Thermodynamics of Micelle Formation of Ionic Surfactants: A Critical Assessment for Sodium Dodecyl Sulfate, Cetyl Pyridinium Chloride and Dioctyl Sulfosuccinate (Na Salt) by Microcalorimetric, Conductometric, and Tensiometric Measurements

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The thermodynamics of micelle formation of ionic surfactants, sodium dodecyl sulfate (SDS), cetyl pyridinium chloride (CPC), and sodium salt of dioctyl sulfosuccinate (Aerosol OT or AOT) have been thoroughly assessed from microcalorimetric, conductometric, and tensiometric measurements, and the results have been rationalized in terms of physicochemical concepts and relations. The past and recent critical micellar concentration (CMC) data on SDS have been considered and compared; the CMCs of SDS, CPC, and AOT determined in this and earlier studies have been processed to evaluate the energetic parameters (free energy, enthalpy, entropy, and heat capacity) of micellization. The effect of the salt, NaCl, on the CMC and energetics of micellization of the surfactants has been also examined.

Introduction

The micellization of surfactants (amphiphiles) after a critical concentration (called the critical micellar concentration, CMC) is an important solution property which needs evaluation to know the existence of micelles in solution as well as evaluating the thermodynamics of the process which is essential for characterization and comparison in the light of spontaneity and stability. The determination of thermodynamic parameters for 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 case. However, both nonionic and ionic micelles are normally not amenable to appropriate energetic treatment for the variation in the micellar aggregation number and change of shape which are environment dependent, particularly to evaluate the enthalpy of micellization from the temperature dependence of CMC by the use of van't Hoff equation. It is essential to mention in this connection that direct determination of the enthalpy of micellization in a calorimeter can be made (although such determinations are not abundant) but the van't Hoff enthalpy often does not agree[1-4] with the calorimetric enthalpy. Further, the energetic parameters are not always evaluated on the basis of a single standard state; the results are, therefore, not comparable.

In the van't Hoff method, the CMC of a surfactant is measured at different temperatures and the energetic parameters can be evaluated by the mass action and pseudo-phase models.[5-10] In the mass action model following the line of Moroi[10] we have

$$\Delta G_m^\circ = RT \ln X_{CMC} \text{ (for nonionic micelle)} \quad (1A)$$

and

$$\Delta G_m^\circ = \left(1 + \frac{m}{n}\right)RT \ln X_{CMC} + \frac{RT}{n}\ln[2n(n + m)]$$
$$\text{(for ionic micelle)} \quad (1B)$$

$$\Delta H_m^\circ = -RT^2\frac{\mathrm{d}\ln X_{CMC}}{\mathrm{d}T} \text{ (for nonionic micelle)} \quad (2A)$$

and

$$\Delta H_m^\circ = -RT^2\left[\left(1 + \frac{m}{n}\right)\frac{\mathrm{d}\ln X_{CMC}}{\mathrm{d}T} + \ln X_{CMC}\frac{\mathrm{d}\left(\frac{m}{n}\right)}{\mathrm{d}T} + \frac{\mathrm{d}\left[\left(\frac{1}{n}\right)\ln\{2n(n + m)\}\right]}{\mathrm{d}T}\right] \text{ (for ionic micelle)} \quad (2B)$$

$$\Delta S_m^\circ = \frac{\Delta H_m^\circ - \Delta G_m^\circ}{T} \quad (3)$$

where X_{CMC} is the CMC in molefraction unit, ΔG_m°, ΔH_m° and ΔS_m° are the standard Gibbs free energy, enthalpy and entropy of micellization respectively expressed per mole of monomer unit, n is the aggregation number, m is the number of counterions bound per micelle and the other terms have their usual significance. We have used f for m/n in subsequent presentation and discussion.

In the evaluation of energetic parameters, the second and the third terms in the eqs 1B and 2B, respectively, have been neglected for their low weightage[10a] on the results. The used equations are thus

$$\Delta G_m^\circ = (1 + f)RT \ln X_{CMC} \quad (1C)$$

and

$$\Delta H_m^\circ = -RT^2\left[(1 + f)\frac{\mathrm{d}\ln X_{CMC}}{\mathrm{d}T} + \ln X_{CMC}\frac{\mathrm{d}f}{\mathrm{d}T}\right] \quad (2C)$$

A point to note here is that for 100% counterion binding to the

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micelle, $f = 1$ and $\Delta G_m^\circ = 2RT \ln X_{CMC}$ by eq 1C. Under this condition, the micelle has no net charge and eq 1C becomes twice of eq 1A valid for nonionic micelle. This difference arises because the monomers of nonionic surfactant self-aggregate to form a neutral micelle, whereas the ionic surfactant monomers assemble by reacting with equal number of counterions to form the neutral species. Equal numbers of the two species interact to form the micelle and hence the ΔG_m° is twice that of nonionic micelle where a single species aggregate to form a neutral micelle.

For the evaluation of the energetics of micellization, the counterion binding of the ionic micelles was seldom considered in the past; the choice of the concentration scale was also not consistent. In the recent literature, the role of the counterion binding has been considered, and the mole fractional scale has been used in the evaluation of the energetics of the process. But the effects of the temperature on the aggregation number and the shape of the micelle in relation to the energetics have not been reasonably presented. The CMCs are usually measured by the surface tension, conductance, fluorescence, light scattering methods, etc.

In the calorimetric method, both the CMC and the enthalpy are obtained from a single run and is, therefore, much convenient.[1,2,11-14] In recent years, the availability of high sensitive microcalorimeter has made the determination accurate and authentic.[1,2,11-14] This gives a scope to test the van't Hoff enthalpy and the calorimetric enthalpy by processing the CMC at different temperatures according to eq 2C with the direct results from calorimetry.

In the present study, for a comparative understanding, three typical ionic surfactants have been chosen. These are sodium dodecyl sulfate (SDS), dioctyl sulfosuccinate (sodium salt) called Aerosol OT (or AOT) and cetyl (hexadecyl) pyridinium chloride (CPC). Their CMCs are determined at different temperatures by the methods of microcalorimetry, conductometry and tensiometry. Such measurements are also made in salt (NaCl) environment. The results are processed to derive energetic information on the self-aggregation (organization) of the amphiphiles and to check the agreement between the enthalpies realized by the indirect and direct methods. A pragmatic discussion of the results is presented.

Experimental Section

Materials. The surfactants sodium dodecyl sulfate (SDS), dioctyl sulfosuccinate (sodium salt) (AOT) and cetyl pyridinium chloride (CPC) were 99% pure and characterized products of Sigma used in earlier studies.[11] The surfactants did not show minimum in surface tension-concentration profiles and, hence, were free from contamination by other surface active impurities. The NaCl was A. R. grade product of BDH, India. Doubly distilled water was used in all preparations.

Methods. In the conductance method, a concentrated solution of a surfactant was added in installments with a Hamilton microsyringe in water 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 with an accuracy of $\pm 0.01°$. After each addition, conductance of the solution was measured (after thorough mixing and temperature equilibration) with a Jenway conductometer, UK. The measurements were duplicated. The conductance values were uncertain within the limits of $\pm 2\%$.

The surface tension of the surfactant solutions was measured with a Krüss (Germany) tensiometer by the platinum ring detachment method after appropriate calibration.[15,16] Here, also
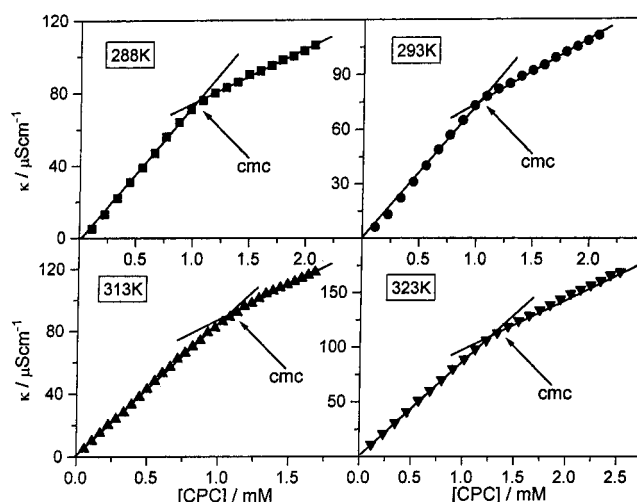
Figure 1. Conductometric determination of the CMC of CPC at different temperatures.
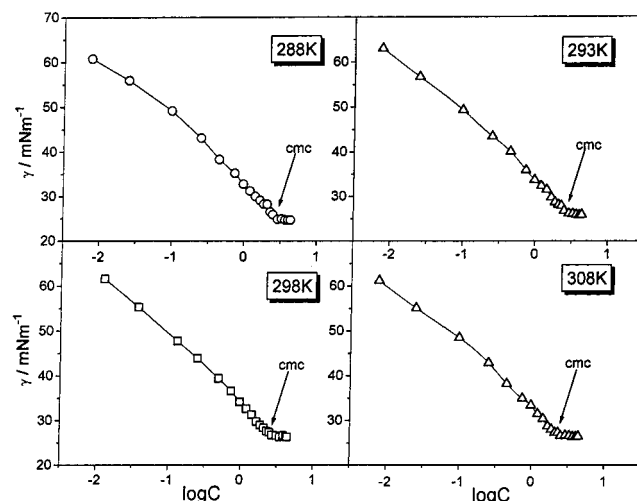

Figure 2. Tensiometric determination of the CMC of AOT at different temperatures.

the addition of the concentrated surfactant solution in installments using a Hamilton microsyringe was done 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 dyne.

The microcalorimetric measurements were taken in an OMEGA ITC microcalorimeter of Microcal Inc., USA. Aliquots of a concentrated surfactant solution of volume 5-20 μL were added in several installments in water (1.325 mL) taken in the cell and the heat flow for the dilution was measured.[1,11-14] 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 repeated at least twice to check reproducibility and were performed in the temperature range of 288-323K.

Results and Discussion

Critical Micellar Concentration (CMC). The CMCs of SDS, CPC and AOT have been measured by the conductometric, tensiometric and microcalorimetric methods. Typical experimental illustrations are presented in Figures 1-3. From the conductance vs concentration plot, the ratio of the slopes of the post and the pre CMC straight lines (the fraction of micellar dissociation)[17] was obtained; its difference from unity gives the
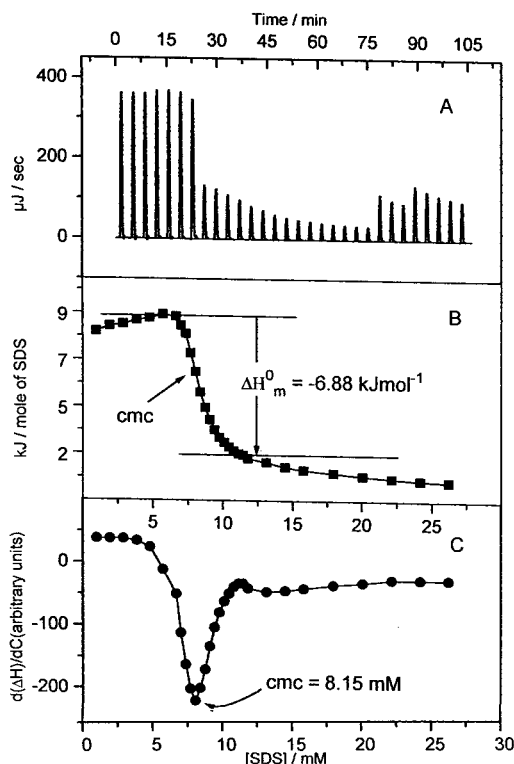
Figure 3. Titration of 237 μL aliquots of SDS micelles (160.55 mM) into 1.325 mL of water in 30 steps at 308 K: (A) heat flow vs time; (B) enthalpy change per mole of SDS vs [SDS]; (C) differential enthalpy change with respect to concentration vs [SDS].
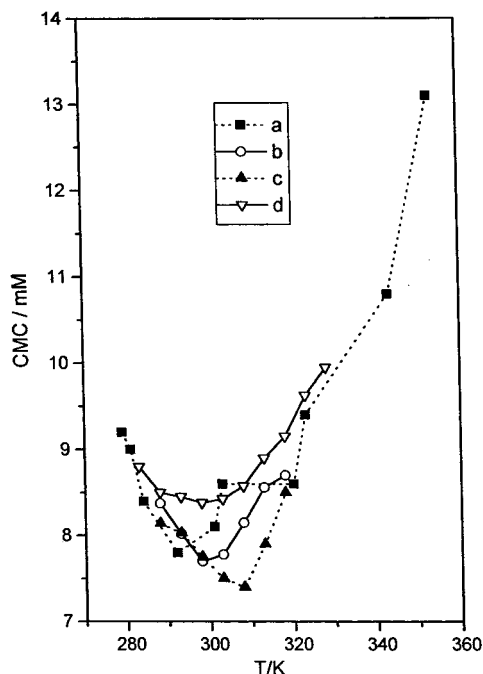
Figure 4. Temperature-dependent CMC of SDS from old and recent works: (a) Blume et al.,[12] microcalorimetry; (b) this work, microcalorimetry; (c) this work, conductometry; (d) Goddard and Benson,[18] conductometry.

fraction of counterions bound to the micelle. This is the f of equation (1C).

In Figure 4, the CMC-temperature profiles of SDS, by different methods are presented. In this representation, the past results of Goddard and Benson[18] and recent results of Blume et al.[12] are compared. It is observed that the CMC is method dependent as well as laboratory dependent of course for

microcalorimetry laboratory-wise dependence is within tolerated limits. The conductance results of Goddard and Benson[18] are significantly different from our observation. The CMC values of SDS obtained by others and us are presented in Table 1.

The agreement between the CMC results by microcalorimetry and surface tension methods for AOT is fairly good; the results on CPC by the methods of microcalorimetry and conductance exhibit tolerable difference in the middle range of the studied temperature. These results are presented in Tables 2 and 3. We conclude that the microcalorimetric method is sensitive and versatile in the determination of accurate CMC of surfactants. This is in line with recent observations.

Thermodynamics of Micellization. The thermodynamic parameters for micelle formation in the studied range of temperature have been evaluated from the equations (1−3) in which $d\ln X_{CMC}/dT$ and df/dT values at different temperatures are required. The $\ln X_{CMC}$ vs T as well as f vs T plots are not linear. Therefore, to evaluate ΔH_m° and ΔCp_m°, polynomial forms of variation of both $\ln X_{CMC}$ and f with temperature have been used. This is a standard procedure for handling the practical situation.[1,12,19−21] The relations and the followed procedure are given below

$$\ln X_{CMC} = a + bT + cT^2 \tag{4}$$

and

$$f = a' + b'T + c'T^2 \tag{5}$$

where a, b, and c as well as a', b', and c' are respective polynomial constants.

Then

$$\frac{d\ln X_{CMC}}{dT} = b + 2cT \tag{6}$$

and

$$\frac{df}{dT} = b' + 2c'T \tag{7}$$

were used in the eq 2C to evaluate the ΔH_m° according to the relation

$$\Delta H_m^\circ = -RT^2[(1 + f)(b + 2cT) + (b' + 2'cT)\ln X_{CMC}] \tag{8}$$

To obtain ΔCp_m°, the polynomial eq 9 was used

$$\Delta H_m^\circ = \alpha + \beta T + \gamma T^2 \tag{9}$$

The differentiation of 9 with respect to T then yields eq 10 to calculate the ΔCp_m°

$$\Delta Cp_m^\circ = \frac{d\Delta H_m^\circ}{dT} = \beta + 2\gamma T \tag{10}$$

All polynomial fittings have been made in a computer.

It is known that different kinds of fitting procedure of CMC with temperature are used to derive thermodynamic information. We have tried another fitting procedure used by Kresheck[1] in addition to those described above. This is given below

$$\ln X_{CMC} = k + \frac{l}{T} + m\ln T \tag{11}$$

$$f = k' + \frac{l'}{T} + m'\ln T \tag{12}$$

TABLE 1: CMC, f, and Thermodynamic Parameters of SDS at Different Temperatures[a]

| temp/K | f[b] | CMC/mM | | ΔG_m°/kJmol⁻¹ | ΔH_m°/kJmol⁻¹ | ΔS_m°/JK⁻¹mol⁻¹ | ΔCp_m°/JK⁻¹mol⁻¹ |
		cond[b]	cal[c]				
279	- - - - -	- - - - -	- - - (9.2)	- - - - -	- - - (- - -) [9.1]	- - - - -	- - - (- - -) [−468]
281	- - - - -	- - - - -	- - - (9.0)	- - - - -	- - - (- - -) [8.2]	- - - - -	- - - (- - -) [−467]
283	- - - (0.675)	- - - (8.80)	- - - - -	- - - - -	- - - - -	- - - - -	- - - - -
284	- - - - -	- - - - -	- - - (8.4)	- - - - -	- - - (- - -) [6.6]	- - - - -	- - - (- - -) [−464]
288	0.625 (0.660)	8.14 (8.50)	8.37 (- - -)	−34.2	5.2 (−14.7) [- - -]	137 (68)	−607 (−607) [- - -]
292	- - - - -	- - - - -	- - - (7.8)	- - - - -	- - - (- - -) [2.4]	- - - - -	- - - (- - -) [−457]
293	0.605 (0.647)	8.03 (8.45)	8.02 (- - -)	−34.6	2.4 (−17.8) [- - -]	126 (57)	−601 (−614) [- - -]
298	0.590 (0.632)	7.75 (8.38)	7.70 (- - -)	−35.0	−0.81 (−20.9) [- - -]	115 (47)	−595 (−622) [- - -]
301	- - - - -	- - - - -	- - - (8.1)	- - - - -	- - - (- - -) [−1.9]	- - - - -	- - - (- - -) [−449]
303	0.570 (0.622)	7.50 (8.43)	7.78 (8.6)	−35.0	−3.5 (−24.0) [−2.5]	104 (37)	−589 (−629) [−447]
308	0.553 (0.609)	7.40 (8.55)	8.15 (- - -)	−35.0	−6.9 (−27.1) [- - -]	92 (26)	−584 (−636) [- - -]
313	0.543 (0.600)	7.90 (8.88)	8.56 (- - -)	−35.3	−9.6 (−30.3) [- - -]	82 (16)	−578 (−644) [- - -]
318	0.531 (0.579)	8.50 (9.10)	8.70 (- - -)	−35.5	−12.3 (−33.7) [- - -]	73 (5.7)	−572 (−651) [- - -]
320	- - - - -	- - - - -	- - - (8.6)	- - - - -	- - - (- - -) [−10.0]	- - - - -	- - - (- - -) [−432]
323	- - - (0.582)	- - - (9.60)	- - - (9.4)	- - - - -	- - - (- - -) [−10.9]	- - - - -	- - - (- - -) [−430]
328	- - - (0.563)	- - - (9.95)	- - - - -	- - - - -	- - - - -	- - - - -	- - - - -
343	- - - - -	- - - - -	- - - (10.8)	- - - - -	- - - (- - -) [−16.8]	- - - - -	- - - (- - -) [−412]
353	- - - - -	- - - - -	- - - (13.1)	- - - - -	- - - (- - -) [−25.2]	- - - - -	- - - (- - -) [−403]

[a] The error limits of the CMC, ΔG_m°, ΔH_m°, ΔS_m° and ΔCp_m° are ±5, ±3, ±4, ±5, and ±5% respectively. [b] The parentheted values are of Goddard and Benson.[18] [c] The parentheted values are of Blume et al.[12] ΔH_m°, the nonparentheted values are our calorimetric data, the first bracketed values are calculated from van't Hoff equation using calorimetric CMC values, the third bracketed values are of Blume et al.[12] ΔS_m°, the nonparentheted values are calculated using calorimetric ΔH_m° values, the first bracketed values are calculated using van't Hoff ΔH_m° values. ΔCp_m°, the nonparentheted values are calculated using calorimetric ΔH_m° values, the first bracketed values are calculated using van't Hoff ΔH_m° values, the third bracketed values are of Blume et al.[12]

TABLE 2: CMC and Thermodynamic Parameters of CPC at Different Temperatures[a]

| temp/K | f | CMC/mM | | ΔG_m°/kJ mol⁻¹ | ΔH_m°/kJ mol⁻¹ | | ΔS_m°/JK⁻¹mol⁻¹ | | ΔCp_m°/JK⁻¹mol⁻¹ | |
		cond	cal		van·t Hoff	cal	van·t Hoff	cal	van·t Hoff	cal
288	0.60	1.01	1.0	−41.8	−31.4	3.65	36.2	158	−686	−794
293	0.57	1.01	1.0	−41.8	−34.9	0.50	23.4	144	−712	−768
298	0.55	0.96	1.03	−41.8	−38.5	−4.5	11.1	125	−739	−741
303	0.54	1.00	1.09	−42.0	−42.3	−7.8	−0.81	113	−765	−714
308	0.52	1.04	1.13	−42.1	−46.2	−10.4	−13.4	103	−792	−688
313	0.50	1.10	1.14	−42.1	−50.3	−14.4	−26.1	89	−818	−661
318	0.46	1.15	1.19	−41.4	−54.3	−17.9	−40.8	74	−845	−634
323	0.45	1.31	1.26	−41.6	−58.7	−20.6	−53.0	65	−871	−608

[a] The error limits of the f, CMC, ΔG_m°, ΔH_m°, ΔS_m° and ΔCp_m° are ±5, ±5, ±3, ±4, ±5, and ±5%, respectively.

TABLE 3: CMC and Thermodynamic Parameters of AOT at Different Temperatures[a]

| temp/K | CMC/mM | | ΔG_m°/kJ mol⁻¹ | ΔH_m°/kJ mol⁻¹ | | ΔS_m°/JK⁻¹mol⁻¹ | | ΔCp_m°/JK⁻¹mol⁻¹ | |
	s. t.	cal		van·t Hoff	cal	van·t Hoff	cal	van·t Hoff	cal
288	2.85	2.75	−32.0	−4.1	10.4	97	147	−23.1	−657
293	2.57	2.58	−32.8	−4.2	7.36	98	137	−23.2	−630
298	2.72	2.68	−33.2	−4.3	3.12	97	122	−23.3	−603
303	2.77	2.80	−33.7	−4.4	1.50	97	116	−23.4	−577
308	2.76	2.95	−34.1	−4.5	−2.58	96	102	−23.4	−550
313		3.10	−34.4	−4.7	−4.02	95	97	−23.5	−523
318		3.12	−34.9	−4.8	−6.50	95	89	−23.6	−497
328		3.05	−36.1	−5.0	−12.0	95	73	−23.8	−443

[a] The error limits of the CMC, ΔG_m°, ΔH_m°, ΔS_m° and ΔCp_m° are ±4, ±3, ±3, ±5, and ±5%, respectively.

Following the same treatment as above, the ΔH_m° was obtained from the relation

$$\Delta H_m^\circ = -RT^2\left[(1+f)\left(-\frac{l}{T^2}+\frac{m}{T}\right)+\left(-\frac{l'}{T^2}+\frac{m'}{T}\right)\ln X_{CMC}\right] \quad (13)$$

To obtain ΔCp_m°, the fitting eq 14 was used, the differentiation of which with respect to T then yields eq 15 to evaluate the ΔCp_m°

$$\Delta H_m^\circ = K + \frac{L}{T} + M\ln T \quad (14)$$

$$\Delta Cp_m^\circ = \frac{d\Delta H_m^\circ}{dT} = -\frac{L}{T^2} + \frac{M}{T} \quad (15)$$

where k, l, m, k', l', m', K, L, and M are the fitting parameters, obtained by the method of computation.

The results derived by the above two methods have nice agreement. Therefore, the set of eqs 4−10 is considered in deriving thermodynamic information. The standard Gibbs free energy of micellization, ΔG_m° refers to the hypothetical standard state of unit mole fraction. The working solutions were very dilute, and hence, the concentrations of the solutes were taken equal to their activities. The enthalpy and entropy of micellization obtained by the calorimetric method were also the standard state values as considered by different workers.[1,11−13,19]

The way of determination of CMC and ΔH_m° by the calorimetric method is given in Figure 3. The sets of enthalpy-[Surfactant] profile for the determination of CMCs of SDS, CPC and AOT are presented in Figures 5−7. The CMC and the

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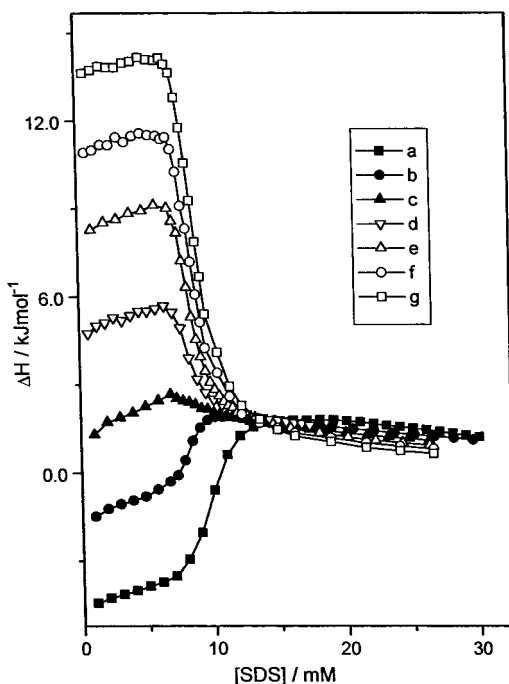
Figure 5. Microcalorimetric determination of ΔH_m° of SDS at different temperatures. (a) 288 K: titration of 251 μL aliquots of SDS micelles (162.90 mM) into 1.325 mL of water in 30 steps; (b) 293 K: titration of 271 μL aliquots of SDS micelles (160.37 mM) into 1.325 mL of water in 30 steps; (c) 298 K: titration of 233 μL aliquots of SDS micelles (162.90 mM) into 1.325 mL of water in 30 steps; (d) 303 K: titration of 240 μL aliquots of SDS micelles (160.55 mM) into 1.325 mL of water in 30 steps; (e) 308K: titration of 237 μL aliquots of SDS micelles (160.55 mM) into 1.325 mL of water in 30 steps; (f) 313 K: same as in d; (g)318 K: same as in d.

energetic parameters obtained on the three surfactant systems are presented in Tables 1−3. For revealing comparison of the past and recent works and the van't Hoff and microcalorimetric ways of evaluation of the thermodynamic parameters, all the processed results are illustrated in Figures 8−12. It is observed that the results based on the van't Hoff treatment and microcalorimetry without the consideration of *f* are close. If *f* is considered in the calculation (which is more appropriate), the discrepancy between the two is significant. The near agreement between the van't Hoff and calorimetric results without consideration of *f* as stated above is considered fortuitous.

Although the CMCs of surfactants determined by the calorimetric and other methods may fairly agree, the ΔH_m° obtained by the direct method of calorimetry in most cases appreciably differ[1−4] from that calculated from the temperature effect on CMC using the van't Hoff equation. Herein, we have observed significant difference between the results obtained by the two procedures. The changing aggregation number and shapes, and the counterion binding of micelles are considered to influence the ΔH_m° of the process which are usually not rigorously considered in the data treatment by the van't Hoff analysis. In the direct determination of the ΔH_m° by calorimetry, the consequence of the above effects is, on the other hand, included in the measurement. Corkill[22] has proposed a relation for the evaluation of ΔG_m° and ΔH_m° 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[23] to show the inefficiency of the van't Hoff method. In the past, there were even reports of agreement of ΔH_m°
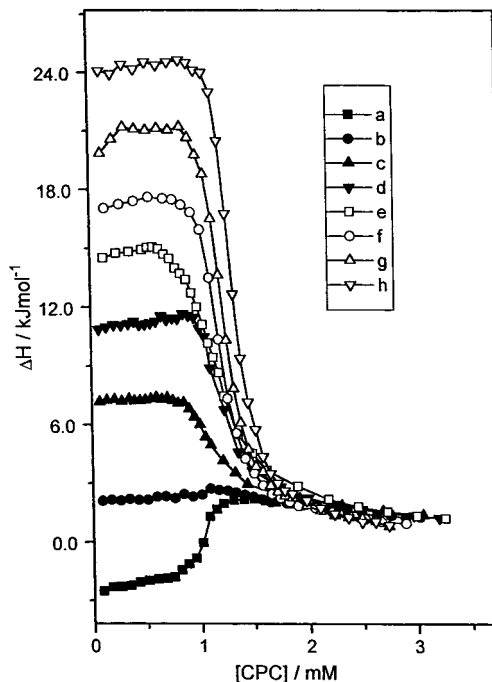

Figure 6. Microcalorimetric determination of ΔH_m° of CPC at different temperatures. (a) 288 K: titration of 134 μL aliquots of CPC micelles (22.75 mM) into 1.325 mL of water in 25 steps; (b) 293 K: titration of 190 μL aliquots of CPC micelles (22.61 mM) into 1.325 mL of water in 30 steps; (c) 298 K: titration of 191 μL aliquots of CPC micelles (22.73 mM) into 1.325 mL of water in 28 steps; (d) 303K: titration of 201 μL aliquots of CPC micelles (22.73 mM) into 1.325 mL of water in 30 steps; (e) 308 K: titration of 205 μL aliquots of CPC micelles (22.73 mM) into 1.325 mL of water in 28 steps; (f) 313 K: titration of 180 μL aliquots of CPC micelles (22.75mM) into 1.325 mL of water in 26 steps; (g)318 K: titration of 164 μL aliquots of CPC micelles (23.47 mM) into 1.325 mL of water in 30 steps; (h) 323 K: same as in g.

obtained by the methods of van't Hoff and calorimetry.[18] A number of past and recent measurements,[1−4] on the other hand, have revealed disagreement between the results obtained from the two methods.

Because the energetic parameters are expressed per mole of the amphiphile monomer, the contribution of the altered amphiphile aggregation by the effect of temperature evens out if the configurational changes[19] in the micelle contributes minimal to the process. It is considered that the molar enthalpy of the surfactant in micelles of different average sizes at a given temperature is likely to be small.[24,25] The altered aggregation changes the electrostatic surface potential to control the counterion condensation (binding) and is reflected on the value of *f*. Its estimation and use in the equation thus take care of the aggregation and the temperature related contributions of the bound counterions toward the overall free energy, and hence, the enthalpy change i.e., on the energetics of the process of micellization. With this rationale, the discrepancy between the results by the van't Hoff and calorimetric methods is sought elsewhere. The calorimetry measures the integral heat of the process (amphiphile-monomer association and otherwise) whereas the van't Hoff method gives differential heat of micellization.[2,4] The heats of solvation-desolvation of the species, their ionization, molecular rearrangement, mixing, etc may contribute their shares (significant or insignificant) toward the overall enthalpy change in the calorimetric measurements. Such contributions are normally absent in the equilibrium mass action concept of micelle formation seen in the light of $n(S^+$ or S^- or $S) \rightleftharpoons$ (S_n^+ or S_n^- or S_n) model (where, S^+ or S^- or $S =$ surfactant
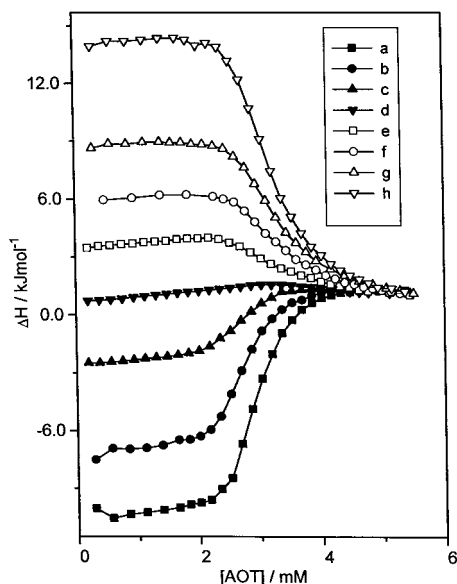
Figure 7. Microcalorimetric determination of ΔH_m° of AOT at different temperatures. (a) 288 K: titration of 320 μL aliquots of AOT micelles (25.17 mM) into 1.325 mL of water in 28 steps; (b) 293 K: same as in a; (c) 298 K: titration of 326 μL aliquots of AOT micelles (25.13 mM) into 1.325 mL of water in 30 steps; (d) 303 K: same as in a; (e) 308 K: same as in c; (f) 313 K: titration of 325 μL aliquots of AOT micelles (25.13 mM) into 1.325 mL of water in 25 steps; (g) 318 K: titration of 330 μL aliquots of AOT micelles (25.13 mM) into 1.325 mL of water in 27 steps; (h) 328 K: same as in a.
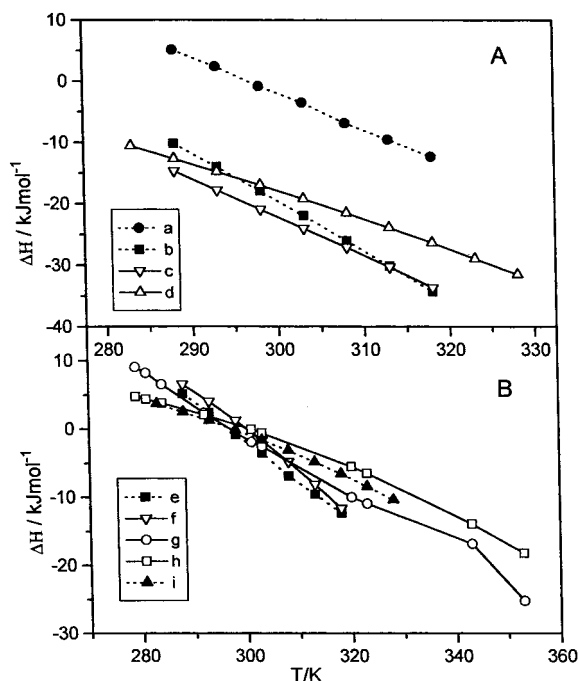
Figure 8. Temperature-dependent enthalpy of micellization of SDS evaluated in different ways and compared. (A) with f: (a) this work, microcalorimetry; (b) this work, conductometry by van't Hoff method; (c) this work, microcalorimetry by van't Hoff method; (d) Goddard and Benson,[18] conductometry by van't Hoff method. (B) without f: (e) this work, microcalorimetry; (f) this work, microcalorimetry by van't Hoff method; (g) Blume et al.,[12] microcalorimetry; (h) Blume et al.,[12] microcalorimetry by van't Hoff method; (i) Goddard and Benson,[18] conductometry by van't Hoff method.

monomer, S_n^+ or S_n^- or S_n = micelle and n = aggregation number) affected by the temperature to derive the ΔH_m° by the van't Hoff rationale. The difference in the two sets of results is better reflected on ΔS_m° (see Table). The large difference in
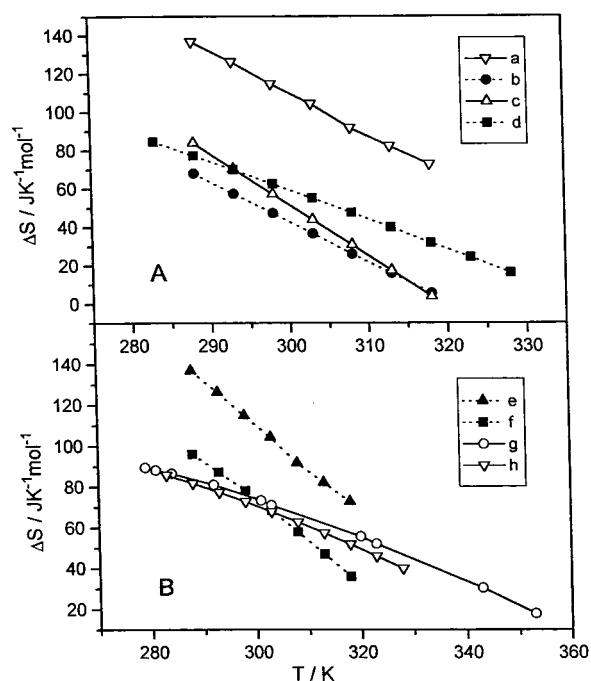
Figure 9. Comparison of temperature-dependent entropy of micellization of SDS evaluated in different ways. (A) with f: (a) this work, microcalorimetry; (b) this work, microcalorimetry by van't Hoff method; (c) this work, conductometry by van't Hoff method; (d) Goddard and Benson,[18] conductometry by van't Hoff method. (B) without f: (e) this work, microcalorimetry; (f) this work, microcalorimetry by van't Hoff method; (g) Blume et al.,[12] microcalorimetry by van't Hoff method; (h) Goddard and Benson,[18] conductometry by van't Hoff method.
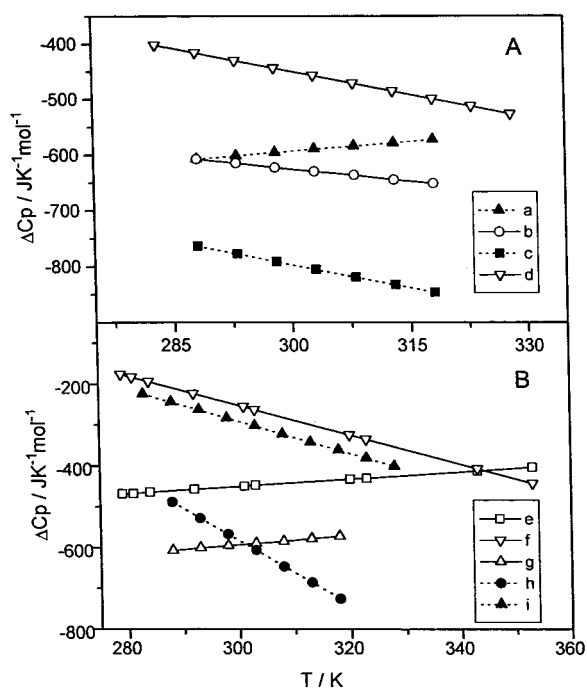
ΔH_m° produces larger difference in ΔS_m°. The $\Delta(\Delta H_m^\circ) = [(\Delta H_m^\circ)_{cal} - (\Delta H_m^\circ)_{vH}]$ and $\Delta(\Delta S_m^\circ) = [(\Delta S_m^\circ)_{cal} - (\Delta S_m^\circ)_{vH}]$ can be a measure of the additional effects that contribute toward the overall enthalpy and hence the entropy change during amphiphile self-aggregation leading to micellization. The differences between the calorimetric and van't Hoff enthalpies and hence entropies and heat capacities given in Table 4 mainly arise from the "hydrophobic" and "hydrophilic" hydration of the ionic surfactant monomers. During micellization, the monomers get rid of their hydrophobic hydration[26] (known as "icebergs" or "flickering clusters" around their nonpolar tails). The hydration of their headgroups upon incorporation in the micelles also gets readjusted according to the surface charge density consequent of monomer association and counterion condensation. Both of the processes are endothermic in nature and are associated with positive entropy change. The $\Delta(\Delta Cp_m^\circ) = [(\Delta Cp_m^\circ)_{cal} - (\Delta Cp_m^\circ)_{vH}]$ term likewise is expected to become positive. The results in Table 4, show $\Delta(\Delta H_m^\circ)$ to be significantly positive for both SDS and CPC (the latter is higher), and are slightly temperature dependent. The values for AOT are much lower and appreciably depend on temperature; at higher temperature the values are even negative. For the micellization of SDS and CPC, the shares of the contributing factors get compensated with increasing temperature which is not so for AOT. The low counterion association of AOT micelles (cf. Table 3) and its decline at higher temperature can be the reason for the low negative $\Delta(\Delta H_m^\circ)$; the increased solvation of the nonshielded micellar headgroups also contributes to the negative $\Delta(\Delta H_m^\circ)$. The $\Delta(\Delta S_m^\circ)$ evidences that the calorimetric entropy is appreciably higher than that by the van't Hoff method. The structural and solvation aspects discussed above in connection with the enthalpy change are also applicable to the trend of $\Delta(\Delta S_m^\circ)$. At higher temperature, the van't Hoff

TABLE 4: Differences between the Thermodynamic Parameters Realized by the Calorimetric and van't Hoff Methods for SDS, CPC and AOT Surfactants at Different Temperatures
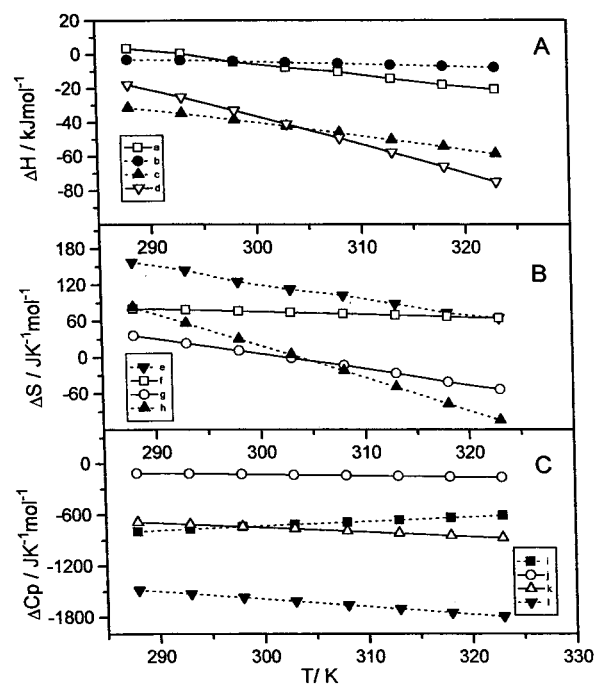
temp/K	$\Delta(\Delta H_m^\circ)$/kJ mol^{-1}			$\Delta(\Delta S_m^\circ)$/JK^{-1}mol^{-1}			$\Delta(\Delta Cp_m^\circ)$/JK^{-1}mol^{-1}		
	SDS	CPC	AOT	SDS	CPC	AOT	SDS	CPC	AOT
288	20	35	15	69	122	50	0	−108	−634
293	20	35	12	69	121	39	13	−56	−607
298	20	34	7	68	114	25	27	−2	−580
303	21	34	6	68	114	19	40	51	−554
308	20	36	2	66	116	6	52	104	−527
313	21	36	0.6	66	115	2	66	157	−500
318	21	36	−2	67	114	−6	79	211	−473
323		38			106			263	
328			−7			−22			−419

TABLE 5: Salt (NaCl) Effect on the CMC and Thermodynamic Parameters of SDS and CPC at 303 K, and of AOT at 293 K Determined by Microcalorimetry

|	SDS				CPC					AOT				
[NaCl]/ M	CMC/ mM	$-\Delta G_m^\circ$/kJ mol^{-1}	$-\Delta H_m^\circ$/kJ mol^{-1}	ΔS_m°/JK^{-1} mol^{-1}	[NaCl]/ M	CMC/ mM	$-\Delta G_m^\circ$/kJ mol^{-1}	$-\Delta H_m^\circ$/kJ mol^{-1}	ΔS_m°/JK^{-1} mol^{-1}	[NaCl]/ M	CMC/ mM	$-\Delta G_m^\circ$/kJ mol^{-1}	ΔH_m°/kJ mol^{-1}	ΔS_m°/JK^{-1} mol^{-1}
0	7.78	22.4	3.50	62	0	1.09	27.3	7.80	64	0	2.58	32.8	1.49	117
0.02	3.68	24.2	3.77	68	0.005	0.41	29.8	7.10	75	0.005	2.03	33.6	6.66	137
0.05	2.33	25.4	4.52	69	0.01	0.23	31.3	7.85	77	0.0075	1.62	34.3	6.49	139
0.1	1.72	26.2	5.60	68	0.02	0.17	31.9	8.38	78	0.01	1.54	34.5	5.24	136
0.2	0.90	27.8	5.74	73	0.04	0.12	32.9	9.02	79	0.015	1.37	34.9	2.90	129
0.4	0.54	29.1	7.21	72	0.1	0.08	33.9	9.86	79					
0.8	0.30	30.6	7.36	77										

Figure 10. Comparison of temperature dependent ΔCp_m° of SDS evaluated in different ways. (A) with f: (a) this work, microcalorimetry; (b) this work, microcalorimetry by van't Hoff method; (c) this work, conductometry by van't Hoff method; (d) Goddard and Benson,[18] conductometry by van't Hoff method. (B) without f: (e) Blume et al.,[12] microcalorimetry; (f) Blume et al.,[12] microcalorimetry by van't Hoff method; (g) this work, microcalorimetry; (h) this work, microcalorimetry by van't Hoff method; (i) Goddard and Benson,[18] conductometry by van't Hoff method.

Figure 11. Comparison of temperature dependent thermodynamic parameters for CPC micellization evaluated in different ways. (A) ΔH_m°: (a) this work, microcalorimetry; (b) this work, microcalorimetry by van't Hoff method without f; (c) same by considering f; (d) this work, conductometry by van't Hoff method with f. (B) ΔS_m°: (e) this work, microcalorimetry; (f) this work, microcalorimetry by van't Hoff method without f; (g) same by considering f; (h) this work, conductometry by van't Hoff method with f. (C) ΔCp_m°: (i) this work, microcalorimetry; (j) this work, microcalorimetry by van't Hoff method without f; (k) same by considering f; (l) this work, conductometry by van't Hoff method with f.

enthalpy related entropy of micellization of AOT exceeds that from calorimetry yielding negative $\Delta(\Delta S_m^\circ)$ showing minimal contribution of the hydrophobic effect on micellization. The $\Delta(\Delta Cp_m^\circ)$ for the micellization of SDS and CPC are small and they marginally increase with temperature. The positive values for SDS and that at higher temperature for CPC speak in favor of organizational lability in the micellar association. The negative and large values of $\Delta(\Delta Cp_m^\circ)$ for AOT micellization

means organization of amphiphiles to form micelles with enhanced hydration of the exposed interfacial ester headgroups.

The ΔCp_m° values for SDS, CPC, and AOT are all negative, and are more or less of comparable magnitudes. Negative ΔCp_m° are normally observed for the self-association of amphiphiles leading to micelle formation.[1,3,12] This is in line with
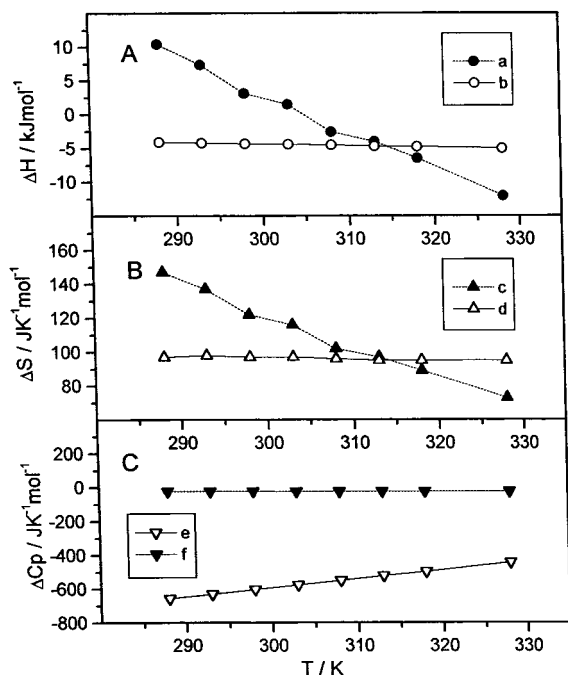
Figure 12. Comparison of temperature dependent thermodynamic parameters for AOT micellization evaluated in different ways. (A) ΔH_m°: (a) this work, microcalorimetry; (b) this work, microcalorimetry by van't Hoff method. (B) ΔS_m°: (c) this work, microcalorimetry; (d) this work, microcalorimetry by van't Hoff method. (C) ΔCp_m°: (e) this work, microcalorimetry; (f) this work, microcalorimetry by van't Hoff method.

the transfer of amphiphiles from their hydrophobically hydrated (ordered) state in the aqueous medium to the more labile solvent free micellar interior. For an increase in temperature of 30 K, 35 K, and 40 K, the $\Delta(\Delta Cp_m^\circ)$ values have increased by 0.079, 0.361, and 0.215 kJK^{-1}mol^{-1} for SDS, CPC, and AOT, respectively; the behavior of SDS is much different in this
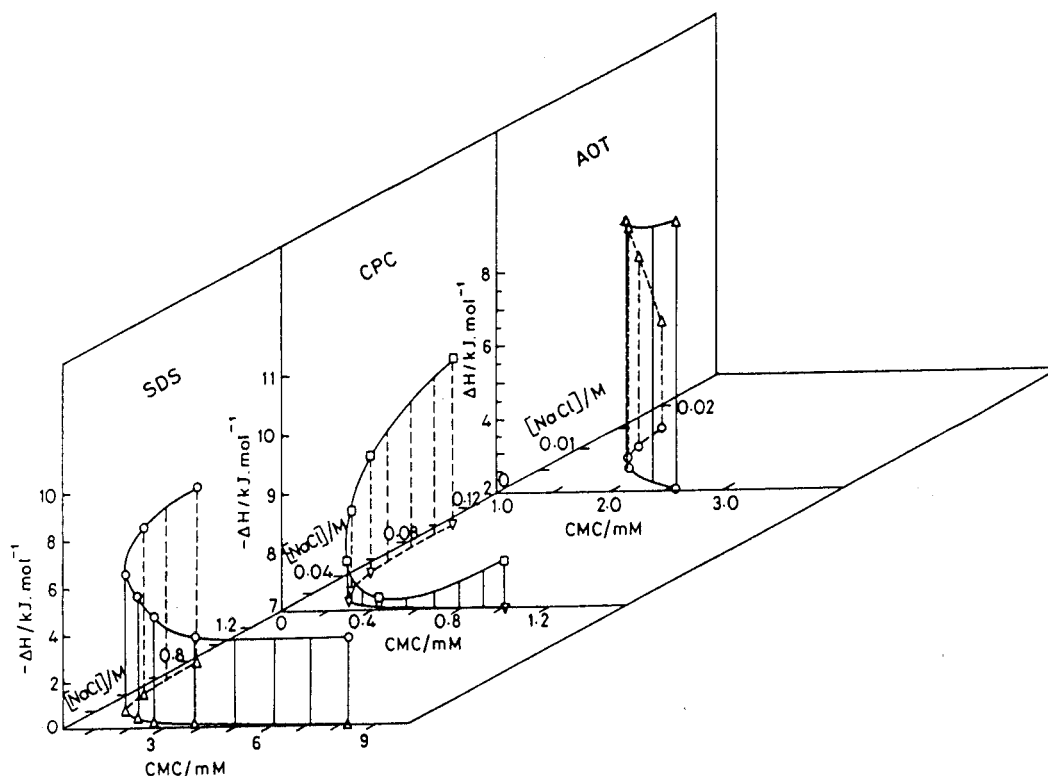
respect. The nonspecific processes registered in calorimetry virtually get eliminated at elevated temperature for the micellization of SDS but they fairly sustain in the cases of CPC and AOT. The ΔCp_m° varies linearly with temperature producing much greater slopes for CPC and AOT compared to SDS because the structural changes in the formers (CPC and AOT) are more than that in the latter (SDS).

Salt (NaCl) Effect on the CMC and the Energetics. The CMC and the energetics of micellization of the studied surfactants are affected by the addition of NaCl. The CMC has significantly decreased in the cases of SDS and CPC; the latter is more susceptible to the salt. The NaCl has shown a comparatively mild effect on the CMC of AOT.

In the computation of ΔG_m° from eq 1C, the f values of SDS, CPC, and AOT are required. The f values obtained from the slope ratio method (mentioned in the Results and Discussion section, page 4) at 303 K for SDS and CPC are 0.57 and 0.54, respectively. The counterion binding of ionic micelles with varied [counterion] in salt environment can be also evaluated using the Corrin-Harkins[8,27] equation

$$\log \text{CMC} = \text{CONSTANT} - f\log[\text{counter ion}] \quad (16)$$

Such plots (not shown) in the present study using the values of CMC and [NaCl] given in Table 5 have produced f values of 0.69 and 0.53 for SDS and CPC, respectively. The f for AOT obtained at 293K following the above procedure has been 0.35. The f values obtained at different temperatures for SDS and CPC from the slope ratio method are consistent. The Corrin−Harkins[8,27] method has shown a difference for SDS and not for CPC; the f for AOT is unavailable in the literature. We have, therefore, used the f value for SDS as obtained from the slope ratio method and that for AOT from the Corrin-Harkins[8,27] method in the energetic calculations in the presence of NaCl. The CPC has no discrepancy in this matter. It may be mentioned that in the Corrin−Harkins[8,27] rationale the counterion binding

Figure 13. Three-dimensional representation of ΔH_m°, CMC and [NaCl] of SDS and CPC at 303 K and AOT at 293 K.

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has been considered to be independent of [salt]. The effect of changed aggregation number in the salt environment on the counterion condensation has been also ignored.

The micellization process of SDS and CPC are both exothermic whereas that of AOT is endothermic; the ΔH_m° has decreased with increasing [NaCl] for both SDS and CPC whereas it has passed through a maximum for AOT. The exo- and endothermicities of micellization herein observed advocate differences in the kinds and strengths of the involved physicochemical processes during surfactant self-aggregation. At equal levels of [NaCl], the ΔS_m° for SDS and CPC are comparable whereas that for AOT is higher. This is in line with the exo- and endothermicity situations, the former produces more disorder in the system than the latter. The thermodynamic results of SDS and CPC at 303 K and AOT at 293 K are presented in Table 5.

In Figure 13, the simultaneous dependence of CMC and ΔH_m° on the [NaCl] is shown in three dimensions. The SDS and CPC show similar kind of dependence whereas that of AOT is distinctly different. For the increasing presence of NaCl, the first two amphiphiles have shown increased exothermicity of micellization, which is more endothermic for the third i.e., AOT.

Conclusions

The CMC of SDS obtained by the method of microcalorimetry differs from that obtained by the method of conductance. In this comparison the results on CPC by microcalorimetry and conductance, and AOT by microcalorimetry and surface tension reasonably agree. The ΔH_m° and ΔCp_m° values calculated by van't Hoff method and directly determined by the microcalorimetric method are significantly different. This difference is considered to arise from the physicochemical processes other than the amphiphile aggregation that contribute to the overall heat measured in the calorimeter. The salt NaCl has been found to significantly depress the CMC; the effect is prominent on SDS and CPC, and mild on AOT. The ΔH_m° has been found to be more exothermic for SDS and CPC, and more endothermic for AOT in the presence of increasing [NaCl].

References and Notes

(1) Kresheck, G. C. *J. Phys. Chem.* **1998**, *102*, 6596.
(2) Naghibi, H.; Tamura, A.; Sturtevant, J. M. *Proc. Natl. Acad. Sci. U.S.A.* **1995**, *92*, 5597.
(3) Kresheck, G. C.; Hargraves, W. A. *J. Colloid Interface Sci.* **1974**, *48*, 481.
(4) Franks, F.; Reid, D. S. *Water: A Comprehensive Treatise*; Franks, F., Ed.; Plenum Press: New York, 1975: Vol. II, p 337.
(5) Attwood, D.; Florence, A. T. *Surfactant Systems, Their Chemistry, Pharmacy and Biology*; Chapman and Hall: London, New York, 1983; pp 72−117.
(6) Mukerjee, P. *Adv. Colloid Interface Sci.* **1967**, *1*, 241.
(7) Moulik, S. P. *Current Sci.* **1996**, *71*, 368.
(8) Nakamura, A. A.; Hisatomi, M.; Sugihara, G.; Fujiwara, M.; Okano, T. *J. Surf. Sci. Technol.* **1998**, *14*, 23.
(9) Sugihara, G.; Mukerjee, P. *J. Phys. Chem.* **1981**, *85*, 1612.
(10) Moroi, Y. *Micelles, Theoretical and Applied Aspects*; Plenum Press: New York, 1992. (10a) The reports on temperature dependence of micellar aggregation number are scanty in the literature. The aggregation number of micelles of nonionic and ionic surfactants has weak to very weak dependence on temperature. An increase in aggregation number from 117 to 159 for a temperature increase of 25° (from 288 to 313K) has been obtained for TritonX-100 (Chatterjee, A.; Dey, T.; Sanyal, S. K.; Moulik, S. P. *J. Surf. Sci. Technol.* (accepted)). We have shown therein that the use of the aggregation number in the equation of Corkill et al. (Corkill, J. M.; Goodman, J. F.; Harrold, S. P. *Trans. Faraday Soc.* **1964**, *60*, 202) has a minor effect on the free energy of micellization. Of course TritonX-100 may show increased aggregation of monomer at temperature near to its cloud point. The ionic surfactants N-cetyl-N-ethanolyl-N, N-dimethyl and N-cetyl-N, N-diethanolyl-N-methyl ammonium bromides (CEDAB and CDMAB, we have studied) have shown practically unchanged aggregation number for a rise in temperature of 30° (from 293 to 323K) (Chatterjee, A.; Maity, S.; Sanyal, S. K.; Moulik, S. P. *Langmuir* (under consideration)).
(11) Majhi, P. R.; Moulik, S. P. *Langmuir* **1998**, *14*, 3986.
(12) Paula, S.; Süs, W.; Tuchtenhagen, J.; Blume, A. *J. Phys. Chem.* **1995**, *99*, 11742.
(13) Majhi, P. R.; Blume, A. *Langmuir* **2001**, *17*, 3844.
(14) Lah, J.; Pohar, C.; Vesnaver, G. *J. Phys. Chem.* **2000**, *104*, 2522.
(15) Moulik, S. P.; Ghosh, S. *J. Mol. Liq.* **1997**, *72*, 145.
(16) Ghosh, S.; Moulik, S. P. *J. Colloid Interface Sci.* **1998**, *208*, 357.
(17) Lianos, P.; Lang, J. *J. Colloid Interface Sci.* **1983**, *96*, 222.
(18) Goddard, E. D.; Benson, G. C. *Can. J. Chem.* **1957**, *35*, 986.
(19) Onori, G.; Santucci, A. *J. Phys. Chem.* **1997**, *101*, 4662.
(20) Blume, A.; Tuchtenhagen, J.; Paula, S. *Prog. Colloid Polym. Sci.* **1993**, *93*, 118.
(21) Blandamer, J.; Cullis, P. M.; Engberts, J. B. F. N. *Pure Appl. Chem.* **1996**, *68*, 1577.
(22) Corkill, J. M.; Goodman, J. F.; Harrold, S. P. *Trans. Faraday Soc.* **1964**, *60*, 202.
(23) Holtzer, A.; Holtzer, M. F. *J. Phys. Chem.* **1974**, *78*, 1442.
(24) Desnoyers, J. E.; Caron, G.; De Lisi, R.; Roberts, D.; Roux, A.; Perron, G. *J. Phys. Chem.* **1983**, *87*, 1397.
(25) Olofsson, G. *J. Phys. Chem.* **1985**, *89*, 1473.
(26) Muller, N. *Acc. Chem. Res.* **1990**, *23*, 23.
(27) Corrin, M. L.; Harkins, W. D. *J. Am. Chem. Soc.* **1947**, *69*, 684.