Self-Aggregation of Ionic C$_{10}$ Surfactants Having Different Headgroups with Special Reference to the Behavior of Decyltrimethylammonium Bromide in Different Salt Environments: A Calorimetric Study with Energetic Analysis

Indranil Chakraborty and Satya P. Moulik*

Centre for Surface Science, Department of Chemistry, Jadavpur University, Kolkata 700 032, India

Received: October 3, 2006; In Final Form: February 13, 2007

Self-aggregation of C$_{10}$ ionic surfactants with different head groups, viz., decylpyridinium chloride, sodium decylsulfate, decylammonium bromide, decyldimethylammonium bromide, and decyltrimethylammonium bromide, was studied in the aqueous medium by microcalorimetric and conductometric methods. The effects of temperature and different salts (NaF, NaCl, NaBr, NaI, Na$_2$SO$_4$, Na$_2$S$_2$O$_7$, Na-benzoate, and Na-salicylate) were also studied on decyltrimethylammonium bromide representatives. The cmc, counterion binding, and energetics of micellization were evaluated and discussed. The energetic parameters, enthalpy, entropy, and specific heat of micellization obtained from direct calorimetry and the indirect van't Hoff method were compared and discussed.

Introduction

Self-aggregation or micellization of surfactants in solution is a well-studied phenomenon, in which types of the surfactants and their environmental conditions play important roles.[1] The ionic and nonionic surfactants manifest distinct solution behaviors, and overall physicochemical treatment for the latter is simpler than the former. The presence of ionic charges in the former produces additional effects by electrostatic interactions. The phenomenon of counterion binding needs estimation for quantification of the micellization process. The micellar aggregation number, their shape, and polarity are other physicochemical parameters, knowledge on which is essential for a pragmatic characterization of the micelle.

The important basic property of self-aggregation of amphiphiles is the critical micellar concentration or cmc, which is an essential parameter for evaluation of energetics of the process. There are a number of methods for cmc determination of which tensiometry, conductometry, fluorimetry, and dye solubilization are very frequently used. Its determination at different temperatures helps to evaluate the enthalpy change associated with the process by the use of the van't Hoff equation, which is a time-consuming experimental procedure. The accuracy of the derived enthalpy essentially depends on the accuracy and the range of temperature used for the measurements.

In recent years, microcalorimetric determination of enthalpy of dilution of a concentrated surfactant solution in an isothermal titration calorimeter (ITC) has emerged as a potential method to determine both the parameters. This has surpassed all other methods for the ability of the accurate determination of both cmc and ΔH_m from a single run. Like other workers,[2,3] we have employed the method of ITC on different micelle-forming systems to estimate energetics of the process.[4−10] In this venture, we also became interested to compare the ITC results with that of van't Hoff and have found major discrepancies between the two, particularly for ionic surfactants.[6−8,11−13] This has been explained on the basis of a basic difference between the two

procedures. The van't Hoff way is a differential procedure concerning the monomer ↔ micelle equilibrium process based on the relation $\Delta H_m = R \ [d \ \log \ cmc/d(1/T)]$, whereas the calorimetric enthalpy is an integral quantity related to the micellization and other associated processes, both specific and nonspecific, that may arise in the system. In this consideration, change in the structure of the solvent, solvation of the species formed, their orientation in the aggregates, etc. contribute to the overall energetics of the process.

In understanding the micellization process and its energetics, although surfactants of different types have been experimented upon, systematic studies on small alkyl chain representatives have remained unattempted. In the present study, several micelle-forming amphiphiles with varied head groups and a fixed alkyl chain of ten carbon atoms were chosen and physicochemistry of their micellization was studied by microcalorimetry and conductometry. The amphiphile representatives used were sodium decylsulfate (C$_{10}$DS), decylammonium bromide (C$_{10}$AB), decyldimethylammonium bomide (C$_{10}$-DMAB), decyltrimethylammonium bromide (C$_{10}$TMAB), and decylpyridinium chloride (C$_{10}$PC). Of these five representatives, the self-aggregation of C$_{10}$TMAB at different temperatures and salt environments was also investigated. Details of this energetic study have been presented to shed light on the role of the head groups on the energetic parameters as well as the differences between the integral and differential method dependent enthalpy changes and hence the associated entropy changes. In the above context, a short account of the reported solution properties of C$_{10}$TMAB would not be out of place here. The C$_{10}$TMAB is an infrequently studied surfactant. Mukerjee and Mysels[14] reported a cmc of 65 mM at 298 K from electrical transport measurements. Alkhamis et al.[15] obtained cmc values of 53.5 and 60.6 mM at 298 and 310 K, respectively. In a recent work, the value has been found to be 66.3 and 66.9 mM at 310 K by tensiometry and conductometry, respectively.[9] From a simulation procedure, Pal et al.[16] reported an aggregation number of 47 for C$_{10}$TMAB assuming all counterions (Br$^-$) condensed on the micellar surface, which was in close agreement with the light

Self-Aggregation of Ionic C$_{10}$ Surfactants

J. Phys. Chem. B, Vol. 111, No. 14, 2007 **3659**

scattering results of Debye.[17] Neutron scattering[18] and mass spectrometry[19] experiments have reported cmc and transport properties of C$_{10}$TMAB wherein the reported aggregation number was quoted to be 40. The counterion condensation on C$_{10}$TMAB micelles has remained mostly undone, particularly at varied temperatures.

Materials

C$_{10}$TMAB (98%) and C$_{10}$DS (98%) were products of Fluka (Germany) and Sigma (USA), respectively. The other surfactants C$_{10}$AB, C$_{10}$DMAB, and C$_{10}$PC (99% pure samples) were gifted by Professor R. Palepu, St. Francis Xavier University, Nova Scotia, Canada. All solutions were prepared in doubly distilled conductivity water of specific conductance 2−3 μS cm^{-1} at 313 K.

Methods

Microcalorimetry. An OMEGA, ITC, microcalorimeter of Microcal, Northampton (USA) was used for thermometric measurements. A concentrated solution of the surfactant (∼20× cmc) was taken in the microsyringe, and 320 μL of it was added at equal time intervals of 210 s in multiple stages (50 additions) to 1.325 mL doubly distilled, filtered (through Millipore filter), degassed water, taken in the calorimeter cell under constant stirring (300 rpm) condition. Then, 1.6 mL of the same water was taken in the reference cell. The heat released or absorbed at each step of injection of the surfactant in water was measured by recording the power elapsed by the instrument to bring the sample cell to its initial condition (thermal equlibrium with the sample cell), and the enthalpy per mole of the surfactant was calculated using the ITC software. Each run was duplicated to check reproducibility. All measurements were taken at thermo-stated conditions maintained by a Neslab RTE100 circulating water bath (below 5 K of the experimental temperature). The temperature of the sample and reference cells was scanned to the desired level, which was maintained in the calorimetric system within the accuracy of ±0.01 K. Basically, in the experiments, heats of dilution of a concentrated surfactant solution was measured in multisteps, which showed a rapid change in the micellization region of concentration in the cell solution enabling us to locate the cmc point in the thermo-gram.[20,21] The enthalpy of the micellization process can also be estimated from the choice of specific points in the enthal-pogram to be discussed subsequently.

Conductometry. Conductometric experiments were per-formed in a Jenway (UK) conductivity meter. Doubly distilled conductivity water (10 mL) was taken in a closed container placed in a water bath of accuracy ±0.01 K. Concentrated surfactant solutions (∼20× cmc) were progressively added in water in stages with a Hamilton microsyringe. At each stage, the specific conductance (κ) was measured with a cell of unit cell constant. The [surfactant] corresponding to the break point in the κ vs [surfactant] profile corresponded to the cmc at the temperature of measurement. The degree of counterion con-densation on the micelle was calculated using the slope−ratio method wherein the pre- and post-cmc slopes of the linear plots S_1 and S_2 were determined by the least-squares method and the fraction of the condensed counterion at the micellar interface (β) was obtained from the relation[22,23] $\beta = (1 - S_2/S_1)$.

Results and Discussion

General Background and the Five Decyl Representatives. Determination of the cmc of an amphiphile using microcalo-
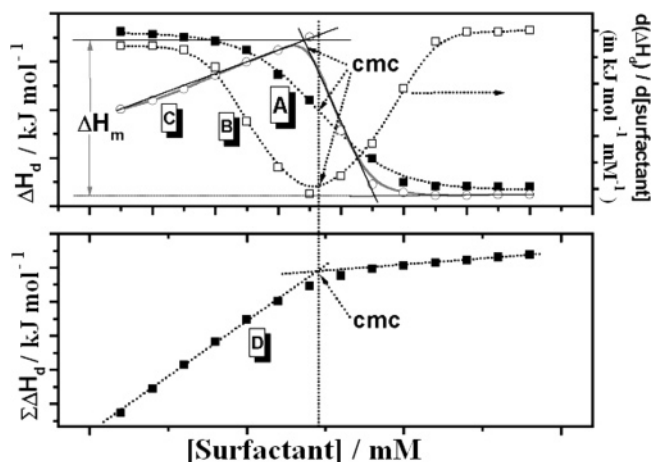

Figure 1. Typical microcalorimetric profiles for the enthalpy of dilution of surfactants. (A) Ideal curve. (B) Differential plot of A. (C) Nonideal dilution curve (C$_{10}$ surfactants behavior). (D) van Os method of cumulative (ΣH_d) plotting. The dotted vertical line passes through the cmc points of A, B, and D. Being a generalized representative illustration, the axes magnitudes are not used.

rimetry requires titration of a concentrated surfactant solution in water up to a concentration beyond the cmc of the surfactant in the calorimeter cell under isothermal, constant stirring conditions. During the course of this titration, initially, the solution undergoes demicellization associated with monomer dilution. This process corresponds nearly to a nonvarient enthalpy change (ΔH_i) expressed per unit concentration of the amphiphile that results for non-interacting or weakly interacting species (ions or molecules) in solution. At the state of micel-lization and above, the solution undergoes micellar dilution (and no further demicellization) with an appreciable change in the enthalpy that remains fairly constant with increasing [am-phiphile]. The whole enthalpy course, therefore, consists of three different regions; two more or less horizontal regions intervened by a sharply declining or increasing one, and the height between the final and the initial horizontal stages correspond to the enthalpy of micellization. The surfactant concentration corre-sponding to the inflection point in the first derivative plot corresponds to the cmc of the surfactant.[7,8,22−24] The above description is depicted in Figure 1.

Curve A represents an ideal situation of sigmoidal variation of enthalpy of dilution with [surfactant] whose derivative plot is depicted in curve B. The perpendicular dotted line crosses the curves at points that correspond to the cmc. Curve C represents a nonideal system where the initial enthalpies of dilution vary. The first inflection point in the curve (herein shown by the arrowhead) essentially corresponds to the point of micelle formation.

Hait et al.[25] reported a convenient method for the determi-nation of cmc using the sigmoidal Boltzman fitting (SBF) procedure using the relation

$$\Delta H_d = \frac{(\Delta H_{d(i)} - \Delta H_{d(f)})}{[1 + \exp([\text{surfactant}] - \text{cmc})/\Delta[\text{surfactant}]]} + \Delta H_{d(f)} \quad \text{(A)}$$

where ΔH_d is the enthalpy of dilution of the surfactant, $\Delta H_{d(i)}$ and $\Delta H_{d(f)}$ are the values at the initial and final states, respectively, [surfactant] is the surfactant concentration in the system, and Δ[surfactant] is the constant interval of [surfactant]. Mathematically, this is similar to the first derivative method as cmc values in both the processes correspond to the inflection
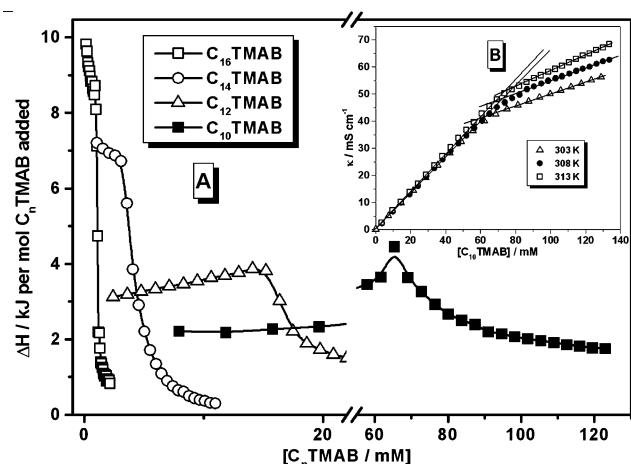
Figure 2. Enthalpy of dilution profiles for the self-aggregating alkyltrimethylammonium bromides with varied chain lengths. Inset: the specific conductance−concentration profiles of $C_{10}TMAB$ at 303, 308, and 313 K.

point in the ΔH_d vs [surfactant] plots. The SBF procedure is more elegant because it gives the cmc as a fitting parameter with associated experimental error and also gives the initial and final asymptote values for the evaluation of the enthalpy of micellization (ΔH_m) also with experimental error; arbitrariness in the visual estimation process does not influence the results.

For nonideal (interacting) amphiphilic systems, the initial enthalpies of dilution do not remain constant over the [amphiphile] (Figure 1, curve C). The non-sigmoidal pattern makes the SBF procedure inapplicable and incurs error in cmc and associated enthalpy evaluation. The point that corresponds to the change in the initial slope is considered in enthalpy calculation.[26] The cmc can be evaluated from the inflection point or the derivative plot as mentioned above. The van Os method of cumulated enthalpy ($\Sigma\Delta H_d$) analysis[27] procedure can also be used, which produces a break in the $\Sigma\Delta H_d$ vs [surfactant] profile (curve D, Figure 1) that normally tallies well with the cmc obtained by the other methods, viz., differential and SBF.

Although Blandamer et al. [2,3] reported ΔH_d as a quantity nearly independent of the [$C_{16}TMAB$], we have found a finite dependence of ΔH_d on the surfactant concentration for the C_n-TMAB surfactants as shown in Figure 2. The inclination of the initial slope of ΔH_d decreases with increasing surfactant chain length. The SBF procedure for the C_{16}, C_{14}, and $C_{12}TMAB$ led to moderately satisfactory results,[9] whereas the enthalpogram for $C_{10}TMAB$ deviated strongly. The cmc realized by the first derivative procedure yielded a higher value. We have, therefore, considered the initial sharp break point as the cmc in line with Blandamer et al.[3] and McClements et al.[28,29] The non-sharp transition pathway in the enthapogram resulted from the contributions of different physicochemical factors to the thermodynamics of the self-aggregating process. The change in micellar structure, their solvation, change in aggregation number, etc. were the specific and nonspecific factors that contributed to the calorimetric ΔH_m, a discussion on which will be taken up subsequently. The value was in close agreement with our previously reported data[9] by tensiometry (66.3 mM) and conductometry (66.9 mM). The past reports[14] were 64.6−67 mM at 298 K. The close resemblance in cmc between conductometry (Figure 2A) and microcalorimetry (Figure 2B) was also herein evidenced for $C_{10}TMAB$. The data are reported in Table 1. The cumulative method of van Os produced two inflections at 11.8 and 28.5 mM (illustration not shown), and both were different from the expected cmc value. This was an unusual manifestation of the analytical procedure.

TABLE 1: Critical Micellar Concentration and Related Thermodynamic Parameters of Different C_{10} Surfactants at 30 °C[a]

surfactant	cmc$_B$	cmc$_{SB}$	cmc$_D$	cmc$_C$	β	ΔH_m^0	ΔG_m^0	ΔS_m^0
$C_{10}PC$	19.2	23.3	24.7	19.8	0.59	−1.93	−31.9	99
$C_{10}DS$	34.2	44.6	42.6	32.3	0.74	−1.22	−32.4	103
$C_{10}AB$	50.8	61.0	60.8	52.3	0.75	−1.59	−30.9	97
$C_{10}TMAB$	60.2	69.7		62.7	0.67	−1.59	−28.7	90
$C_{10}DMAB$	61.7	73.9	77.7	62.1	0.70	−1.05	−29.1	93

[a] The cmc values are expressed in mM. ΔH_m^0 and ΔG_m^0 are expressed in kJ mol^{-1} and ΔS_m^0 in J K^{-1} mol^{-1}, respectively. The subscripts B, SB, D, and C to cmc correspond to the cmc obtained from the first break in the enthapogram, SBF, first derivative of enthalpy, and conductometry, respectively. The cmc$_B$ and cmc$_C$ were in fair agreement. For energetic analysis, β from conductometry and cmc$_B$ were used.
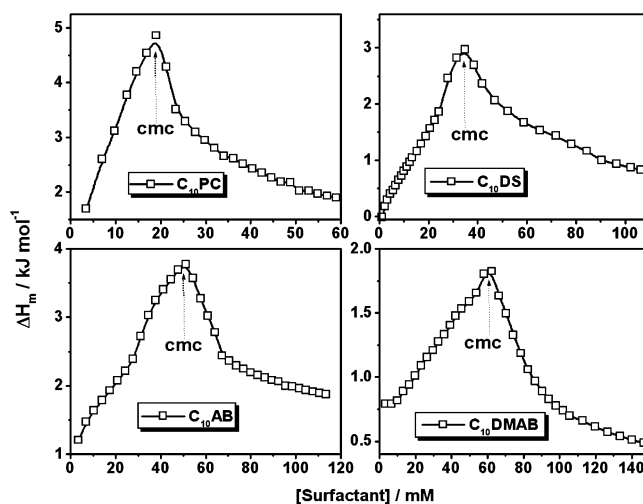

Figure 3. Enthalpograms for self-aggregation of different C_{10} surfactants with different head groups. (A) $C_{10}PC$. (B) $C_{10}DS$. (C) $C_{10}AB$. (D) $C_{10}DMAB$. The cmc points are indicated by arrowheads.

The enthalpograms for $C_{10}AB$, $C_{10}DMAB$, $C_{10}TMAB$, C_{10}-DS, and $C_{10}PC$ are shown in Figure 3. The cmc values are included in Table 1. For $C_{10}DS$, the observed cmc (34.2 mM) closely resembled the earlier reports[14] by conductometry (33.1 and 32.6 mM by specific conductance and average equivalent conductance plotting procedures, respectively). Israelachvili reported a value of 33 mM.[30] The ΔH_m values are also reported in Table 1. The standard Gibbs free energy change for the micellization process was calculated from the relation

$$\Delta G_m^0 = (1 + \beta)RT \ln X_{cmc} \tag{1}$$

where β is the fraction of counterions condensed on the micellar interface (obtained from conductometry discussed earlier), X_{cmc} is the cmc of the surfactant in the mole-fraction unit, and T is the absolute temperature. The entropy change associated with the process was obtained from the Gibbs−Helmholtz equation,

$$\Delta S_m^0 = \frac{1}{T}(\Delta H_m^0 - \Delta G_m^0) \tag{2}$$

assuming $\Delta H_m^0 \cong \Delta H_m$. The energetic parameters are given in Table 1. In the table, the surfactants are placed down the column in the order of decreasing cmc, which matched almost with the order of their ΔG_m^0 values. Their β values were found to be fairly high. The ΔH_m^0 values had shown moderate dependence on the nature of their head groups. The exothermicity of micellization for both the cationic and the anionic surfactants

Self-Aggregation of Ionic C$_{10}$ Surfactants

J. Phys. Chem. B, Vol. 111, No. 14, 2007 **3661**

TABLE 2: Temperature Effect on the Micellization of C$_{10}$TMAB in Aqueous Medium^a

T/K	cmc/mM			β (N)	ΔH_m^{0C}	ΔH_m^{0vH}	ΔG_m^0	ΔS_m^{0C}	ΔS_m^{0vH}
	cond	μcal	av						
288.0	63.7	63.2	63.5	0.81(46)	3.57	9.8	−29.4	114	136
290.5	62.3	61.1	61.7	0.79(45)	2.80	4.2	−29.4	111	116
293.0	61.0	59.1	60.1	0.77(42)	2.25	−1.4	−29.4	108	96
298.0	58.0	57.0	57.5	0.72(40)	0.89	−13.0	−29.2	101	54
303.0	62.7	61.2	62.0	0.68(38)	−1.44	−24.1	−28.8	90	15
308.0	66.9	64.1	65.5	0.63(36)	−2.85	−35.5	−28.1	82	−24
313.0	68.3	64.6	66.5	0.59(34)	−3.97	−47.2	−27.8	76	−62

^{a} ΔH and ΔG_m^0 are expressed in kJ mol^{-1} and ΔS_m^0 in J K^{-1} mol^{-1}. $\Delta C_{p,m}^0$ values were −0.31 and −2.28 kJ mol^{-1} K^{-1}, respectively, by microcalorimetry and van't Hoff methods.
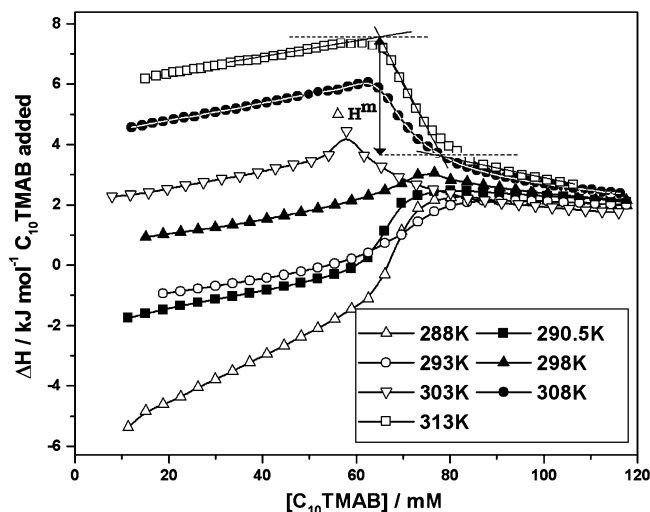
Figure 4. Temperature-dependent enthalpograms of C$_{10}$TMAB.

suggested fair electrostatic interaction in the self-association process. The process was favorably entropy controlled.

Detailing of C$_{10}$TMAB. *1. Temperature Effect on Micellization.* Besides conductometric and microcalorimetric evaluaion of the cmc and the counterion binding of the studied decyl surfactants at 303 K, the temperature dependence of cmc and β of C$_{10}$TMAB was also studied in order to evaluate the energetics by the van't Hoff procedure for a comparison with calorimetry.

Conductometry. Conductometric profiles (κ vs [surfactant]) of micellization of C$_{10}$TMAB at three different temperatures are documented in Figure 2B, in which the breakpoints corresponded to the cmc values. The extent of counterion dissociation (α) from the micellar interface was calculated from the slopes of the pre-micellar (S_1) and post-micellar (S_2) regions as, $\alpha = S_2/S_1$, and the degree of counterion condensation (β) at the micellar interface was determined from the relation $\beta = 1 - \alpha$.
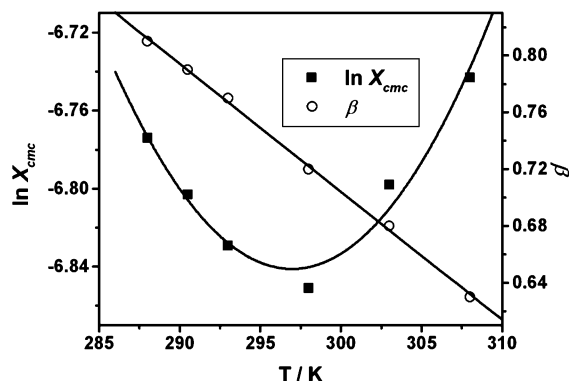
The cmc and β values for C$_{10}$TMAB at several different temperatures in the range 288−313 K are given in Table 2. The results show a minimum (∼296 K) in cmc, whereas the β was found to decrease with temperature (Figure 5). The cmc vs T profile obeyed a second degree polynomial equation of the form

$$cmc = a + bT + cT^2 \quad (3)$$

The β followed a linear course of the form

$$\beta = p + qT \quad (4)$$

The a, b, and c values obtained were 4681.5 ± 546.9, −31.13 ± 3.67, 0.052 ± 0.006, respectively whereas the p and q values were 3.38 ± 0.03 and −0.01 ± 0.0001, respectively.

Figure 5. Variation in ln X_{cmc} and β with absolute temperature for C$_{10}$TMAB.

Microcalorimetry. The enthalpograms for dilution of C$_{10}$-TMAB at seven different temperatures are exemplified in Figure 4. The cmc and the ΔH_m were evaluated as discussed earlier and are given in Table 2. The cmc followed a second degree polynomial equation with a minimum at ∼296 K as reported for ionic surfactants.[4−8,31] According to the mass action model for the micellization of an ionic surfactant with aggregation number "n" and number of counterions per micelle "m", the standard Gibbs free energy change (ΔG_m^0), enthalpy change (ΔH_m^0), and entropy change (ΔS_m^0) can be obtained from the following relations[31]

$$\Delta G_m^0 = (1 + m/n)RT \ln X_{cmc} + (RT/n) \ln[2n(n + m)] \quad (5)$$

$$\Delta H_m^0 = -RT^2\Big[(1 + m/n)\frac{\partial \ln X_{cmc}}{\partial T} + \ln X_{cmc}\frac{\partial(m/n)}{\partial T} + \ln X_{cmc}\frac{\partial[(1/n)\ln\{2n(n + m)\}]}{\partial T}\Big] \quad (6)$$

and

$$\Delta S_m^0 = 1/T(\Delta H_m^0 - \Delta G_m^0) \quad (7)$$

where the second and third terms in eqs 5 and 6 are insignificant for micelles with large aggregation numbers ($n = 40$ and 47) reported for C$_{10}$TMAB.[16−19,31]

Under this approximation, eqs 8 and 9 are applicable

$$\Delta G_m^0 = (1 + \beta)RT \ln X_{cmc} \quad (8)$$

$$\Delta H_m^0 = -RT^2\Big[(1 + \beta)\frac{\partial \ln X_{cmc}}{\partial T} + \ln X_{cmc}\frac{\partial(\beta)}{\partial T}\Big] \quad (9)$$

A second degree polynomial equation (eq 10) along with eq 4 were used for the evaluation of ΔH_m^0

$$\ln X_{cmc} = A + BT + CT^2 \quad (10)$$

with A, B, and C values of 67.64 ± 9.50, -0.50 ± 0.06, and 0.0008 ± 0.0001, respectively. Variation in $\ln X_{cmc}$ and β with temperature is shown in Figure 5.

The differential forms of eqs 4 and 10 were used in eq 9 to get ΔH_m^0. Thus,

$$\Delta H_m^0 = -RT^2[(1 + \beta)(B + 2CT) + q \ln X_{cmc}] \quad (11)$$

The experimentally observed ΔH_m^0 and that obtained from the above-described van't Hoff procedure were found to differ significantly (Table 2). The van't Hoff method yielded much larger enthalpy than calorimetry. Both endo- and exothermic features of the self-association process were observed by the direct method, which was only endothermic by the van't Hoff method. The common features were the decline in the enthalpy with increasing temperature by both the methods. In the past, we have shown discrepancies between ΔH_m^{0C} and ΔH_m^{0vH} for ionic surfactants like AOT, SDS, $C_{16}PC$, $C_{16}TMAB$, and its modified head group analogues, tetradecyltriphenylphosphonium bromide ($C_{14}TPB$), etc., which were fairly large but that herein observed were much larger. The temperature dependence (Figure 6) of both kinds of enthalpies (i.e., $\Delta C_{p,m}^0$) were not similar. The values were -0.31 kJ K^{-1} mol^{-1} by calorimetry and -2.28 kJ K^{-1} mol^{-1} by van't Hoff. The difference in $\Delta C_{p,m}^0$ by the two methods was also observed by us earlier.[6,7,11-13] At this stage, a discussion on the minimum in cmc with respect to its temperature dependence, linear dependence of β on temperature, and the difference between ΔH_m^{0C} and ΔH_m^{0vH} for the $C_{10}TMAB$ system has been considered to be relevant. This has been presented below.

In solution, the ionic headgroups, $-(CH_3)_3N^+$ of $C_{10}TMAB$ repelled one another hindering their association. The ordered water molecules surrounding the nonpolar tails (the hydrophobic hydration or Frank's "iceberg") protected the monomers disfavoring their association; as a result, the cmc was fairly large at the lowest studied temperature of 288 K. Increased temperature reduced the protection of monomers by hydrophobic hydration, and despite electrostatic repulsion among the head groups, they aggregated by way of easier melting of the icebergs (the entropy effect) and consequently cmc decreased. After a certain temperature, thermal energy in association with electrostatic repulsion operated as a deterrent to micelle formation, making the cmc increase. The temperature (T_m) for minimum in cmc would be somewhere in between, which for ionic surfactants normally ranges between 295-305 K.

The temperature dependence of β was found to be nicely linear following eq 4. The decrease in β with rise in temperature resulted from the decrease in aggregation number[32] and hence the charge density of micellar interface.

Over the range of temperature 298-313 K, β reduced by 26% (Table 2), which was taken as the percent decrease also of the aggregation number (N) of $C_{10}TMAB$ micelles. This meant a 1% change in N per degree. On the basis of this rationale and the experimentally reported value of $N = 40$ at 298 K,[33] the values at the other temperatures were estimated and are included in parenthesis in Table 2 (column 5).

The cmc determined by ITC was accurate enough to process the data taken at different temperatures in terms of van't Hoff equation to evaluate ΔH_m^0. The values of ΔH_m^{0vH} and ΔS_m^{0vH} found were much different from ΔH_m^{0C} and ΔS_m^{0C}. The major factors influencing ΔH_m^{0C} and hence ΔS_m^{0C} were solvation/desolvation phenomena during the formation and growth of

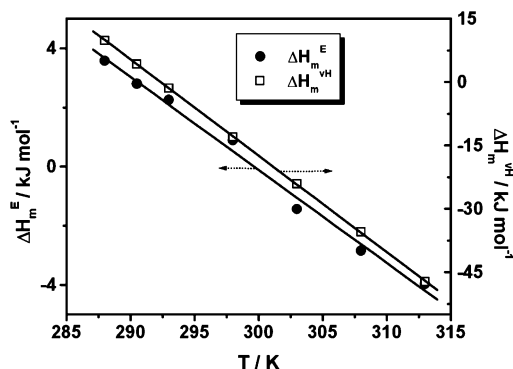**Figure 6.** Enthalpy of micellization vs temperature profiles for C_{10}-TMAB. (•) From direct calorimetry. (□) From van't Hoff analysis.

micelles and structural changes in the micelles and the surrounding solvent medium. Other nonspecific processes also had their shares in the overall thermodynamic event. Their contributions were additive and subtractive; that originating from the process of amphiphile self-aggregation got mixed up with the contributions coming from other involved processes, making the magnitudes and directions of both ΔH_m^{0C} and ΔS_m^{0C} different from actual. Thus, the ΔH_m^{0vH} and ΔS_m^{0vH} derived from calorimetric cmc values stood as better energetic representatives for the self-association of $C_{10}TMAB$. The discrepancies between the two procedures were found to be much larger at temperatures higher than 298 K. The additional processes influenced the micellization event under elevated thermal conditions. The overall issue is substantially complex, but the manifestation needs acknowledgment and analysis for comprehension.

2. Salt Effect on $C_{10}TMAB$ Micellization at 303 K. Salts normally cause reduction in the self-aggregation of ionic amphiphiles. It has been reported that the growth of SDS micelles depend on the counterions; the coions nominally affect the micellar growth. Salts, like sodium salicylate and sodium bezoate, have been known to significantly affect the micellar morphologies of $C_{16}TMAB$, $C_{16}PC$, etc; rod shaped and worm-like micelles have been found to be formed.[34-37] Thread-like micelle formation of anionic surfactants (sodium tetra- and hexadecylsufate) by the interaction with pentylammonium bromides and *p*-toluidine halides has been recently reported.[38] SANS measurements on $C_{16}TMAB$ have shown[39,40] that, although micellar size remains constant over a wider range of [KCl], a significant micellar growth can take place in presence of small amount of NaBr.

Figure 7A shows enthalpograms for the micellization of C_{10}-TMAB in the presence of varied [NaBr] at 303 K. The cmc and ΔH_m^0 values obtained are reported in Table 3. The cmc decreased exponentially with increasing [NaBr] (see inset). A pronounced reduction in cmc was observed at lower [NaBr]. The addition of Br$^-$ screened the repulsion between the anionic head groups of the surfactant, and the double layer potential was thereby lowered. The decreased surface charge density helped in the easier formation of micelle. At higher [NaBr], the screening effect was nearly complete and the cmc lowering effect was less effective. The [salt] had mild influence on the ΔH_m^0, which had shown a maximum at 0.27 M of NaBr found from a second degree polynomial fit of the ΔH_m^0 data with [NaBr]. The endothermicity of the self-association process was comparable with that without salt. Thus, electrostatic interaction weakly influenced the heat of micellization or got compensated in the presence of salt. The distinctions between Br$^-$ and I$^-$ and F$^-$ and Cl$^-$ was evident, although the formation of thread- or worm-like micelles in the presence of the former pair of
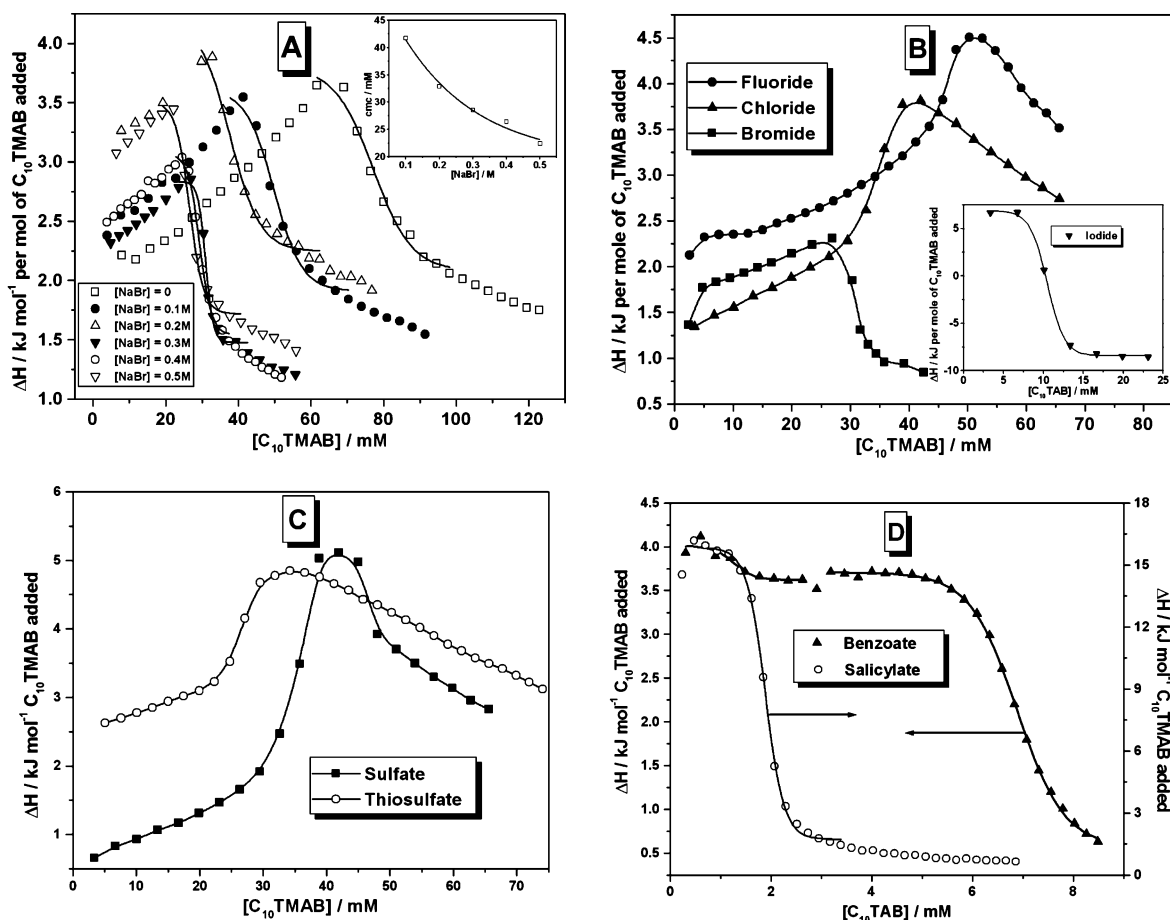
Self-Aggregation of Ionic C_{10} Surfactants

J. Phys. Chem. B, Vol. 111, No. 14, 2007 **3663**

Figure 7. Effect of added salts on the enthalpic and self-aggregation behavior of C_{10}TMAB at 303 K. (A) Effect of increasing [NaBr]. (B) 0.3 M sodium halides. (C) 0.3 M Na-sulfate and Na-thiosulfate. (D) 0.3 M Na-benzoate and Na-salicylate.

TABLE 3: Salt[a] Effects on the Micellization of C_{10}TMAB in Aqueous Medium at 30 °C

[NaBr]/M	cmc/mM	ΔH_m^0/J mol^{-1}
0.1	41.7	−1.56
0.2	32.9	−1.35
0.3	28.5	−1.40
0.4	26.4	−1.50
0.5	24.4	−1.68
	halides	
F$^-$	41.7	1.65
Cl$^-$	30.2	1.74
Br$^-$	28.4	−1.40
I$^-$	8.00	−1.50
	other salts	
SO$_4^{2-}$	31.3	3.21
S$_2$O$_7^{2-}$	23.5	1.67
Ben$^-$	5.9	−1.34
Sal$^-$	1.5	−1.41

[a] The salt concentration was 0.30 M in all experiments.

counterions for the C_{10}TMAB was not possible as realized for C_{16}TMAB, C_{16}PC. The Br$^-$ and I$^-$ ions showed some special influence on the self-association of C_{10}TMAB.

Enthalpograms for the micellization of C_{10}TMAB in the presence of 0.3 M sodium halides at 303 K are documented in Figure 7B. Larger halide ions had more cmc reducing effect. They have higher polarizability and more charge neutralizing effect at the cationic micellar interface to efficiently reduce the cmc. NaF and NaCl produced endothermic enthalpy of micellization, whereas NaBr and NaI produced exothermic enthalpy for the self-aggregation process.

At 0.3 M concentration, thiosulfate reduced the cmc of C_{10}-TMAB more than sulfate (Figure 7C). The bulkier counterion influenced the cmc to a larger extent. The ΔH_m^0 values were positive, and it was higher with sulfate than thiosulfate.

Salicylate and tosylate have been reported to induce a sphere to rod transition to hexadecyltrimethylammonium bromide micelles at a low concentration because they can intercalate with the micellar core by hydrophobic interaction, whereas the ionic part can neutralize the micellar charge at the palisade layer. In our experiments, benzoate and salicylate were found to lower the cmc of C_{10}TMAB to a large extent, salicylate being more effective (Figure 7D). We have found a bisigmoidal enthalpogram for benzoate with a weak enthalpy change for the first process and an appreciable enthalpy change for the second process. The two steps might have corresponded to the formation of spherical aggregates followed by that of elongated rod-like species. The aggregation process ended up with negative change in enthalpy.

In relation to the salt effect on the micellization of C_{10}TMAB, the relevance of the "Hoffmeister Series" (HS) or the "Lyotropic Series" in this matter may be examined.[41] The HS for the salting out effect of the anions of a lyophilic substance from colloidal solution follows the efficiency order citrate^{3-} > tartrate^{4-} > SO$_4^{2-}$ > PO$_4^{3-}$ > acetate$^-$ > Cl$^-$ > NO$_3^-$ > I$^-$ > CNS$^-$. Considering cmc reducing activity of the anions comparable with salting out phenomenon, the following effectivity order of the counter anions herein studied equimolar concentration (0.3 M) level has been found: Sal^{-1} > Ben$^-$ > I$^-$ > Cl^{-1} > SO$_4^{2-}$ > F$^-$. The ions common to HS and used in this study

$(SO_4^{2-}, Cl^-, $ and $I^-)$ have shown a reverse order. The series was formulated on the basis of lyophilic compounds, but the surfactants are amphiphiles, and hence effectivity order was reversed.

Conclusions

The results obtained in this study led to the following conclusions.

(1) The studied C_{10} surfactants have shown large cmc and fair degree of counterion binding but low endothermic enthalpy of micellization at 303 K. In this matter, the headgroup difference has no major effect say except for $C_{10}PC$, which has shown lower cmc, β, and ΔH_m.

(2) The $C_{10}TMAB$ has evidenced the cmc minimum at $\sim$296 K but decreasing β with increasing temperature.

(3) Large difference between the enthalpy of micellization of $C_{10}TMAB$ obtained from calorimetry and that derived from the van't Hoff relation was observed. The ΔH_m^{0C} was much greater than ΔH_m^{0vH}; the $\Delta C_{p,m}^{0C}$ was also greater than $\Delta C_{p,m}^{0vH}$. The integral method of calorimetry was thus much different from the differential method of van't Hoff.

(4) The salts produced appreciable effects on both the cmc and the ΔH_m^0. In this process, NaI, NaBen, and NaSal showed drastic effects. Most of the salts produced negative ΔH_m^0 by calorimetry, which for NaF, NaCl, Na_2SO_4 and $Na_2S_2O_7$ were positive.

References and Notes

(1) Rosen, M. J. In *Surfactants and Interfacial Phenomenon*, 2nd ed.; John Wiley: New York, 1989.

(2) Blandamer, M. J.; Briggs, B.; Cullis, P. M.; Engberts, J. B. F. N. *Phys. Chem. Chem. Phys.* **2002**, *2*, 5146.

(3) Blandamer, M. J.; Cullis, P. M.; Soldi, L. G.; Chowdiji Rao, K.; Subha, M. C. S. *J. Therm. Anal.* **1996**, *46*, 1583.

(4) Prasad, M.; Moulik, S. P.; MacDonald, A.; Palepu, R. *J. Phys. Chem. B* **2004**, *108*, 355.

(5) Prasad, M.; Moulik, S. P.; Palepu, R. *J. Colloid Interface Sci.* **2005**, *284*, 658.

(6) Prasad, M.; Chakraborty, I.; Rakshit, A. K.; Moulik, S. P. *J. Phys. Chem. B* **2006**, *110*, 9815.

(7) Chatterjee, A.; Moulik, S. P.; Sanyal, S. K.; Mishra, B. K.; Puri, P. M. *J. Phys. Chem. B* **2001**, *105*, 12823.

(8) Chatterjee, A.; Maity, S.; Sanyal, S. K.; Moulik, S. P. *Langmuir* **2002**, *18*, 2998.

(9) Basu Ray, G.; Chakraborty, I.; Ghosh, S.; Moulik, S. P.; Plepu, R. *Langmuir* **2005**, *21*, 10958.

(10) Basu Ray, G.; Chakraborty, I.; Ghosh, S.; Moulik, S. P. *Colloid Polym. Sci.* **2007**, *285*, 457.

(11) Kresheck, G. C. *J. Phys. Chem. B* **1998**, *102*, 6596.

(12) Kresheck, G. C.; Hargraves, W. A. *J. Colloid Interface Sci.* **1974**, *48*, 481.

(13) Naghibi, H.; Tamura, A.; Sturtevant, J. M. *Proc. Natl. Sci. Acad. Sci. U.S.A.* **1995**, *92*, 5597.

(14) Mukerjee, P.; Mysels, K. J. In *Critical Micellar Concentration of Aqueous Surfactant Systems*; U.S. National Bureau of Standards: Washington, DC, 1971.

(15) Alkhamis, K. A.; Allaboun, H.; Al-Momani, W. Y. *J. Pharm. Sci.* **2003**, *92*, 839.

(16) Pal, S.; Bagchi, B.; Balasubramanian, S. *J. Phys. Chem. B* **2005**, *109*, 12879.

(17) Debye, P. *J. Phys. Chem.* **1949**, *53*, 1.

(18) Berr, S.; Jones, R. R. M.; Johnson, J. S. Jr. *J. Phys. Chem.* **1992**, *96*, 5611.

(19) Nohara, D.; Bitoh, M. *J. Mass. Spectrom.* **2000**, *35*, 1434−37.

(20) Garidel, P.; Hildebrand, A.; Neubert, R.; Blume, A. *Langmuir* **2000**, *16*, 2567.

(21) Majhi, P. R.; Blume, A. *Langmuir* **2001**, *17*, 3844.

(22) Majhi, P. R.; Mukherjee, K.; Moulik, S. P.; Sen, S.; Sahu, N. P. *Langmuir* **1999**, *15*, 6624.

(23) Chaterjee, A.; Dey, T.; Sanyal, S. K.; Moulik, S. P. *J. Surf. Sci. Technol.* **2001**, *17*, 1.

(24) Bhattacharya, S.; Haldar, J. *Langmuir* **2004**, *20*, 7940.

(25) Hait, S. K.; Moulik, S. P.; Palepu, R. *Langmuir* **2002**, *18*, 2471.

(26) Stodghill, S. P.; Smith, A. E.; O'Haver, J. H. *Langmuir* **2004**, *20*, 11387.

(27) van Os, N. M.; Haandrikman, G. *Langmuir* **1987**, *3*, 1051.

(28) Thongngam, M.; McClements, D. J. *Langmuir* **2005**, *21*, 79−86.

(29) Thongngam, M.; McClements, D. J. *J. Agric. Food Chem.* **2004**, *52*, 987.

(30) Israelachvili, J. N. In *Intermolecular and Surface Forces*, 2nd ed., Academic Press: London, 1992.

(31) Paula, S.; Sus, W.; Tuchtenhagen, J.; Blume, A. *J. Phys. Chem.* **1995**, *99*, 11742.

(32) Moroi, Y. In *Micelles: Theoretical and Applied Aspects*, ; Plenum Press: New York, 1992; p 85, First Indian Reprint 2005 by Springer (India) Pvt. Ltd., and references therein.

(33) Evans, D. F.; Allen, M.; Ninham, B. W.; Fonda, A. *J. Solution Chem.* **1984**, *13*, 87.

(34) Cate, M. E.; Candau, S. J. *J. Phys. Condens. Matter* **1990**, *2*, 6869.

(35) Oda, R.; Narayanan, J.; Hassan, P. A.; Manohar, C.; Salkar, R. A.; Kern, F.; Candau, S. J. *Langmuir* **1998**, *14*, 4364.

(36) Cates, M. E. *J. Phys. Condens. Matter* **1996**, *8*, 9167.

(37) Roy, B. K.; Moulik, S. P. *J. Dispersion Sci. Technol.* **2000**, *21*, 161.

(38) Nakamura, K.; Shikata, T. *Langmuir* **2006**, *22*, 9853.

(39) Aswal, V. K.; Goyal, P. S. *Phys. Rev. E* **2000**, *61*, 2947.

(40) Goyal, P. S.; Menon, S. V. G.; Dasannacharya, B. A.; Rajagopalan, V. *Chem. Phys. Lett.* **1993**, *211*, 559.

(41) Glasstone, S. In *Text Book of Physical Chemistry*, 2nd ed.; Macmillian: London, 1960; p 1254.