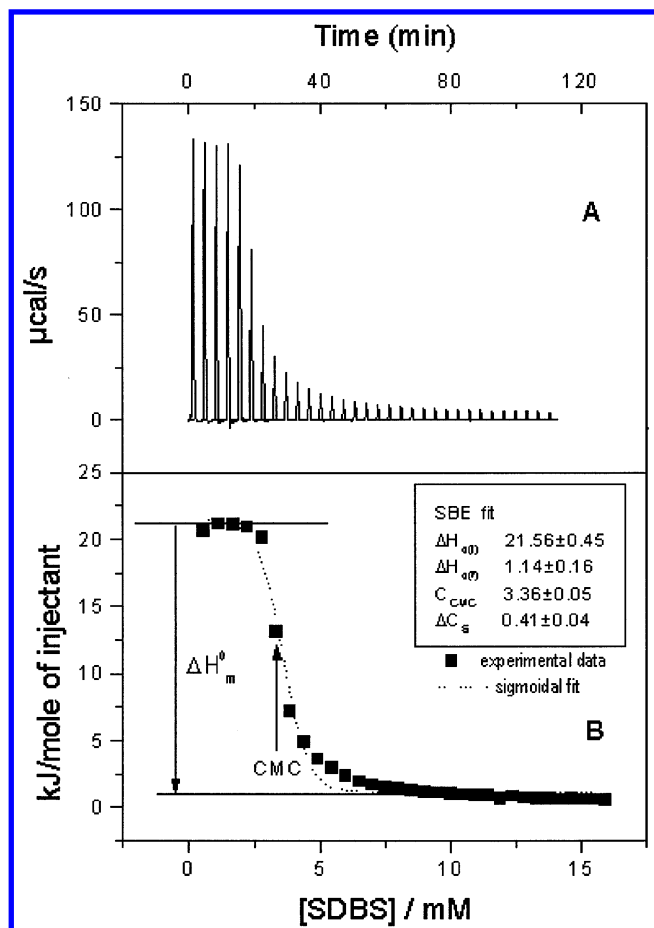
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Figure 5. Titration of a total volume of 320 μL of 75 mM SDSB solution into 1.325 mL of water in 32 steps with 10 μL titration volume at 323 K: (A) calorimetric traces of heat flow against time; (B) reaction enthalpy against concentration of SDBS in the cell with SBE fitting curve.

298 K just to get support of the reported cmc in terms of an otherwise established method. The result is shown in Table 1.

The results of the microcalorimetric runs are documented in Figure 5. In section A, the heat flow at different stages of micellar dilution is witnessed. The enthalpy of dilution with [SDBS] is profiled in section B. The cmc and ΔH_m^0 were obtained from the SBE fitting.[26] The temperature-dependent cmc values are presented in Table 1.

The commercial samples of SDBS may contain different isomers, $2\phi C_{12}$, $3\phi C_{12}$, $4\phi C_{12}$, $5\phi C_{12}$, and $6\phi C_{12}$. The separation of these isomers from their mixture and their identification therein are really a difficult task. It is obvious that the self-aggregation and interfacial properties of these isomers are different. The sample of SDBS obtained from Aldrich was >97% pure product of molecular formula $C_{12}H_{25}\phi SO_3^-$ Na^+, but its isomeric form was not known. We could not get the isomeric composition of the sample from the company. There are also reports in the literature in which the purity of the sample with respect to the presence of isomers is not mentioned.[29−32] We checked the purity of the compound by HPLC (80:20 ratio of phosphate buffer at pH 2.5 and acetonitrile as mobile phase) and found a major component in it with indications for two minor components of proportion within 5%. In the literature, there are reports on the micellization characteristics of isomeric SDBS.[33−37] They are listed in Table 2. It is seen from the table that the cmc's of the isomers increase with increasing number of carbon atoms in the branched chain. The maximum attainable value of cmc is 2.4. A linear regression of the carbon-number-

TABLE 2: The Reported cmc Values of Isomeric SDBS

isomer	temp, K	cmc, m mol dm^{-3}	ref
$3\phi C_{12}$	298	1.30	33
$3\phi C_{12}$	298	1.50	34
$3\phi C_{12}$	303	2.39	35
$4\phi C_{12}$	298	1.40	33
$4\phi C_{12}$	298	1.70	34
$5\phi C_{12}$	298	2.20	33
$5\phi C_{12}$	298	2.40	34
$6\phi C_{12}$	298	2.40	33
$6\phi C_{12}$	298	2.40	36
$6\phi C_{12}$	298	2.25	37
$6\phi C_{12}$	298	2.78	this work

TABLE 3: The cmc, f, and Thermodynamic Parameters of Micellization of SDBS at Different Temperatures Based on Pseudophase Principle[a]

temp, K	f	cmc, mM cal	ΔG_m^0, kJ mol^{-1}	ΔH_m^0, kJ.mol^{-1} van·t Hoff	ΔH_m^0, kJ.mol^{-1} cal	ΔS_m^0, J K^{-1} mol^{-1} van·t Hoff	ΔS_m^0, J K^{-1} mol^{-1} cal	ΔC_{pm}^0, J K^{-1} mol^{-1} van·t Hoff	ΔC_{pm}^0, J K^{-1} mol^{-1} cal
288	0.34	2.72	−31.8	−8.6	6.4	80.4	132	−648	−784
293	0.33	2.76	−32.2	−11.9	3.4	69.0	121	−683	−784
298	0.32	2.81	−32.5	−15.4	−1.0	57.1	106	−718	−784
303	0.32	2.88	−32.7	−19.1	−5.1	45.0	91.1	−753	−784
308	0.31	2.95	−32.9	−23.0	−9.0	32.3	77.5	−788	−784
313	0.30	3.07	−33.1	−27.0	−13.4	19.3	62.8	−823	−784
318	0.28	3.19	−33.2	−31.2	−17.2	6.12	50.2	−858	−784
323	0.27	3.32	−33.1	−35.6	−20.1	−7.63	40.3	−893	−784

[a] The error limits in f, cmc, ΔG_m^0, ΔH_m^0, ΔS_m^0, and ΔC_{pm}^0 are ±3%, ±4%, ±3%, ±5%, ±7%, and ±10%, respectively.

dependent cmc provided an expected value of 2.44 for the cmc of the $6\phi C_{12}$ isomer. The average value of the cmc obtained by us at 298 K using six different methods is 2.78; the result is higher. Recognizing the method-dependent variation of cmc, the present finding is acceptable. Because the $6\phi C_{12}$ isomer provides the maximum cmc, we consider that the compound herein studied was essentially the $6\phi C_{12}$, the major component of the HPLC analysis.

Counterion Binding of Micelle. The counterion (Na^+) dissociated from the micelle has been estimated from the ratio of the right and left asymptotes (A_2 and A_1) in the post- and premicellar regions, respectively, obtained by plotting differential conductance vs [SDBS]. The quantity $(A_2/A_1) = f$ is, therefore, the fraction of counterions bound to a micelle.[9,24] The results are given in Table 3. It is observed that f varies in the range of 0.27−0.34. The counterions moderately bind to the SDBS micelle. The surface charge density of the SDBS micelle is, therefore, moderate. The monomers here sparsely packed in the micelle. The variation of f weakly depends on temperature; there is a decline in f with increasing temperature. It may be mentioned that for sodium dodecyl sulfate (SDS) and cetyl trimethylammonium bromide (CTAB) f tends to pass through a minimum analogous to cmc.[9,24] The extents of counterion binding are also higher for both SDS and CTAB than for SDBS. Sein and Engberts[37] have reported f values of 0.36 and 0.26 for their samples of polydisperse SDBS and its pure 5/6 isomer at 298 K, which are comparable with the f values herein obtained.

Aggregation Number of Micelle. The aggregation number n of SDBS micelle at 298 K was obtained by processing the static quenching of the fluorescence data according to the equation

$$\ln \frac{F_0}{F} = \frac{n[Q]}{[SDBS] - cmc} \qquad (1)$$

where F_0 and F are the fluorescence intensities of pyrene without and with the quencher, Q (cetylpyridinium chloride, CPC), respectively, at SDBS concentration fairly larger than its cmc. The Stern−Volmer constant K_{SV} (the equilibrium constant for the complex between CPC and pyrene) was obtained using the equation

$$\frac{F_0}{F} = 1 + K_{SV}[Q] \qquad (2)$$

The average values of n and K_{SV} obtained by the static quenching method were 61 and 8858 mol^{-1} dm^3, respectively. Inset of Figure 3 illustrates the I_1/I_3 vs [SDBS] plot to demonstrate the polarity change in the system. The nonpolar pyrene molecule has been conveniently solubilized in the micellar interior yielding a fairly sharp transition in the plot. The data processing in terms of SBE has resulted in the transition point or cmc being 2.62 m mol dm^{-3} at 298 K. The Stern−Volmer constant K_{SV} (8858 mol^{-1} dm^3) is fairly large demonstrating appreciable quencher−probe interaction in the excited state in the micellar environment. The n value obtained is fairly large compared to that for SDS ($n = 55$ at 298 K).[38] It is known that along with other environmental factors, n also depends on the concentration of surfactant; it increases with increasing surfactant concentration above cmc.[38−41] The value of 61 herein obtained is thus considered higher than that at the cmc. In a subsequent section, dealing with the thermodynamics of micellization according to the mass action model, the n values at cmc determined from a simulation procedure are presented and discussed.

Thermodynamics of Micellization. In the evaluation of the thermodynamic parameters for the micellization of SDBS, the enthalpy of micellization is obtained directly from calorimetry, as well as by estimating it from the van't Hoff equation using the calorimetric cmc values at different temperatures. The set of differential enthalpy of dilution−[SDBS] profiles obtained by the isothermal titration calorimetric (ITC) method at different temperature is presented in Figure 6. The fitting of the data according to the SBE helped to derive the cmc and the ΔH_m^0.

$$\Delta H_m = \Delta H_{d(f)}\left[1 + \left(\frac{\Delta H_{d(i)} - \Delta H_{d(f)}}{\Delta H_{d(f)}}\right)(1 + \exp(C_s - $$

$$C_{cmc})/\Delta C_s)^{-1}\right] \quad (3)$$

where C_s and C_{cmc} are the stoichiometric concentration of SDBS and its cmc, respectively, at a particular temperature, ΔC_s is the increment in concentration of SDBS between two successive additions, and $\Delta H_{d(i)}$ and $\Delta H_{d(f)}$ are the initial and final asymptotes, respectively, in the sigmoidal plot. A representative fitting plot according to the eq 3 is illustrated in Figure 5B.

We have used both the "mass action" and "pseudophase" micellization principles for the thermodynamic calculation. In terms of the mass action principle, the standard Gibbs energy of micellization, ΔG_m^0 (expressed per mole of monomer unit) is given by the following equation.[20]

$$\Delta G_m^0 = \left(1 + \frac{m}{n}\right)RT \ln X_{cmc} + \frac{RT}{n}\ln[2n(n + m)] \quad (4)$$

where the new terms m and n are the number of counterions bound per micelle and the aggregation number of a micelle, respectively. The factor m/n is thus equal to the fraction of the counterions bound to a micelle, that is, f. The other term, X_{cmc}, is the mole fractional concentration of cmc. The standard
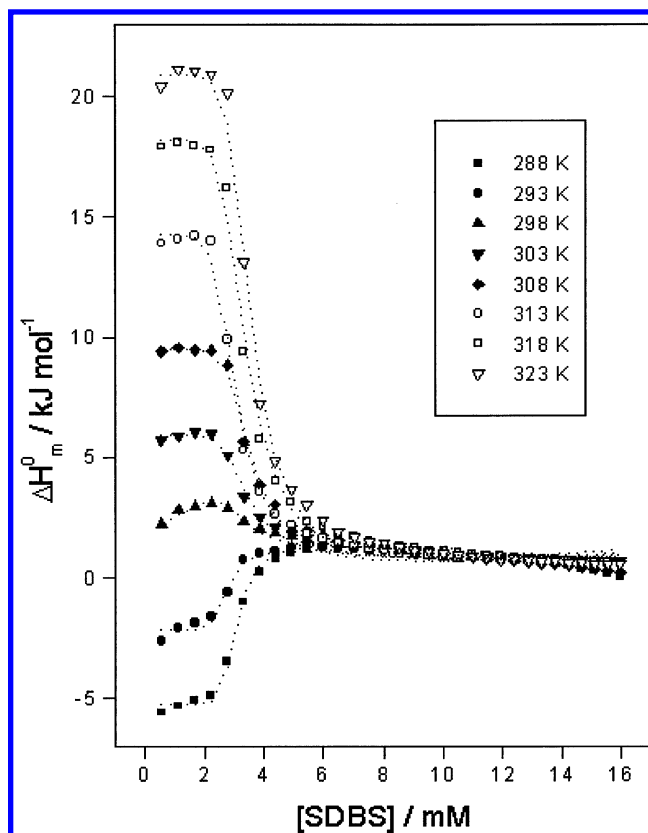

Figure 6. Microcalorimetric determination of enthalpy of dilution of SDBS at different temperature. The points are experimentally determined. The dotted curve is according to the simulated mass action model.[41,42]

enthalpy of micellization, ΔH_m^0, and the standard entropy of micellization, ΔS_m^0, are obtained by the procedure given by Chatterjee et al.[9]

The thermodynamic parameters in the pseudophase rationale are evaluated by the procedure of Chatterjee et al.[9] The cmc and the energetic parameters obtained by the pseudophase model are presented in Table 3.

It is observed that although the cmc's of SDBS determined by the calorimetric and other methods fairly agree, the ΔH_m^0 obtained by the direct method of calorimetry appreciably differs from that calculated by the van't Hoff equation. This is in conformity with our recent observations particularly on ionic surfactants.[9,24] The changing aggregation number and shapes and the counterion binding of micelles, which are usually not accommodated in the data processing in the van't Hoff rationale, are considered to influence the ΔH_m^0 of the process. In the present mass action principle based analysis,[42,43] the shares of the aggregation number and counterion binding to the energetic parameters have been considered; the contribution associated with the changing shape of the micelles has been considered to be minor. In the direct determination of the ΔH_m^0 by calorimetry, the contributions of the above effects were, on the other hand, included in the measurement. The observed discrepancy between the results of the two methods is thus not unusual. Corkill[44,45] has proposed a relation for the evaluation of ΔG_m^0 and ΔH_m^0 of nonionic surfactants accounting for the contribution of the aggregation number. The effect of the altered aggregation number on the micellar surface charge and hence the electrostatic free energy of the micellization process of ionic surfactants has been explained by Holtzer and Holtzer[46] to show the inefficiency of the van't Hoff method.

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It is known that, while calorimetry provides integral heat of micellization, the van't Hoff method gives the differential heat.[5,6] Thus, the direct method of calorimetry registers all sorts of heat changes, amphiphile self-organization and otherwise, the sum of which is registered as the heat of micellization. This may include the contributions (significant or insignificant) from solvation–desolvation of the species, their ionization, molecular rearrangement, mixing, etc. These are not related to the equilibrium concept of micelle formation envisaged in the mass action model or pseudophase model.

$$(\text{monomer}^-) + \frac{m}{n}(\text{counterion}^+) \leftrightarrow \text{micelle} \qquad (5)$$

The difference in the two sets of results is as well reflected on ΔS_m^0 and ΔC_{pm}^0 (Table 3). The calorimetric ΔS_m^0 values are more positive; the self-organization involves greater disorderedness. Other processes (over and above the releasing of the hydrophobic hydration around the amphiphile tail and their increased lability in the micellar interior) contribute to the increased entropy of the system. The $\Delta C_{pm}^0(\text{cal})$ is to some extent greater (less negative) than $\Delta C_{pm}^0(\text{van't Hoff})$ at temperatures of ≥ 308 K; the former has been found to be independent of temperature. The entropies and heat capacities during micelle formation mainly arise from the change in the "hydrophobic" and "hydrophilic" hydration of the ionic surfactant monomers and their counterions. During micellization, both the hydrophobic hydration of the amphiphilic monomers and the hydrophilic hydration of the ionic headgroups and the counterions (due to their mutual association) decrease. The processes are expected to be associated with positive entropy change normally observed. The significantly higher entropy values in the direct calorimetric measurements suggest the contributions coming from other associated processes operative in the system. The ΔC_{pm}^0 values for SDBS are all negative and are more or less of comparable magnitudes (a mild increasing trend in the magnitude has been observed with temperature by the van't Hoff procedure). The negative ΔC_{pm}^0 are normally observed for the self-associating amphiphiles leading to micelle formation. This is in line with the transfer of amphiphiles from their hydrophobically hydrated (ordered) state in the aqueous medium to the free and oily micellar interior. The associated heat is of course inclusive of the contributions from other related processes.

In deriving ΔG_m^0 and ΔH_m^0 by the mass action model (using eqs 4 and 5), the knowledge of the micellar aggregation number at cmc is essential because the aggregation number depends on the surfactant concentration above cmc. In a recent work,[41,42] a simulation procedure has been used employing the ITC results (Figure 6) to obtain the aggregation number at cmc and the thermodynamic parameters based on the "mass action" model. This procedure has been herein used and the results are presented in Table 4. It is observed that the values of n are low (range between 9 and 16) and pass through a minimum at 303 K. The low values of n tally with the low values of f for SDBS micelles. They correspond to the aggregation at the cmc point, which is expected to be lower than that obtained using [SDBS] > cmc normally employed in the fluorescence quenching method. The static quenching method herein used (and discussed in previous section) is also known to yield n less accurate than actual. The n values obtained by the simulation method thus fit to the requirements of the present thermodynamic evaluation procedure. There is a difference between the ΔG_m^0 values obtained by the mass action and pseudophase models; the latter is more

TABLE 4: Thermodynamic Parameters of Micellization of SDBS in Water as a Function of Temperature Calculated from Simulation of ITC Data Based on the Mass Action Model[a]

temp, K	mass action model			
	ΔH_m^0, kJ mol^{-1}	ΔG_m^0, kJ mol^{-1}	$T\Delta S_m^0$, kJ mol^{-1}	n
288	6.5	−28.9 (−30.8)	35.3	16
293	3.2	−29.5 (−31.1)	32.7	15
298	−2.5	−28.5 (−31.1)	26.0	11
303	−5.2	−28.1 (−31.2)	22.9	9
308	−8.9	−28.5 (−31.5)	19.6	10
313	−13.9	−28.7 (−31.5)	14.8	9
318	−18.2	−28.5 (−31.6)	10.3	9
323	−20.8	−29.0 (−31.6)	8.2	10

[a] The error limits in f, cmc, ΔG_m^0, ΔH_m^0, ΔS_m^0, ΔC_{pm}^0, and n are ±3%, ±4%, ±3%, ±5%, ±7%, ±10%, and ±10%, respectively.

TABLE 5: Interfacial Adsorption Parameters of SDBS at Different Temperatures Obtained from Tensiometric Measurements

temp, K	$\Gamma_{max} \times 10^6$, mol m^{-2}	A_{min}, nm^2	$-\Delta G_{ad}^0$, kJ mol^{-1}	$-\Delta H_{ad}^0$, kJ mol^{-1}	$-\Delta S_{ad}^0$, J K^{-1} mol^{-1}
288	2.1	0.81	53.0	157	361
293	2.3	0.74	49.9	152	347
298	2.3	0.74	49.1	145	323
303	2.4	0.69	48.5	139	297
308	2.7	0.62	45.6	131	278

negative. When the n values thus obtained are employed and when ΔG_m^0's are calculated in terms of the eq 4 of Moroi,[20] the results improve, but still the pseudophase values are found to be less (shown in parentheses of column 3, Table 4). The difference thus lies in the nonequivalence of the calorimetric enthalpy with the enthalpy of the actual process of micellization (i.e., the van't Hoff enthalpy) modeled in eq 5. A quantitative accounting by way of concept and additional measurements is thus wanted for rationalization of the discrepancy.

Interfacial Adsorption of SDBS. The slope of the initial straight line between the plot of π and ln [SDBS] in Figure 2 was used to calculate the maximum surface excess of SDBS, Γ_{max} at the cmc. These and the related thermodynamic parameters (ΔG_{ad}^0, ΔH_{ad}^0, and ΔS_{ad}^0) were evaluated according to the method discussed by Chatterjee et al.[9,15]

All of the interfacial adsorption parameters (presented in Table 5) are very weakly dependent on temperature up to 298 K and mildly dependent above it. With increased temperature, the transfer of SDBS at the interface increased leading to delayed formation of micelle in solution. The exothermicity of the adsorption process has obviously diminished with increasing temperature resulting in a decrease in negative ΔS_{ad}^0. The interfacial phase becomes less-ordered with rise in temperature. Compared to the micellization (Table 3), the process of interfacial adsorption of SDBS is thermodynamically more favorable. This property is related to the hydrophobic nature of the amphiphile.

Interaction of SDBS with Polymers. The interaction of SDBS with PVP, LM 200, and JR 400 was studied by the conductometric and the calorimetric methods. The conductance vs [SDBS] plots in the presence of the polymer PVP have shown two breaks; the first break corresponds to the critical aggregation concentration (cac),[47] and the second one denotes the normal micelle formation (cmc) of SDBS in PVP medium. The conductance behavior of SDBS in the presence of LM 200 and JR 400 in solution is depicted in Figure 7. The cac and cmc values are well spread; the cmc/cac ratios both for PVP and LM 200 increase nearly linearly with polymer concentration.
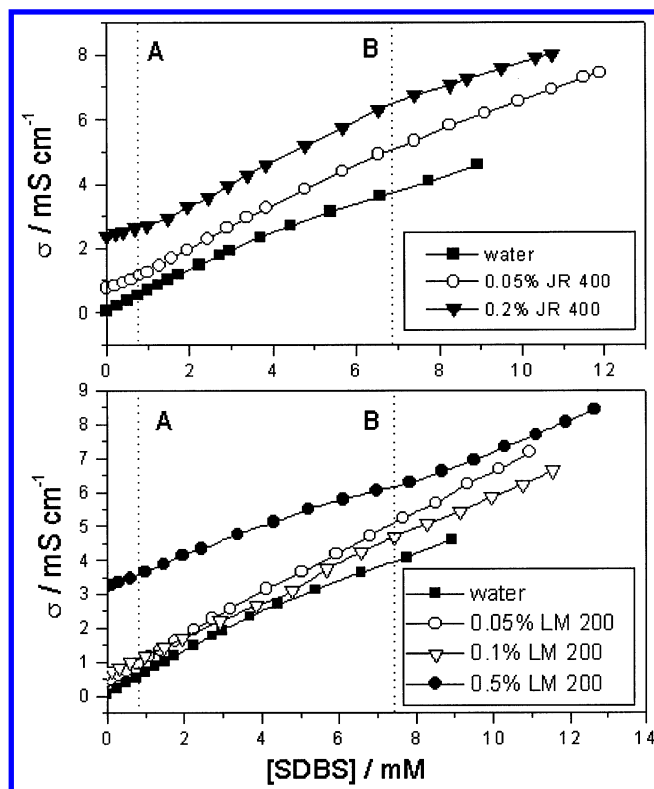
Figure 7. Conductometric evaluation of cac and cmc of SDBS in the presence of LM 200 (bottom) and JR 400 (top). The viscous region falls between lines A and B.

Figure 8. (A) Titration of a concentrated SDBS solution into PVP solution at 303 K. (B) Variation of subtracted enthalpy values against [SDBS] at different PVP concentrations.

TABLE 6: Conductometrically Evaluated cac, cmc, and Counterion Binding of SDBS Aggregates in Aqueous PVP Medium at 303 K

[PVP], mass %	cac, mM	cmc, mM	cmc/cac	f_1	f_2
0.1	1.1	5.6	4.9	0.06	0.20
0.2	1.1	6.2	5.4	0.08	0.34
0.4	1.3	10.7	8.1	0.11	0.36
0.5	1.4	12.4	8.6	0.12	0.38
0.7	1.5	13.3	8.9	0.18	0.51

TABLE 7: Conductometrically Evaluated cac and cmc of SDBS in Aqueous LM 200 and JR 400 Medium at 303 K

[polymer], mass %	cac, mM	cmc, mM
	LM 200	
0.05	1.80	4.80
0.075	2.10	5.20
0.1	1.80	5.25
0.2	3.20	5.70
0.5	3.90	9.20
	JR 400	
0.05	0.79	6.43
0.1	1.39	7.10
0.2	1.65	7.25

The SDBS−JR 400 system has evidenced decreasing cmc/cac ratio with increasing polymer. The process of binding of amphiphile with a polymer essentially depends on the size of the amphiphile aggregate, its affinity toward the polymer segment, and the environmental conditions, such as viscosity, temperature, and the presence of additives. This is an interesting area of research because the interacted (surfactant−polymer) products have potential applications in chemical, pharmaceutical, and medicinal fields.

It has been observed that for the SDBS−PVP system the slopes of the linear conductance vs [SDBS] plots successively decline in the postbreak regions of the cac and cmc. The fraction of the counterions bound to the SDBS aggregates were evaluated in the usual way from the $f_1 = 1 - (S_2/S_1)$ and $f_2 = 1 - (S_3/S_1)$ rationale,[48] where S_1, S_2, and S_3 are the first, second, and third slope of the three straight lines, respectively, and f_1 and f_2 are the fractions of counterions bound to the polymer-bound aggregate and the free micelle in solution, respectively.[18] The f_1 and f_2 values are presented in Table 6. It has been observed that in the SDBS−JR 400 system $S_2 > S_1$ and $S_3 < S_2$. The observation on the SDBS−LM 200 system has been reverse. There, $S_2 < S_1$ and the $S_3 > S_2$. These results are apparently anomalous because of the highly viscous nature of the solutions in addition to the counterion association by the aggregates (at
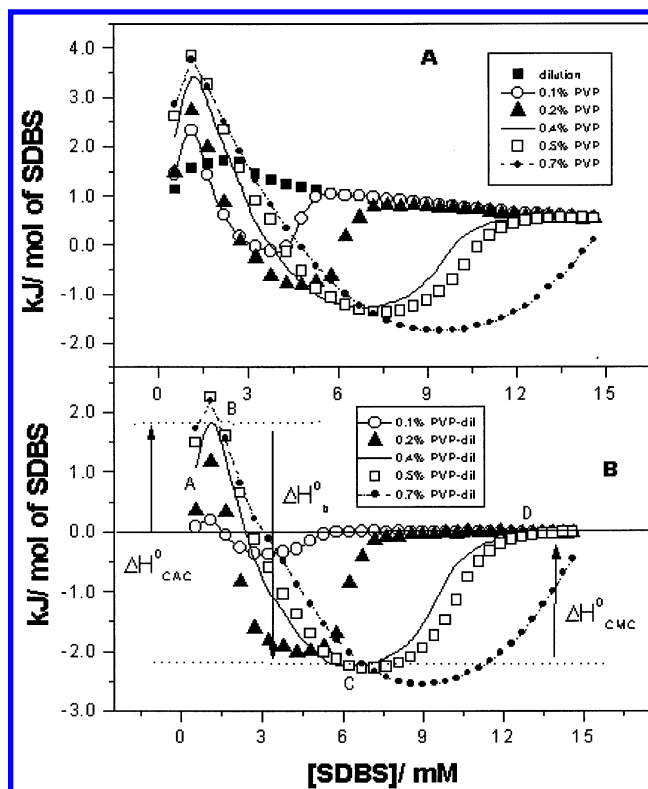
and above cac and cmc). The change in solution viscosity (most common in this type of amphiphile−polymer system) can influence the system conductance. The addition of SDBS into the solutions of both JR 400 and LM 200 polymer has initially increased the viscosity of the solution, which has decreased at higher SDBS concentration. This has a contribution to the conductance, in addition to that resulting from the SDBS aggregation (cac formation). Thus, the conductance of SDBS in JR 400 and LM 200 solution did not follow the expected trends in the pre- and post-cac and -cmc regions. The influence of the solution viscosity on the conductance depends on the nature of the internal consistency of the solution. The combined effects of the counterion binding and internal consistency change (increased or decreased) controlled the overall conductance course. Thus, the observed cac and cmc values by the conductance method (Table 7) are approximate and may not tally with those realized from the calorimetric method at all concentrations of the polymers (Table 9).

The differential enthalpies of dilution of SDBS in the absence and presence of PVP at 303 K with respect to the overall SDBS

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TABLE 8: Calorimetrically Obtained cac, cmc, and Energetic Parameters of Interaction of SDBS with PVP at 303 K

[PVP], mass %	cac, mM	ΔH^0_{cac}, kJ mol^{-1}	$-\Delta G^0_{cac}$, kJ mol^{-1}	ΔS^0_{cac}, J mol^{-1} K^{-1}	$-\Delta H^0_{b}$, kJ mol^{-1}	cmc, mM	cmc/cac	ΔH^0_{cmc}, kJ mol^{-1}	$-\Delta G^0_{cmc}$, kJ mol^{-1}	ΔS^0_{cmc}, J mol^{-1} K^{-1}
0.1	1.10	0.20	29.0	96	0.59	5.3	4.81	0.40	28.0	94
0.2	1.10	1.18	29.6	102	3.23	7.6	6.93	2.04	30.1	106
0.4	1.10	1.82	30.3	106	4.09	12.0	10.9	2.27	29.0	103
0.5	1.10	2.21	30.5	108	4.54	12.6	11.4	2.33	29.2	104
0.7	1.10	2.21	32.2	114	4.78	15.5	14.1	2.57	31.1	111

TABLE 9: Calorimetrically Obtained cac, cmc, and Energetic Parameters of Interaction of SDBS with JR 400 and LM 200 at 303 K

[polymer], mass%	cac, mM	ΔH^0_{cac}, kJ mol^{-1}	$-\Delta G^0_{cac}$, kJ mol^{-1}	ΔS^0_{cac}, J mol^{-1} K^{-1}	ΔH^0_{b}, kJ mol^{-1}	ΔH^0_{cmc}, kJ mol^{-1}	cmc, mM	cmc/cac	$-\Delta G^0_{cmc}$, kJ mol^{-1}	ΔS^0_{cmc}, J mol^{-1} K^{-1}	$-\Delta G^0_{ps}$, kJ mol^{-1}
					LM 200						
0.05	2.13	0.67	33.7	114		0.49	4.1	1.93	31.5	106	2.19
0.075	2.17	0.62	33.7	113	0.27	0.93	5.5	2.54	30.5	104	3.14
0.1	2.04	0.58	33.9	114	0.76	1.04	7.7	3.76	29.5	101	4.37
					JR 400						
0.01	2.26	1.10	33.5	114		0.38	5.2	2.32	30.7	103	2.79

concentration are presented in Figure 8, section A. It is observed that in the presence of PVP a peak appears at 1.1 m mol dm^{-3} at all concentrations of PVP. In section B of Figure 8, the enthalpies of dilution in the presence of PVP relative to its absence are plotted against the SDBS concentration. The overall pattern of the plots is the same as in that section A, but the curves level off at zero enthalpy. For 0.7% PVP, the zero-enthalpy state has remained unreached for want of enough data points on the higher side of SDBS concentration, but the tendency is evident from the trend. It is seen in Figure 8B that each curve has ups and downs and can be dissected in different enthalpic terms. It is considered that by induction premicellar aggregation of SDBS occurs on the polymer chain at a concentration less than cmc, which is called the cac. This constitutes the initial rising of the ΔH_d vs [SDBS] curve. From the crest, the enthalpy then descends to a minimum, which is regarded as the completion of binding/attachment of the aggregated SDBS to the PVP. Thereafter, the enthalpy change climbs up to the zero ΔH_d value, consequent upon the formation of free micelles in solution. Thus, with reference to the curve for the 0.4% PVP, the enthalpy change from A → B stands for the enthalpy of polymer induced cac formation with B as the cac point, B → C represents the enthalpy of binding of the aggregated SDBS with PVP, and C → D accounts for the enthalpy change for the formation of free micelle in solution, with D as the cmc point. These dissected enthalpies, along with cac and cmc at different PVP concentrations, are presented in Table 8. The cac values are nonvariant on PVP concentration. Unaltered cac with increasing polymer concentration is seldom reported in the literature. Because the process is initiated by the polymer, decreasing cac with increasing polymer concentration was the expectation, but the observation was contrary. Like conductometry, the cmc/cac ratios obtained from calorimetry have also evidenced overall linear dependence on PVP concentration and LM 200 concentration. Such a behavior with JR 400 could not be checked because of difficulty in calorimetric experiments at different polymer concentration subsequently discussed in this section. In Table 8, the standard Gibbs energies of cac formation (ΔG^0_{cac}) have been calculated using the equation

$$\Delta G^0_{cac} = (1 + f_1)RT \ln X_{cac} \tag{6}$$

where X_{cac} is the mole fractional concentration of SDBS at the cac and f_1 is the counterion binding extent of the SDBS

aggregate given in Table 6. The above relation is comparable with the relation for the Gibbs energy of micellization. The f_1 values are low and contribute increment in ΔG^0_{cac} only within 18%.

Unlike the cac, the ΔH^0_{cac} is not independent of PVP concentration; it has increased with PVP concentration. The entropy of the process is large. The arrangement of amphiphiles on the polymer segment is associated with sizable disorder. The process is entropy-controlled. Normally, the surfactant aggregation is associated with positive entropy change. In the present system, the organized solvent molecules of the solvated polymer segment undergo disruption during the process of association of SDBS molecules induced by the PVP. The enthalpy of aggregate binding (ΔH^0_{b}) to the PVP segments is exothermic, and the magnitude increases with increasing PVP concentration. When more SDBS assemblies were anchored on the PVP segments, the heat release was more. Upon completion of the binding process, the amphiphile molecules organized in solution to form free micelles with increasing cmc values for increased PVP in solution. The Gibbs energy for micellization has been calculated by the relation[49]

$$\Delta G^0_{cmc} = (1 + f_2)RT \ln X_{cmc} \tag{7}$$

The thermodynamic parameters have shown appreciable difference between PVP of 0.1% and 0.2% (w/v); for the other concentrations, the difference is small.

The calorimetric findings on the interaction between SDBS and LM 200 are presented in Table 9. The cac and cmc values agree with the conductometric evaluation (Table 7) for 0.1% LM 200; higher concentrations of the polymer than 0.1% could not be used in calorimetry because of increased viscosity causing baseline fluctuation and shift. In Table 9, all of the thermodynamic and related parameters are presented. Because of unexpected dependence of conductance of SDBS in LM 200 and JR 400 solution, the evaluation of f_1 and f_2 values was not feasible. The thermodynamic parameters have been, therefore, calculated without using f_1 and f_2 values. The aggregation and the binding of the aggregates with the polymer segments ended up with minor absorption of heat. The aggregation and the micellization processes of SDBS in both are entropy-controlled. The differential enthalpy of dilution curves of SDBS at 0.075% and 0.1% LM 200 have shown kinks in the postaggregate binding stage. This was a reflection of low-energy-related organizational change in the polymer bound aggregates the

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assessment of which has been kept pending until results of further studies are available. The conductometrically evaluated cac and cmc values with reference to the interaction of SDBS with JR 400 presented in Table 9 evidence increase in the parameters with increasing polymer concentration. The calorimetric measurements were taken only at a single concentration of JR 400; such measurements at higher polymer concentration were not feasible for decreased fluidity of the solution. Nevertheless, the thermodynamic and related parameters are comparable with those realized for LM 200.

Conclusions

The cmc's of SDBS determined by various methods are close and thus unambiguous.

The thermodynamic parameters for the micellization of SDBS obtained from the pseudophase principles assessed on the basis of enthalpies obtained from the van't Hoff rationale and by the direct ITC method and by the mass action model do not agree. Processes other than simple micelle formation need to be considered to account for the difference.

The aggregation number of SDBS at the cmc point and the Gibbs energy of micellization can be derived from a simulation method based on the mass action principle.

The SDBS can significantly interact with the polymers PVP, LM 200, and JR 400. The polymers induce early aggregation of SDBS at concentrations less than the cmc, and the aggregates exothermically bind to the polymer segments.

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