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Effect of Headgroup Size on the Thermodynamic Properties of Micellization of Dodecyltrialkylammonium Bromides

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S *Supporting Information*

ABSTRACT: The micellization of dodecyltrimethyl/ethyl/propyl/butylammonium bromide (C_{12}NM, C_{12}NE, C_{12}NP, and C_{12}NB) was investigated by electrical conductivity measurements at different temperatures T. In the investigated temperature range, (15 to 45) °C, both the critical micelle concentration (cmc) and the degree of counterion association (β) decreased with the increase of headgroup size. The cmc as a function of T showed a typical U-shaped relationship. The temperature of the minimum of U-shaped curve ($T_{\min}$) increased with the incremental chain length in the headgroups, which was the reverse to the previous results for quaternary ammonium surfactants that $T_{\min}$ decreased with the increment in the hydrophobic tails. The β approximately exhibited a linear decrease with raising T. Nonlinearity was observed both in ln(cmc) versus N_c and in $\Delta_{\mathrm{mic}}G^\circ$ versus T, where N_c was the carbon number in the headgroups and $\Delta_{\mathrm{mic}}G^\circ$ was the standard Gibbs energy of micellization. C_{12}NM and C_{12}NE resembled each other in the thermodynamics of micellization, but they behaved considerably differently from either C_{12}NP or C_{12}NB in the dependence of ln(cmc) on N_c, in the decreasing rate of $\Delta_{\mathrm{mic}}G^\circ$ versus T, and in the variation of thermodynamic properties with T. All of the surfactants exhibited the enthalpy−entropy compensation phenomenon. The large value of standard entropy of micellization ($\Delta_{\mathrm{mic}}S^\circ$) of C_{12}NB compared with the others could be attributed to the strong hydrophobicity of the tributyl headgroup.

INTRODUCTION

The nature of the headgroup is one of the most important structural factors that control the properties of surfactants. It is well-known that the structure of headgroups could influence the aggregate forms and surface adsorption through the packing parameter.[1,2] Besides the significant differences among anionic, cationic, nonionic, and zwitterionic surfactants classified by headgroups,[3] even a subtle difference in headgroups can result in different behaviors of surfactants. For example, the similarly structured sodium alkyl sulfates and sodium alkyl sulfonates exhibit striking differences in their interactions with cationic surfactants[4,5] and polymers,[6,7] which is related to the different charge density between the two headgroups based on quantum chemical calculations. With regards to quaternary ammonium surfactants the structure of headgroup is various and adjustable[8−11] because of the convenience of introducing a different number of different substitution groups onto the nitrogen atom.

The most commonly studied quaternary ammonium surfactants are alkyltrimethylammonium surfactants,[11−13] whereas the research works on the other members in the family of quaternary ammonium surfactants are usually scattered; for example, liquid−liquid phase separation is studied in high concentrations of micellar solution of dodecyltributylammonium bromide (C_{12}NB).[14] Great contributions have been performed to survey the effects of the structure of headgroups. In the series of tetradecyltrialkylammonium bromides [$C_{14}H_{29}N(C_mH_{2m+1})_3Br$, with m = 1 to 4] at 25 °C as studied by Zana,[11] a decrease of critical micelle concentration (cmc) and an increase of ionization degree of micelles upon increasing m have been found. Additionally, the micellization and phase behavior of alkyltrimethyl/ethyl/propyl/butyl/pentylammonium bromide have been investigated by Buckingham et al.[15] ^{1}H NMR was applied to study the aggregation of dodecyltrialkylammonium bromides (alkyl group = methyl, ethyl, *n*-propyl, and *n*-butyl) at 298 K,[16] in which the equilibrium constants of micelle formation (K) increase with increasing headgroup size, but the incremental contribution to the Gibbs free energy per CH_2 group at the interface is small; its value increases from 0.13 kJ to 0.29 kJ per moles of CH_2 in going from the trimethyl to the tri-*n*-propyl and the tri-*n*-butyl analogue, respectively.

In our previous works the surface activity of dodecyltrialkylammonium bromides (alkyl = methyl, ethyl, propyl, and butyl, abbreviated as C_{12}NM, C_{12}NE, C_{12}NP, and C_{12}NB, respectively) and their mixtures with sodium dodecyl sulfate were studied with the surface tension method,[17] and the interactions of C_{12}NM, C_{12}NE, C_{12}NP, and C_{12}NB with polymers were also studied.[18,19] Previous works of this series on the measurements of cmc were performed at 25 °C.[17−19] When thermodynamic properties of micellization are involved, investigations on the series of dodecyltrialkylammonium bromides were only performed at a specific temperature of 20 °C[15] or 25 °C,[16] and

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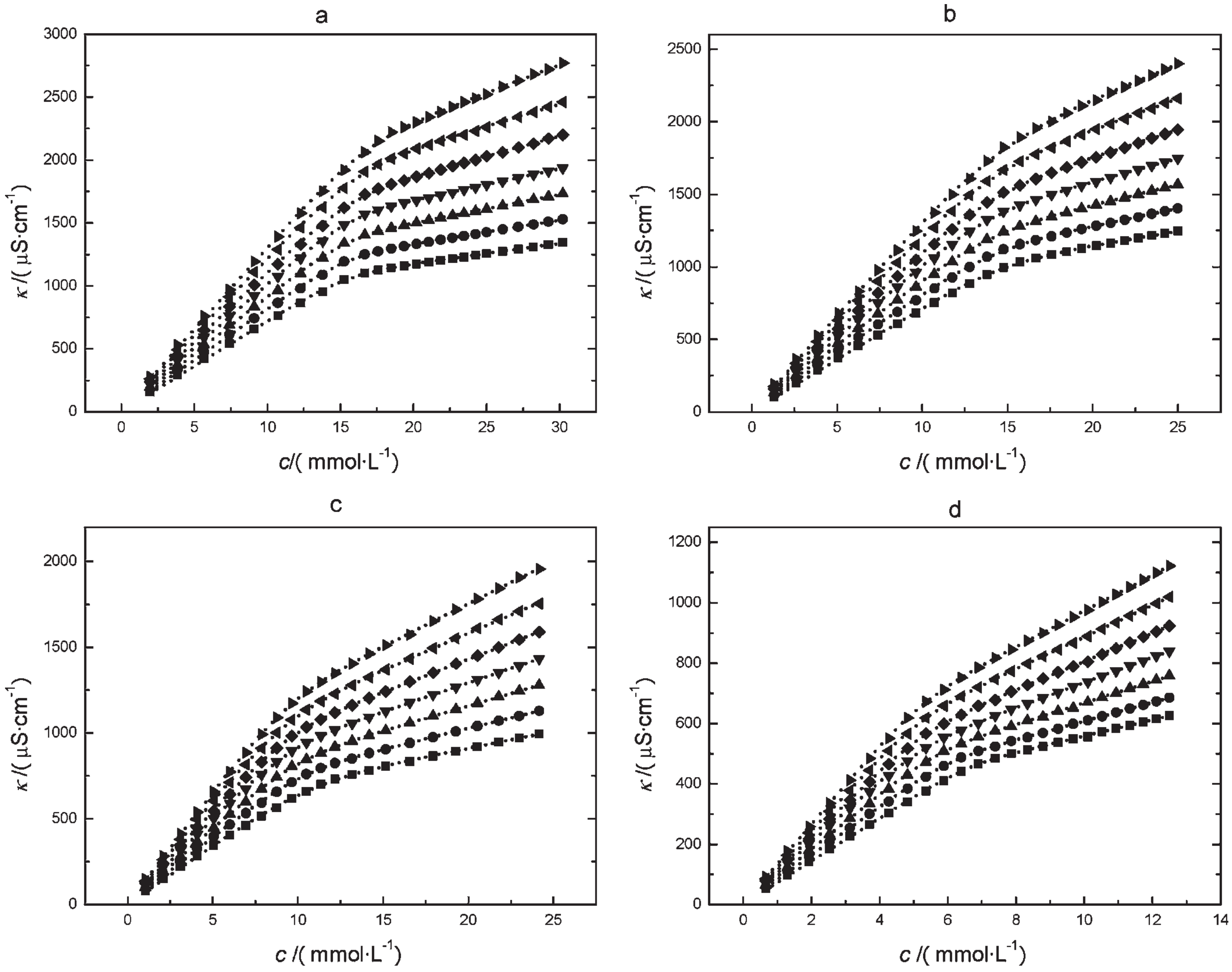

Figure 1. Plots of specific conductivity (κ) vs surfactant concentration (c) for solutions of (a) $C_{12}NM$, (b) $C_{12}NE$, (c) $C_{12}NP$, and (d) $C_{12}NB$ at temperatures (bottom to top) of (15, 20, 25, 30, 35, 40, and 45) °C. The dotted lines are fit to eq 1.

$C_{12}NP$ was not studied in ref 15. To capture the thermodynamics of micellization as a function of temperature in the case of increasing headgroup size, in this work, the micellization of $C_{12}NM$, $C_{12}NE$, $C_{12}NP$, and $C_{12}NB$ was investigated by electrical conductivity measurements over a temperature range from (15 to 45) °C. With the developed method of conductivity data treatment, that is, the integral form of the Boltzmann sigmoidal function,[20] the thermodynamic parameters of standard Gibbs energy, enthalpy, and entropy could be approached.

■ EXPERIMENTAL SECTION

Dodecyltrimethyl/ethyl/propyl/butylammonium bromides [n-$C_{12}H_{25}N(C_mH_{2m+1})_3Br$, $C_{12}NM$ (CAS No. 1119-94-4), $C_{12}NE$ (CAS No. 18186-71-5), $C_{12}NP$, and $C_{12}NB$ for $m = 1$ to 4, respectively] were prepared and purified by the procedure described in our previous work.[5] No minima were observed in plots of surface tension (γ) versus log c for these surfactants,[17] indicating no surface-active impurities.[21] Distilled water with a conductivity of less than 1.4 $\mu S\cdot cm^{-1}$ was used in all of the experiments.

The conductivities of aqueous solutions of the surfactants were measured using an Advanced Conductivity Orion 162A conductivity meter (Thermo) with a resolution of 0.01 $\mu S\cdot cm^{-1}$ and accuracy of ± 0.5 %. The measurements were made in a water bath maintained within ± 0.01 K of the desired temperature.

■ RESULTS AND DISCUSSION

Critical Micelle Concentrations of $C_{12}NM$, $C_{12}NE$, $C_{12}NP$, and $C_{12}NB$ at Different Temperatures. The conductivity curves of aqueous solutions of $C_{12}NM$, $C_{12}NE$, $C_{12}NP$, and $C_{12}NB$ over the temperature range (15 to 45) °C are shown in Figure 1. The experimental conductivity data are included in the Supporting Information (Table S1, S2, S3, and S4).

All of the conductivity plots in Figure 1 showed a shape of two straight lines intersecting at the break point, which corresponds to the formation of micelles. The conductivity data were fitted according to the integral form of the Boltzmann sigmoidal function proposed for the analysis of specific conductivity (κ) versus concentration (c) data for solutions of ionic

Table 1. Determined cmc/(mol·kg^{-1}) Values and Their Uncertainties for the Systems of $C_{12}NM$, $C_{12}NE$, $C_{12}NP$, and $C_{12}NB$

T/K	$C_{12}NM$	$C_{12}NE$	$C_{12}NP$	$C_{12}NB$
288.15	0.01525 ± 0.00015 0.0147[a]	0.01442 ± 0.00020	0.01047 ± 0.00016	0.00651 ± 0.00006
293.15	0.01518 ± 0.00014 0.0143[a] 0.0144[b]	0.01395 ± 0.00018 0.014[b] 0.0136[d]	0.00997 ± 0.00010	0.00597 ± 0.00005 0.0048[c]
298.15	0.01523 ± 0.00014 0.0146[a] 0.0144[d] 0.0146[e] 0.016[f] 0.0154[g] 0.01447[h] 0.0156[i] 0.0145[j]	0.01367 ± 0.00017 0.0140[d] 0.0108[e] 0.013[f] 0.0136[g]	0.00962 ± 0.00008 0.0063[e] 0.0075[f] 0.0105[g]	0.00562 ± 0.00005 0.0048[d] 0.0045[e] 0.0044[f] 0.0057[g]
303.15	0.01548 ± 0.00014 0.0157[k] 0.0153[l] 0.01519[m] 0.0155[n] 0.0151[a] 0.01550[o] 0.015510[p]	0.01358 ± 0.00015	0.00936 ± 0.00007	0.00522 ± 0.00004
308.15	0.01561 ± 0.00016 0.0159[a] 0.015830[p]	0.01364 ± 0.00017	0.00936 ± 0.00007	0.00520 ± 0.00005
313.15	0.01602 ± 0.00017 0.0166[a] 0.01650[o]	0.01377 ± 0.00018	0.00923 ± 0.00008	0.00520 ± 0.00003
318.15	0.01650 ± 0.00019 0.0175[a]	0.01422 ± 0.00024	0.00931 ± 0.00007	0.00517 ± 0.00003

[a] Ref 13, ultrasound velocity. [b] Ref 34, conductivity. [c] Ref 14, conductivity. [d] Ref 15, conductivity. [e] Ref 18, fluorescence. [f] Ref 17, surface tension. [g] Ref 19, conductivity. [h] Ref 38, conductivity. [i] Ref 39, conductivity. [j] Ref 41, conductivity. [k] Ref 12, conductivity. [l] Ref 35, conductivity. [m] Ref 36, conductivity. [n] Ref 37, microcalorimetry. [o] Ref 40, surface tension. [p] Ref 37, ITC method.

surfactants:[20]

$$\kappa = a_0 + a_1 c + a_3(a_2 - a_1)\ln\left(\frac{1+\exp[(c-a_4)/a_3]}{1+\exp(-a_4/a_3)}\right) \quad (1)$$

The parameters a_0, a_1, a_2, a_3, and a_4 represent the value of κ in pure water, the slopes in the pre- and postmicellar regions, the width of transition between the two regions, and the central point of this transition region, respectively. The units of κ and a_0 are μS·cm^{-1}; the units of c, a_3, and a_4 are identical with the unit of surfactant concentration (e.g., mmol·L^{-1} in Figure 1), while the units of a_1 and a_2 are decided by the units of concentration and conductivity. The value of a_4 corresponds to the cmc of the surfactant. Figure 2 shows cmc values for solutions of $C_{12}NM$, $C_{12}NE$, $C_{12}NP$, and $C_{12}NB$ at different temperatures T. The data and the uncertainties of the cmc determined in this work are shown in Table 1. Over the whole temperature range investigated, the cmc values of dodecyltrialkylammonium bromides decreased with increasing headgroup size (Figure 2), which is consistent with previous results at one specific temperature[15,17−19] and the case for tetradecyltrialkylammonium bromides at 25 °C.[11] This could be attributed to the increasing hydrophobicity with the increase of alkyl chain length in the headgroups, which favored the aggregation of surfactant molecules. However, although the incremental

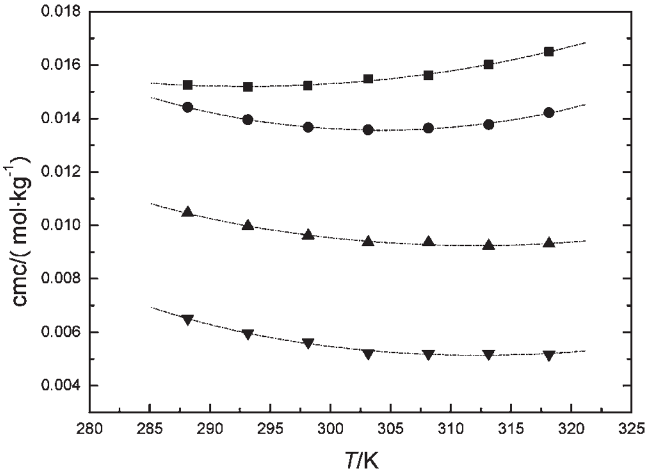

Figure 2. Variation of cmc with temperature (T) for the surfactants: ■, $C_{12}NM$; ●, $C_{12}NE$; ▲, $C_{12}NP$; ▼, $C_{12}NB$. The lines are fit based on the description of ln(cmc) vs T given by eq 7.

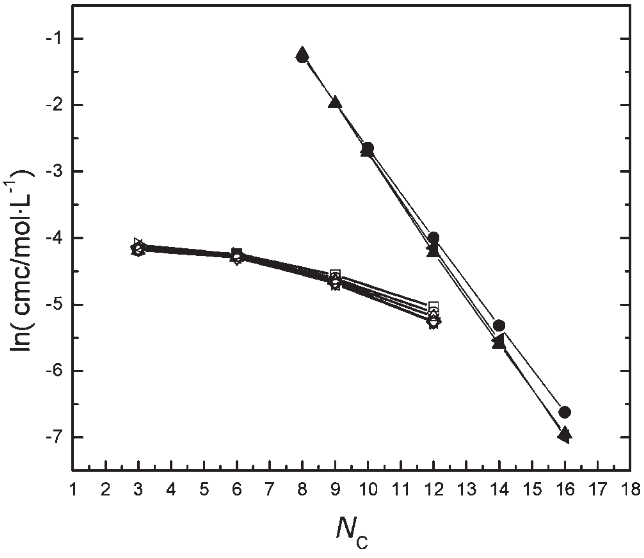

Figure 3. Different effects of the increment of carbon number (N_c) in the headgroups and in the tails of quaternary ammonium surfactants on ln(cmc). Hollow symbols for changing headgroups of $C_{12}H_{25}N(C_mH_{2m+1})_3Br$ ($N_c = 3m$) in this work from (15 to 45) °C; solid symbols for changing tails of C_nTAB ($N_c = n$): from ref 13 at 25 °C (▲) and at 55 °C (●); from ref 12 at 30 °C (left-pointing triangle).

carbon number from C_{12}NM to C_{12}NB was quite considerable, the cmc was not decreased as much as expected when compared with alkyltrimethylammonium bromides (C_nTAB) with a similarly increasing chain length (n),[12,13] as Figure 3 shows.

In Figure 3, the increment of carbon number (N_c) in the headgroups and in the tails induced a different trend of ln(cmc) for quaternary ammonium surfactants. It should be emphasized here that only the comparisons of the rules between this work and the systems referenced[12,13] are valid due to the difference either in the treatment of conductivity data or in the method to determine the cmc. Three interesting points could be concluded in Figure 3:

(1) The increment of N_c in the headgroup induced a lesser decrease of cmc than that in hydrophobic tail did. The reason might be that the hydrophobic contribution arising from dehydration of alkyl group, which should favor micellization, could be partially lost because the headgroup located at the micellar surface. A similar mechanism has been discussed by Buckingham et al.[15] and Bazito et al.[16] with regards to the small Gibbs free energy per CH_2 in headgroup, and the explanation also contains other effects of increasing headgroup size on micellization, including the steric interactions between neighboring headgroups, a change in the micellar surface charge density, and a change to the packing of the alkyl tails.

(2) The dependence of ln(cmc) on N_c in the headgroup was nonlinear, notwithstanding the well-known fact that the relationship between ln(cmc) and the chain length of hydrophobic tail is linear for ordinary surfactants.[21] This could be understood in terms that both the headgroups of C_{12}NM and C_{12}NE had the opportunity for sufficient contact with water; therefore, the difference in ln(cmc) between them was relatively small, while the bulky size of the headgroups of C_{12}NP and C_{12}NB made them to be considerably hydrophobic and even one arm of $—N(CH_2CH_2CH_2CH_3)_3^+$ could partially incorporate in micelle,[15] and thus ln(cmc) dropped more rapidly for C_{12}NP and C_{12}NB.

(3) It showed that if the surfactants are relatively more hydrophilic, for example, with a smaller headgroup (m = 1, 2) and shorter tail (n = 8, 9, 10), the effect of temperature on ln(cmc) was quite limited. However, the effect of temperature on ln(cmc) would become large when the headgroups were bigger (m = 3 and 4) and the surfactant tails were longer ($n \geq 12$). The reason might be the cumulation of the hydrophobicity change upon each CH_2 group induced by iceberg destruction during heating.

The effect of raising temperature on the cmc of C_{12}NM, C_{12}NE, C_{12}NP, and C_{12}NB is shown in Figure 2. It indicates that the curves of cmc versus temperature are typically U-shaped, which is consistent with the relationship between cmc and temperature for ordinary ionic surfactants.[10,13] The temperature of the minimum of the U-shaped curve of cmc versus T is defined as T_{min}. It is known that, for cationic surfactants of quaternary ammonium salts, T_{min} decreases as the chain length of hydrophobic tail increases.[13,22] However, Figure 2 shows that T_{min} for C_{12}NM, C_{12}NE, C_{12}NP, and C_{12}NB were approximately at (292.8, 304.2, 312.0, and 312.4) K, respectively, that is, T_{min} increased with the increase of the chain length in headgroups and T_{min} seemed to approach a top inflection of such increase for tripropyl and tributyl headgroups. In summary, the variation of T_{min} with the increase of headgroup chain length was observed to be completely opposite to that of hydrophobic-tail chain length.

To comprehend the opposite rules of T_{min} for increasing chain length in headgroups and the surfactant tail, it might be better to begin with the cause of U-shaped curve and T_{min}. It is known that T_{min} is a consequence of two opposing effects upon heating: (i) a decrease in the hydration of the ionic headgroup, which induces the growth of hydrophobicity of the surfactant and hence a decrease in the cmc, and (ii) the breakdown of the structure of water which is unfavorable for hydrophobic interactions and hence the growth of the cmc.[23] Thus, the first effect of increasing T became more important than the second one when the headgroup size was increased. In other words, the growth in the hydrophobicity of the headgroup from C_{12}NM and C_{12}NE to C_{12}NP and C_{12}NB would overcome the unfavorable influence on micellization due to the breakdown of the structure of water because of the incremental chain length located in headgroup.

It was noted in Figure 3 that raising the temperature seemed to show different influences on ln(cmc) between the case of long tail and the case of bulky headgroup, which could be ascribed to the same analysis of the cause of T_{min} mentioned above.

These results show that the increment of chain length in headgroup promoted the heating effect to induce poor hydration and bring enhanced hydrophobicity (effect i), which may be why C_{12}NB exhibited rich phase behavior upon heating.[14] On the other side, increment of chain length in tail emphasized the heating effect of breakdown of water structure (effect ii). Therefore, T_{min} decreases with the increase of chain length in tail for quaternary ammonium surfactants,[13,22] but T_{min} increased with the increase of chain length in a headgroup in this work.

Degree of Counterion Association (β) for C_{12}NM, C_{12}NE, C_{12}NP, and C_{12}NB at Different Temperatures. The degree of counterion association of micelle (β) can be determined by conductivity measurements using:

$$\beta = 1 - \frac{a_2}{a_1} \qquad (2)$$

where a_1 and a_2 are the slopes of the straight lines before and after the cmc in the conductivity plots, respectively (see eq 1).[24] The values of β for $C_{12}NM$, $C_{12}NE$, $C_{12}NP$, and $C_{12}NB$ determined from conductivity using eq 2 at different temperatures are shown in Figure 4. The data were treated by linear fitting:

$$\beta = a' + b'T \qquad (3)$$

where a' and b' are fitting parameters whose values are shown in Table 2.

The β versus T curves for dodecyltrialkylammonium bromides in Figure 4 exhibit a linear dependence approximately, which is similar to the linearity of ionization degree of the micelles of dodecyldimethylethylammonium bromide.[10] For ordinary ionic surfactants, raising the temperature would accelerate the motion of particles in the solution, and thus, the degree of counterion association (β) would decrease.[25] In the present systems of $C_{12}NM$, $C_{12}NE$, $C_{12}NP$, and $C_{12}NB$ (Figure 4), β obeyed this rule on temperature for ordinary ionic surfactants.

In Figure 4 it can be seen that β decreased with the increase of headgroup size in the whole temperature range investigated. The complete data of β and the uncertainties are shown in Table 3. It

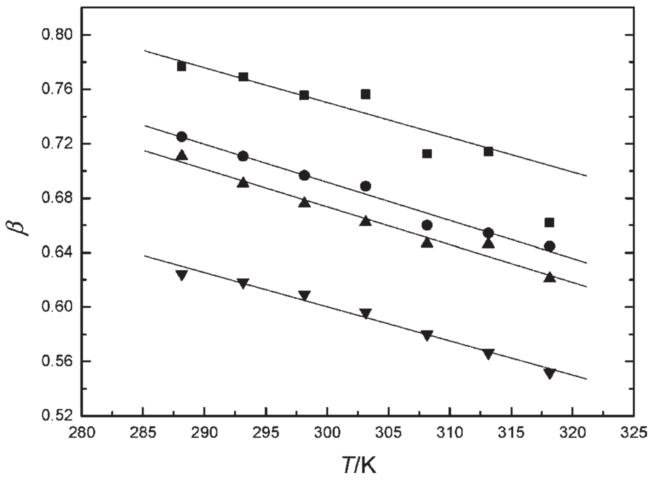

Figure 4. Degree of counterion association (β) of the surfactant aggregates vs temperature (T): ■, $C_{12}NM$; ●, $C_{12}NE$; ▲, $C_{12}NP$; ▼, $C_{12}NB$. The lines are fits to eq 3.

Table 2. Parameters Obtained by Fitting the Plots of β vs T and ln(cmc) vs T with Equation 3 and Equation 7, Respectively, for the Surfactants

	$C_{12}NM$	$C_{12}NE$	$C_{12}NP$	$C_{12}NB$
a	6.75535	17.61441	16.24211	34.05352
b/K^{-1}	−0.07473	−0.14408	−0.13413	−0.25175
$10^4\ c/K^{-2}$	1.27603	2.36812	2.14936	4.02905
a'	1.51591	1.52895	1.50431	1.35472
b'/K^{-1}	−0.00255	−0.00279	−0.00277	−0.00251

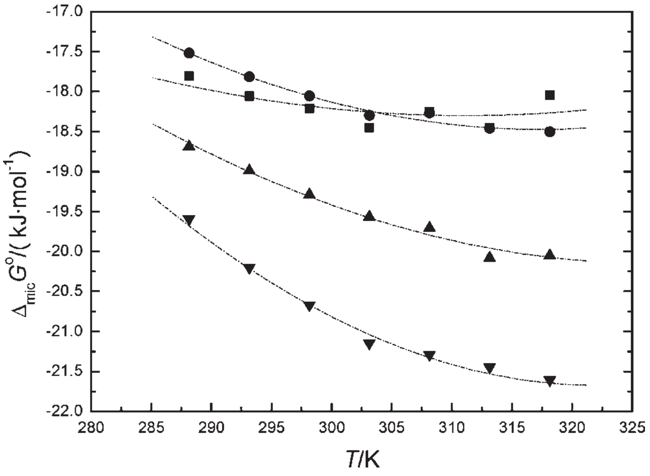

Figure 5. Relationship between $\Delta_{mic}G^\circ$ of the surfactants and temperature (T): ■, $C_{12}NM$; ●, $C_{12}NE$; ▲, $C_{12}NP$; ▼, $C_{12}NB$. The lines are fits based on the description of β vs T and ln(cmc) vs T given by eqs 3 and 7, respectively.

Table 3. Determined Values of Degree of Counterion Association β and Their Uncertainties for the Systems of $C_{12}NM$, $C_{12}NE$, $C_{12}NP$, and $C_{12}NB$

T/K	$C_{12}NM$	$C_{12}NE$	$C_{12}NP$	$C_{12}NB$
288.15	0.7770 ± 0.0116	0.7250 ± 0.0213	0.7109 ± 0.0142	0.6245 ± 0.0097
293.15	0.7689 ± 0.0100	0.7108 ± 0.0186	0.6907 ± 0.0082	0.6185 ± 0.0068
	0.77[a]	0.70[a]		0.61[a]
298.15	0.7555 ± 0.0101	0.6966 ± 0.0167	0.6759 ± 0.0063	0.6094 ± 0.0065
	0.739[b]			
	0.76[c]			
	0.768[d]			
	0.75[e]			
303.15	0.7563 ± 0.0102	0.6886 ± 0.0149	0.6622 ± 0.0052	0.5964 ± 0.0057
	0.718[f]			
	0.726[g]			
308.15	0.7125 ± 0.0121	0.6601 ± 0.0160	0.6465 ± 0.0055	0.5800 ± 0.0062
313.15	0.7141 ± 0.0137	0.6543 ± 0.0170	0.6463 ± 0.0058	0.5664 ± 0.0044
318.15	0.6621 ± 0.0145	0.6446 ± 0.0231	0.6210 ± 0.0055	0.5517 ± 0.0044

[a] Ref 15, conductivity. [b] Ref 38, conductivity. [c] Ref 39, conductivity. [d] Ref 42, conductivity. [e] Ref 41, conductivity. [f] Ref 12, conductivity. [g] Ref 35, conductivity.

has been discussed that the surface charge density of the micelles decreases as the headgroup size of the surfactant increases; therefore, the degree of counterion association also decreases.[15] The explanation of this phenomenon could also be referred to in the study on tetradecyltrialkylammonium bromides at 25 °C by Zana, in which it has been correlated with the changes of surface areas per headgroup.[11]

Gibbs Energy of Micellization ($\Delta_{mic}G°$) for C_{12}NM, C_{12}NE, C_{12}NP, and C_{12}NB at Different Temperatures. To further understand the effect of headgroup size on the micellization of quaternary ammonium surfactants, the standard Gibbs energy of micellization ($\Delta_{mic}G°$) was estimated using the mass-action model:[26]

$$\Delta_{mic}G^{\circ} = (1+\beta)RT\ln(\text{cmc}) \tag{4}$$

where the cmc is given in molality units ($\text{mol}\cdot\text{kg}^{-1}$) and β is the degree of counterion association for the micelle.

The $\Delta_{mic}G°$ estimated using eq 4 is shown in Figure 5. The data and uncertainties in $\Delta_{mic}G°$ determined for the surfactant systems are shown in Table 4. It was surprisingly noted that $\Delta_{mic}G°$ decreased nonlinearly with temperature. It might be a consequence of the trend of cmc and β with raising temperature (Figures 2 and 4).

Figure 5 shows that the curves of $\Delta_{mic}G°$ versus T for C_{12}NM and C_{12}NE were near and entangled, which suggested that the two behaved similarly in micellization. For example, the cmc's of C_{12}NM and C_{12}NE were relatively close, while those of C_{12}NP and C_{12}NB seemed far smaller (Figure 2). Since the ln(cmc) for C_{12}NM is less negative while its β is larger, a $\Delta_{mic}G°$ close to that of C_{12}NE resulted.

The previous result of $\Delta_{mic}G°$ of C_{12}NM, C_{12}NE, and C_{12}NB at 20 °C[15] shows a sequence similar to our work at 20 °C (Figure 5); that is, $\Delta_{mic}G°$ of C_{12}NE is a little less negative than that of C_{12}NM, which could be ascribed to the different influences of headgroup size on cmc and β: Although the cmc decreases with increasing headgroup size, this is offset by decreasing β. However, as shown in this work, the small advantage in $\Delta_{mic}G°$ of C_{12}NM over C_{12}NE was soon overcome by C_{12}NE at higher temperatures (Figure 5). It might suggest that at a relatively low temperature the influence of headgroup size on β seemed a little larger than that on cmc, while upon heating the increase of hydrophobicity for C_{12}NE it became more important than the aspect of β. At high temperature, the sequence of $\Delta_{mic}G°$ was consistent with the sequence of hydrophobicity of surfactants (Figure 5).

As temperature increases in the investigated range, the $\Delta_{mic}G°$ of C_{12}NB was found to decrease at a faster rate than that of C_{12}NP and then significantly faster than C_{12}NM and C_{12}NE (Figure 5). There seemed to be some difference among the categories of C_{12}NB, C_{12}NP, and C_{12}NM/C_{12}NE, in which C_{12}NM and C_{12}NE were included as one category because of their resembled properties. Recall the discussion on the dependence of ln(cmc) on N_c in headgroup above: it could be understood that both the $—N(CH_3)_3^+$ and $—N(CH_2CH_3)_3^+$ headgroup had the opportunity for sufficient contact with water, while the large N_c of bulky $—N(CH_2CH_2CH_3)_3^+$ and $—N(CH_2CH_2CH_2CH_3)_3^+$ headgroups resulted in significant hydrophobicity and even one arm of $—N(CH_2CH_2CH_2CH_3)_3^+$ could partially incorporate in the micelle.[15] A similar opinion has been found for the counterions of tetrapropyl- and tetrabutylammonium perfluorooctanoates, in which these two kinds of counterions are so bulky and hydrophobic that the penetration of tetrapropyl- and tetrabutylammonium ions into micellar surface is inferred from NMR.[27]

Table 4. Determined $\Delta_{mic}G°/(\text{kJ}\cdot\text{mol}^{-1})$ Values and Their Uncertainties for the Systems of C_{12}NM, C_{12}NE, C_{12}NP, and C_{12}NB

T/K	C_{12}NM	C_{12}NE	C_{12}NP	C_{12}NB
288.15	−17.81 ± 0.16	−17.52 ± 0.27	−18.69 ± 0.22	−19.59 ± 0.15
293.15	−18.05 ± 0.14	−17.81 ± 0.25	−18.99 ± 0.13	−20.20 ± 0.12
298.15	−18.21 ± 0.15	−18.05 ± 0.23	−19.29 ± 0.11	−20.67 ± 0.12
	−18.3[a]			
	−35.58[b]			
303.15	−18.45 ± 0.15	−18.30 ± 0.21	−19.57 ± 0.09	−21.14 ± 0.11
	−18.90[c]			
	−35.1[d]			
	−34.2[d]			
	−36.52[e]			
308.15	−18.25 ± 0.17	−18.27 ± 0.23	−19.71 ± 0.10	−21.29 ± 0.12
	−37.03[e]			
313.15	−18.45 ± 0.19	−18.46 ± 0.25	−20.08 ± 0.11	−21.45 ± 0.08
	−19.22[c]			
318.15	−18.04 ± 0.21	−18.50 ± 0.33	−20.05 ± 0.10	−21.61 ± 0.09

[a] Ref 41, conductivity. [b] Ref 38, conductivity. [c] Ref 40, surface tension. [d] Ref 12, conductivity. [e] Ref 37, microcalorimetry.

Enthalpy ($\Delta_{mic}H°$) and Entropy of Micellization ($\Delta_{mic}S°$) for C_{12}NM, C_{12}NE, C_{12}NP, and C_{12}NB at Different Temperatures. The thermodynamic parameters of micellization, such as the standard enthalpy ($\Delta_{mic}H°$) and standard entropy ($\Delta_{mic}S°$), can be obtained according to the following relations:[26]

$$\Delta_{mic}H^{\circ} = \left[\frac{\partial(\Delta_{mic}G^{\circ}/T)}{\partial(1/T)}\right] \tag{5}$$

$$\Delta_{mic}S^{\circ} = \frac{\Delta_{mic}H^{\circ} - \Delta_{mic}G^{\circ}}{T} \tag{6}$$

In eq 4, the ln(cmc) term in $\Delta_{mic}G°$ can be fitted by the following second-order polynomial:[8,28−30]

$$\ln(\text{cmc}) = a + bT + cT^2 \tag{7}$$

where the cmc is given in molality units ($\text{mol}\cdot\text{kg}^{-1}$) and a, b, and c are fitting constants. The values of these parameters used for calculations are given in Table 2. The fitting curves obtained using the relationship between ln(cmc) and T in eq 7 are shown in Figure 2. Thus, combining eqs 4, 3, 5, and 7 gives the following expression for $\Delta_{mic}H°$:[8]

$$\begin{aligned}\Delta_{mic}H^{\circ} &= -RT^2\left[(1+\beta)\frac{\partial\ln(\text{cmc})}{\partial T} + \frac{\partial\beta}{\partial T}\ln(\text{cmc})\right] \\ &= -RT^2[(1+\beta)(b+2cT) + b'\ln(\text{cmc})]\end{aligned} \tag{8}$$

The $\Delta_{mic}H°$ and $\Delta_{mic}S°$ of micellization estimated using eqs 8 and 6, respectively, and their comparisons with $\Delta_{mic}G°$ are shown in Figure 6. The data and uncertainties in $\Delta_{mic}H°$ and $\Delta_{mic}S°$ determined for the surfactant systems are shown in Tables 5 and 6, respectively. It can be seen in Figure 6 that $\Delta_{mic}H°$ and $T\Delta_{mic}S°$ depend linearly on temperature for

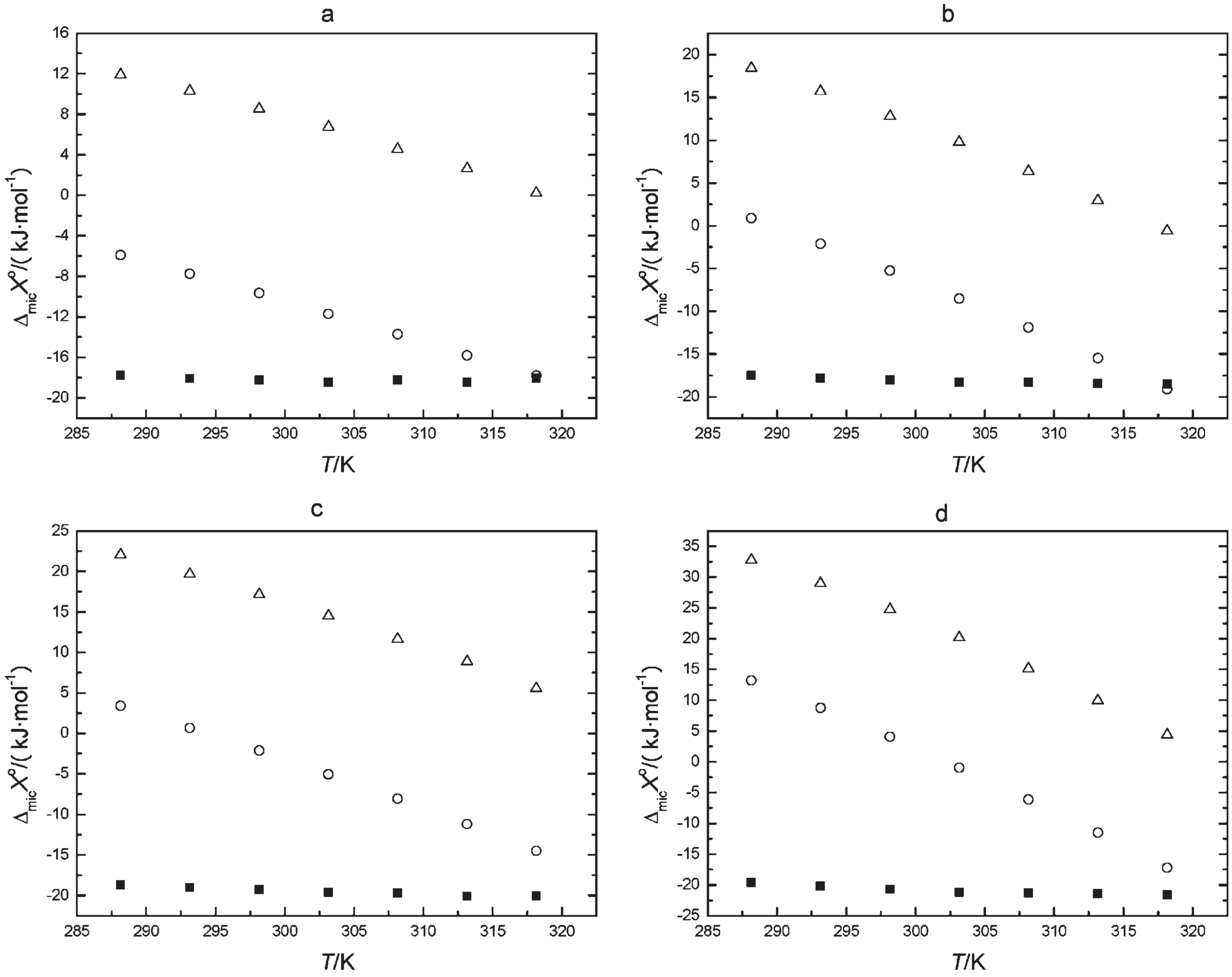

Figure 6. Dependence of the standard Gibbs energy $\Delta_{mic}G°$, standard enthalpy $\Delta_{mic}H°$, and standard entropy $\Delta_{mic}S°$ of the micellization on temperature (T) for (a) $C_{12}NM$, (b) $C_{12}NE$, (c) $C_{12}NP$, and (d) $C_{12}NB$: ■, $\Delta_{mic}G°$; ○, $\Delta_{mic}H°$; △, $T\Delta_{mic}S°$.

dodecyltrialkylammonium bromides. The plots of $\Delta_{mic}G°$, $\Delta_{mic}H°$, $T\Delta_{mic}S°$ vs T for $C_{12}NM$ and $C_{12}NE$ in Figure 6 were very similar to that of dodecyldimethylethylammonium bromide in literature;[10] meanwhile, the plots for $C_{12}NP$ and $C_{12}NB$ in Figure 6 were very similar to that of quaternary ammonium surfactants with the big headgroup $C_{12}H_{25}N^+(CH_3)_2(CHCH_3CH(OH)C_6H_5)Br^-$.[8] Enthalpy—entropy compensation was observed for $C_{12}NM$, $C_{12}NE$, $C_{12}NP$, and $C_{12}NB$, causing the change in $\Delta_{mic}G°$ to be very small. For $C_{12}NM$, $C_{12}NE$, $C_{12}NP$, and $C_{12}NB$, $\Delta_{mic}S°$ decreased with increasing temperature, which could be expected on the basis of "melting" of the "iceberg structure" of water molecules surrounding hydrophobic moieties.[31] This is a common fact of $\Delta_{mic}S°$ for the micellization of ordinary surfactants. The extensive hydrogen bonding in water gradually breaks down with increasing temperature, causing the importance of the entropic term of hydrophobic hydration to decrease and the dispersion interactions to become increasingly dominant.[32,33]

The large $\Delta_{mic}S°$ of $C_{12}NB$ compared with $C_{12}NM$, $C_{12}NE$, and $C_{12}NP$ could be attributed to the strong hydrophobicity of the $—N(CH_2CH_2CH_2CH_3)_3^+$ headgroup, which destroyed the structure of water surrounding the headgroup and induced disorder during association.

SUMMARY

Thermodynamic parameters of cationic surfactants with different headgroup sizes ($C_{12}NM$, $C_{12}NE$, $C_{12}NP$, and $C_{12}NB$) as a function of temperature were studied by conductivity. The increment of chain length in the headgroup brings on different rules compared with that in the hydrophobic tail from several points of view: First, the degree of counterion association (β) decreased with the increase of headgroup size. Second, T_{min}, the temperature of minimum of the U-shaped curve of cmc versus T, increased with the incremental chain length in headgroups. Third, nonlinearity was shown in both plots of $\Delta_{mic}G°$ versus T and ln(cmc) versus carbon number in the headgroups (N_c). These "abnormal" rules, which were reverse to those induced by the incremental chain length in the surfactant tail, could be ascribed to the different roles of the headgroup: the surroundings of headgroup, the promoting effect of raising T on hydrophobicity of headgroup, and the counteractive effect of raising T on

Table 5. Determined $\Delta_{\text{mic}}H^\circ/(\text{kJ}\cdot\text{mol}^{-1})$ Values and Their Uncertainties for the Systems of C_{12}NM, C_{12}NE, C_{12}NP, and C_{12}NB

T/K	C_{12}NM	C_{12}NE	C_{12}NP	C_{12}NB
288.15	-5.90 ± 0.03 2.45^{a}	0.892 ± 0.144	3.40 ± 0.14	13.2 ± 0.2
293.15	-7.74 ± 0.02 0.00^{a}	-2.11 ± 0.10	0.680 ± 0.073	8.77 ± 0.10
298.15	-9.65 ± 0.03 -2.62^{a} -2.34^{b}	-5.25 ± 0.07	-2.12 ± 0.05	4.06 ± 0.08
303.15	-11.7 ± 0.1 -2.18^{c} -4.70^{a} -3.47^{d}	-8.52 ± 0.04	-5.04 ± 0.04	-0.969 ± 0.057
308.15	-13.7 ± 0.1 -6.28^{a} -9.07^{e} -5.33^{d}	-11.9 ± 0.1	-8.05 ± 0.03	-6.13 ± 0.05
313.15	-15.8 ± 0.1 -6.77^{a} -8.71^{b}	-15.5 ± 0.1	-11.2 ± 0.1	-11.5 ± 0.1
318.15	-17.8 ± 0.1 -6.99^{a}	-19.1 ± 0.2	-14.5 ± 0.1	-17.2 ± 0.1

[a] Ref 13, ultrasound velocity. [b] Ref 43, calorimetric measurement. [c] Ref 12, conductivity. [d] Ref 37, microcalorimetry. [e] Ref 40, surface tension.

Table 6. Determined $T\Delta_{\text{mic}}S^\circ/(\text{kJ}\cdot\text{mol}^{-1})$ Values and Their Uncertainties for the Systems of C_{12}NM, C_{12}NE, C_{12}NP, and C_{12}NB

T/K	C_{12}NM	C_{12}NE	C_{12}NP	C_{12}NB
288.15	11.91 ± 0.19 22.2^{a}	18.41 ± 0.42	22.09 ± 0.35	32.79 ± 0.31
293.15	10.31 ± 0.16 20.1^{a}	15.70 ± 0.35	19.67 ± 0.21	28.97 ± 0.22
298.15	8.56 ± 0.18 17.8^{a}	12.80 ± 0.30	17.17 ± 0.16	24.73 ± 0.20
303.15	6.75 ± 0.19 33.0^{b} 16.0^{a} 33.05^{c}	9.78 ± 0.25	14.53 ± 0.13	20.18 ± 0.17
308.15	4.55 ± 0.24 14.6^{a} 9.86^{d} 31.70^{c}	6.37 ± 0.29	11.66 ± 0.13	15.16 ± 0.17
313.15	2.65 ± 0.28 14.3^{a}	2.96 ± 0.34	8.88 ± 0.14	9.95 ± 0.11
318.15	0.24 ± 0.32 14.3^{a}	-0.60 ± 0.51	5.55 ± 0.14	4.41 ± 0.13

[a] Ref 13, ultrasound velocity. [b] Ref 12, conductivity. [c] Ref 37, microcalorimetry. [d] Ref 40, surface tension.

cmc and β with the incremental chain length in headgroup. C_{12}NM and C_{12}NE resembled each other in the thermodynamic properties of micellization, and they showed a considerable discrepancy from either C_{12}NP or C_{12}NB. C_{12}NM, C_{12}NE, C_{12}NP, and C_{12}NB all exhibited the enthalpy−entropy compensation phenomenon. C_{12}NB was found to exhibit large $\Delta_{\text{mic}}S^\circ$ compared with other surfactants because of the strong hydrophobicity of its headgroup. This work could extend a thermodynamic insight for the effect of temperature on surfactants with different headgroup sizes.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Experimental conductivity data for the C_{12}NM, C_{12}NE, C_{12}NP, and C_{12}NB systems at different temperatures. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Nagarajan, R. Theory of Micelle Formation: Quantitative Approach to Predicting Micellar Properties from Surfactant Molecular Structure. In *Structure-Performance Relationships in Surfactants*; Esumi, K., Ueno, M., Eds.; Marcel Dekker, Inc.: New York, 2003; Chapter 1.

(2) Jonsson, B.; Lindman, B.; Holmberg, K.; Kronberg, B. *Surfactants and Polymers in Aqueous Solution*; John Wiley & Sons Ltd.: Chichester, 1998; pp 84−85, 253.

(3) Jonsson, B.; Lindman, B.; Holmberg, K.; Kronberg, B. *Surfactants and Polymers in Aqueous Solution*; John Wiley & Sons Ltd.: Chichester, 1998; pp 8, 37−39.

(4) Zhao, G.-X.; Zhu, B.-Y.; Dou, Z.-P.; Yan, P.; Xiao, J.-X. Effect of Charge Distribution along Surfactant Molecules on Physico-Chemical Properties of Surfactant Systems. *Colloids Surf., A* **2008**, *327*, 122–126.

(5) Chen, L.; Xiao, J.-X.; Ma, J.-M. Striking Differences between Alkyl Sulfate and Alkyl Sulfonate When Mixed with Cationic Surfactants. *Colloid Polym. Sci.* **2004**, *282*, 524–529.

(6) Yan, P.; Xiao, J.-X. Polymer-Surfactant Interaction: Differences between Alkyl Sulfate and Alkyl Sulfonate. *Colloids Surf., A* **2004**, *244*, 39–44.

(7) Wang, C.; Yan, P.; Xiao, J.-X. Differences between Sodium Decylsulfate and Sodium Decanesulfonate When Interacting with Cationic Polyelectrolyte. *Acta Phys. Chim. Sin.* **2009**, *25*, 1775–1778.

(8) Pahi, A. B.; Varga, D.; Kiraly, Z.; Mastalir, A. Thermodynamics of Micelle Formation of the Ephedrine-Based Chiral Cationic Surfactant DMEB in Water, and the Intercalation of DMEB in Montmorillonite. *Colloids Surf., A* **2008**, *319*, 77–83.

(9) Khatua, D.; Gupta, A.; Dey, J. Characterization of Micelle Formation of Dodecyldimethyl-*N*-2-phenoxyethylammonium Bromide in Aqueous Solution. *J. Colloid Interface Sci.* **2006**, *298*, 451–456.

(10) Galan, J. J.; Gonzalez-Perez, A.; Rodriguez, J. R. Micellization of Dodecyldimethylethylammonium Bromide in Aqueous Solution: Thermal Parameters. *J. Therm. Anal. Calorim.* **2003**, *72*, 465–470.

(11) Zana, R. Ionization of Cationic Micelles: Effect of the Detergent Structure. *J. Colloid Interface Sci.* **1980**, *78*, 330–337.

(12) Basu Ray, G.; Chakraborty, I.; Ghosh, S.; Moulik, S. P.; Palepu, R. Self-Aggregation of Alkyltrimethylammonium Bromides (C_{10}-, C_{12}-, C_{14}-, and C_{16}TAB) and Their Binary Mixtures in Aqueous Medium: A Critical and Comprehensive Assessment of Interfacial Behavior and Bulk Properties with Reference to Two Types of Micelle Formation. *Langmuir* **2005**, *21*, 10958–10967.

(13) Zielinski, R.; Ikeda, S.; Nomura, H.; Kato, S. Effect of Temperature on Micelle Formation in Aqueous Solutions of Alkyltrimethylammonium Bromides. *J. Colloid Interface Sci.* **1989**, *129*, 175–184.

(14) Warr, G. G.; Zemb, T. N.; Drifford, M. Liquid-Liquid Phase Separation in Cationic Micellar Solutions. *J. Phys. Chem.* **1990**, *94*, 3086–3092.

(15) Buckingham, S. A.; Garvey, C. J.; Warr, G. G. Effect of Head-Group Size on Micellization and Phase Behavior in Quaternary Ammonium Surfactant Systems. *J. Phys. Chem.* **1993**, *97*, 10236–10244.

(16) Bazito, R. C.; El Seoud, O. A.; Barlow, G. K.; Halstead, T. K. Aggregation of Cationic Surfactants in D_2O: A Proton NMR Study on Effects of the Structure of the Headgroup. *Ber. Bunsen-Ges.* **1997**, *101*, 1933–1941.

(17) Zhao, G.-X.; Xiao, J.-X. Surface Activity of Dodecyltrialkylammonium Bromide and its Mixture with Sodium Dodecylsulfate. *Acta Phys. Chim. Sin.* **1995**, *11*, 785–790.

(18) Yan, P.; Jin, C.; Wang, C.; Ye, J.-P.; Xiao, J.-X. Effect of Surfactant Head Group Size on Polyelectrolyte-Surfactant Interactions: Steady-State and Time-Resolved Fluorescence Study. *J. Colloid Interface Sci.* **2005**, *282*, 188–192.

(19) Wang, C.; Chen, X.-Y.; Zhu, Z.; Xiao, J.-X. Interactions between Cationic Hydrogenated/Fluorinated Surfactants and Neutral Polymers. *Acta Chim. Sin.* **2009**, *67*, 1425–1429.

(20) Pahi, A. B.; Kiraly, Z.; Mastalir, A.; Dudas, J.; Puskas, S.; Vago, A. Thermodynamics of Micelle Formation of the Counterion Coupled Gemini Surfactant Bis(4-(2-dodecyl)benzenesulfonate)-Jeffamine Salt and Its Dynamic Adsorption on Sandstone. *J. Phys. Chem. B* **2008**, *112*, 15320–15326.

(21) Zhao, G.-X.; Zhu, B.-Y. *Principles of Surfactant Action*; China Light Industry Press: Beijing, 2003; Chapter 3, pp250−252.

(22) Rodriguez, J. R.; Gonzalez-Perez, A.; Del Castillo, J. L.; Czapkiewicz, J. Thermodynamics of Micellization of Alkyldimethylbenzylammonium Chlorides in Aqueous Solutions. *J. Colloid Interface Sci.* **2002**, *250*, 438–443.

(23) Chen, L.-J.; Lin, S.-Y.; Huang, C.-C. Effect of Hydrophobic Chain Length of Surfactants on Enthalpy-Entropy Compensation of Micellization. *J. Phys. Chem. B* **1998**, *102*, 4350–4356.

(24) Frahm, J.; Diekmann, S.; Haase, A. Electrostatic Properties of Ionic Micelles in Aqueous Solutions. *Ber. Bunsen-Ges.* **1980**, *84*, 566–571.

(25) Gonzalez-Perez, A.; Ruso, J. M.; Prieto, G.; Sarmiento, F. Self-Assembly of Sodium Heptafluorobutyrate in Aqueous Solution. *Colloids Surf., A* **2004**, *249*, 41–44.

(26) Moroi, Y. *Micelles: Theoretical and Applied Aspects*; Plenum Press: New York, 1992.

(27) Xing, H.; Lin, S.-S.; Lu, R.-C.; Xiao, J.-X. NMR Investigation on Micellization of Ammonium/Tetraalkylammonium Perfluorooctanoates. *Colloids Surf., A* **2008**, *318*, 199–205.

(28) Nusselder, J. J. H.; Engberts, J. B. F. N. Toward a Better Understanding of the Driving Force for Micelle Formation and Micellar Growth. *J. Colloid Interface Sci.* **1992**, *148*, 353–361.

(29) Kiraly, Z.; Dekany, I. A Thermometric Titration Study on the Micelle Formation of Sodium Decyl Sulfate in Water. *J. Colloid Interface Sci.* **2001**, *242*, 214–219.

(30) Chatterjee, A.; Moulik, S. P.; Sanyal, S. K.; Mishra, B. K.; Puri, P. M. 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. *J. Phys. Chem. B* **2001**, *105*, 12823–12831.

(31) Frank, H. S.; Evans, M. W. Free Volume and Entropy in Condensed Systems. 3. Entropy in Binary Liquid Mixtures; Partial Molal Entropy in Dilute Solutions; Structure and Thermodynamics in Aqueous Electrolytes. *J. Chem. Phys.* **1945**, *13*, 507–532.

(32) Tanford, C. *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*; Wiley: New York, 1980.

(33) Blokzijl, W.; Engberts, J. B. F. N. Hydrophobic Effects-Opinions and Facts. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1545–1579.

(34) Haase, A. pH Indicators as Potential Probes in Membranes: Localization and Application. Ph.D. Thesis, Universitat Giessen, Giessen, Germany, 1980.

(35) Ribeiro, A. C. F.; Lobo, V. M. M.; Valente, A. J. M.; Azevedo, E. F. G.; Miguel, M. da G.; Burrows, H. D. Transport Properties of Alkyltrimethylammonium Bromide Surfactants in Aqueous Solutions. *Colloid Polym. Sci.* **2004**, *283*, 277–283.

(36) Rodriguez, A.; Junquera, E.; del Burgo, P.; Aicart, E. Conductometric and Spectrofluorimetric Characterization of the Mixed Micelles Constituted by Dodecyltrimethylammonium Bromide and a Tricyclic Antidepressant Drug in Aqueous Solution. *J. Colloid Interface Sci.* **2004**, *269*, 476–483.

(37) Stodghill, S. P.; Smith, A. E.; O'Haver, J. H. Thermodynamics of Micellization and Adsorption of Three Alkyltrimethylammonium Bromides Using Isothermal Titration Calorimetry. *Langmuir* **2004**, *20*, 11387–11392.

(38) Das, C.; Das, B. Thermodynamic and Interfacial Adsorption Studies on the Micellar Solutions of Alkyltrimethylammonium Bromides in Ethylene Glycol (1) + Water (2) Mixed Solvent Media. *J. Chem. Eng. Data* **2009**, *54*, 559–565.

(39) Bakshi, M. S.; Crisantino, R.; De Lisi, R.; Milioto, S. Volumes, Heat Capacities, and Conductivities of Water-Surfactant-18-Crown-6 Ether Systems. *Langmuir* **1994**, *10*, 423–431.

(40) Anand, K.; Yadav, O. P.; Singh, P. P. Studies on the Surface and Thermodynamic Properties of Some Surfactants in Aqueous and Water + 1,4-Dioxane Solutions. *Colloids Surf.* **1991**, *55*, 345–358.

(41) Graciani, M. M.; Munoz, M.; Rodriguez, A.; Moya, M. L. Water-*N,N*-Dimethylformamide Alkyltrimethylammonium Bromide Micellar Solutions: Thermodynamic, Structural, and Kinetic Studies. *Langmuir* **2005**, *21*, 3303–3310.

(42) Jalsenjak, N.; Tezak, D. A New Method for Simultaneous Estimation of Micellization Parameters from Conductometric Data. *Chem.—Eur. J.* **2004**, *10*, 5000–5007.

(43) Bashford, M. T.; Woolley, E. M. Enthalpies of Dilution of Aqueous Decyltrimethylammonium, Dodecyltrimethylammonium, Tetradecyltrimethylammonium, and Hexadecyltrimethylammonium Bromides at 10 °C, 25 °C, 40 °C, and 55 °C. *J. Phys. Chem.* **1985**, *89*, 3173–3179.