Critical Micellar Concentrations of Quaternary Ammonium Surfactants with Hydroxyethyl Substituents on Headgroups Determined by Isothermal Titration Calorimetry

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The micelle formations in aqueous solutions of a set of quaternary ammonium surfactants, *N*-alkyl-*N*-2-hydroxyethyl-*N*,*N*-dimethyl ammonium bromide (C_nHDAB, $n = 12$, 14, and 16), *N*-alkyl-*N*,*N*-2-dihydroxyethyl-*N*-methyl ammonium bromide (C_nDHAB, $n = 12$, 14, and 16), along with *N*-dodecyl-*N*,*N*,*N*-trimethyl ammonium bromide (DTAB), and *N*-cetyl-*N*,*N*,*N*-trimethyl ammonium bromide (CTAB), were investigated by the isothermal titration calorimetry (ITC). The critical micellar concentrations (CMCs) and the enthalpies of micellization at six different temperatures were determined. The entropies and Gibbs free energies of micellization were then calculated by using the pseudophase separation model. The effects on the thermodynamic data of the temperature, the length of the alkane chain, and the number of hydroxyethyl substituents on the surfactant headgroup were discussed. The CMC value of each surfactant increases slightly with the temperature increase. At a given temperature, both the increases of the length of the alkane chain and the number of hydroxyethyl substituents lead to the decreases of the CMC values.

Introduction

Surfactants have widespread applications in fine industry, medicine, biological systems, petroleum production, and soil remediation techniques. Dispersed in water, surfactant molecules can form different types of aggregations because of the amphiphilic molecular structure, which usually consists of a hydrophilic polar headgroup and a hydrophobic segment. When forming micelles in aqueous solution, the hydrophilic headgroups are located at the surface of the micelles, and the hydrophobic segments are shielded from water. The thermodynamics of the micellization process of surfactants in water were widely studied with many different techniques, such as light scattering,[1−3] conductometry,[4−6] surface tension measurements,[7−9] and calorimetry.[10−12] More and more applications of the isothermal titration calorimetry (ITC) are partly due to the capability for the direct determination of the critical micelle concentration (CMC) and the enthalpy of micellization (ΔH_{mic}). The change in Gibbs free energy (ΔG_{mic}) can then be derived by using different models. In the pseudophase separation model, the micelle part is assumed to be treated as a separate phase, and the value of ΔG_{mic} is calculated from the CMC data from the following equation[13,14]

$$\Delta G_{\mathrm{mic}} = 2RT \ln x_{\mathrm{CMC}} \tag{1}$$

where x_{CMC} is the critical micelle concentration expressed as mole fraction; T is the absolute temperature; and R is the gas constant. ΔS_{mic} can be evaluated by the Gibbs equation

$$\Delta S_{\mathrm{mic}} = (\Delta H_{\mathrm{mic}} - \Delta G_{\mathrm{mic}})/T \tag{2}$$

Recently, several cationic surfactants with one or two hydroxyethyl substituents on the quaternary ammonium headgroup have been synthesized in this laboratory. To further investigate the micellization properties of the surfactants, the ITC method is used to determine the CMC values and the enthalpies of micellization at different temperatures in the present work. The corresponding changes in Gibbs free energy and entropy of the micellization are calculated from the pseudophase separation model. Furthermore, the influences on the thermodynamic functions of the temperature, the length of the alkane chain, and the substituent number on the headgroup are discussed.

Experimental Section

Materials. Six quaternary ammonium surfactants, *N*-alkyl-*N*-2-hydroxyethyl-*N*,*N*-dimethyl ammonium bromide (C_nHDAB, $n = 12$, 14, and 16) and *N*-alkyl-*N*,*N*-2-dihydroxyethyl-*N*-methyl ammonium bromide (C_nDHAB, $n = 12$, 14, and 16), were synthesized from the reactions of 1-bromoalkane (1-bromododecane, 1-bromotetradecane, and 1-bromohexadecane) with dimethylhydroxyethylamine and methyldihydroxyethylamine, respectively, in acetone at about 60 °C for 6 h. They were purified by using the recrystallization method with the mixed solvents of acetone and methanol. The molecular structures were examined by NMR (Bruker Advance 2B/400 Hz), IR spectrum (NEXES 470), and elemental analysis (Carlabo EA1110). *N*-Dodecyl-*N*,*N*,*N*-trimethyl ammonium bromide (DTAB) and *N*-cetyl-*N*,*N*,*N*-trimethyl ammonium bromide (CTAB) were purchased from Sigma and used without further purification. The chemical structures of the investigated surfactants are listed in Table 1. All the surfactant solutions were prepared with ultrapure water with the resistivity above $18.2 \cdot 10^6\ \Omega \cdot \mathrm{cm}$ at 298.15 K produced by the Millipore Q3 system.

Calorimetric Method. The calorimetric experiments were performed with a VP-ITC (Micro-Cal, USA), which has the precision of $0.5\ \mathrm{ncal} \cdot \mathrm{s}^{-1}$. The calorimeter has a sample cell with the fixed volume of 1.45 mL and a gastight syringe with

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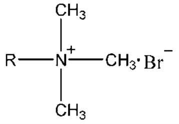
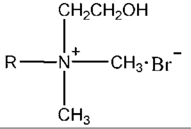
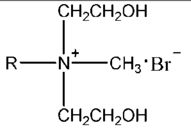
Table 1. Nomenclature and Molecular Structures of the Cationic Surfactants

Structure	R	Name
	$-(CH_2)_{11}CH_3$	*N*-dodecyl-*N*, *N*, *N*-trimethyl ammonium bromide
	$-(CH_2)_{15}CH_3$	*N*-cetyl-*N*, *N*, *N*-trimethyl ammonium bromide
	$-(CH_2)_{11}CH_3$	*N*-dodecyl-*N*-2-hydroxyethyl-*N*, *N*-dimethyl ammonium bromide
	$-(CH_2)_{13}CH_3$	*N*-tetradecyl-*N*-2-hydroxyethyl-*N*, *N*-dimethyl ammonium bromide
	$-(CH_2)_{15}CH_3$	*N*-cetyl-*N*-2-hydroxyethyl-*N*, *N*-dimethyl ammonium bromide
	$-(CH_2)_{11}CH_3$	*N*-dodecyl-*N*, *N*-2-dihydroxyethyl-*N*-methyl ammonium bromide
	$-(CH_2)_{13}CH_3$	*N*-tetradecyl-*N*, *N*-2-dihydroxyethyl-*N*-methyl ammonium bromide
	$-(CH_2)_{15}CH_3$	*N*-cetyl-*N*, *N*-2-dihydroxyethyl-*N*-methyl ammonium bromide

the maximum volume of 250 μL. The sample cell was filled with ultrapure water. The surfactant solution as titrant was added into the sample cell step by step through the syringe. The number of injections, the volume of each injection, and the time interval between each injection were controlled automatically with software. The ITC experiments were carried out at temperatures between (298.15 and 323.15) K in a 5 K interval.

Results and Discussion

Structural Characterization of the Synthesized Surfactants. The molecular structures of the synthesized surfactants were examined by NMR, IR spectrum, and elemental analysis with the following results.

C_{12}HDAB. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ: 0.86 (t, J = 6.8 Hz, 3H), 1.23 to 1.33 (m, 18H), 1.68 to 1.78 (m, 2H), 3.36 (s, 6H), 3.52 (t, J = 8.4 Hz, 2H), 3.75 (t, J = 4.6 Hz, 2H), 4.08 to 4.14 (m, 2H), 4.29 to 4.50 (m, 1H). IR (KBr): ν (3242, 2918, 2850, 1477, 1383, 1077, 1053, 965, 911, 728, 716) cm^{-1}. Elemental analysis results for $C_{16}H_{36}NOBr$ in mass %: N, 4.15; C, 56.70; H, 10.75. Calculated: N, 4.14; C, 56.79; H, 10.72.

C_{14}HDAB. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ: 0.85 (t, J = 6.8 Hz, 3H), 1.22 to 1.31 (m, 22H), 1.71 to 1.74 (m, 2H), 3.35 (s, 6H), 3.52 (t, J = 8.4 Hz, 2H), 3.79 (t, J = 4.6 Hz, 2H), 4.09 to 4.13 (m, 2H), 4.63 to 4.68 (m, 1H). IR (KBr): ν (3243, 2918, 2850, 1476, 1383, 1080, 1056, 917, 731, 602) cm^{-1}. Elemental analysis results for $C_{18}H_{40}NOBr$ in mass %: N, 3.86; C, 59.32; H, 11.22. Calculated: N, 3.81; C, 59.00; H, 11.00.

C_{16}HDAB. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ: 0.85 (t, J = 6.6 Hz, 3H), 1.22 to 1.32 (m, 26H), 1.70 to 1.75 (m, 2H), 3.35 (s, 6H), 3.52 (t, J = 8.2 Hz, 2H), 3.73 (t, J = 4.6 Hz, 2H), 4.08 to 4.12 (m, 2H), 4.30 to 4.54 (m, 1H). IR (KBr): ν (3244, 2917, 2849, 1470, 1383, 1081, 1053, 965, 720) cm^{-1}. Elemental analysis results for $C_{20}H_{44}NOBr$ in mass %: N, 3.52; C, 61.27; H, 11.47. Calculated: N, 3.55; C, 60.90; H, 11.24.

C_{12}DHAB. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ: 0.84 (t, J = 6.8 Hz, 3H), 1.21 to 1.35 (m, 18H), 1.64 to 1.79 (m, 2H), 3.37 (s, 3H), 3.52 (t, J = 8.0 Hz, 2H), 3.66 to 3.80 (m, 4H), 4.03 to 4.15 (m, 4H), 4.59 to 4.77 (m, 2H). IR (KBr): ν (3260, 2918, 2850, 1469, 1384, 1057, 964, 721) cm^{-1}. Elemental analysis results for $C_{17}H_{38}NO_2Br$ in mass %: N, 3.87; C, 55.50; H, 10.54. Calculated: N, 3.80; C, 55.43; H, 10.40.

C_{14}DHAB. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ: 0.86 (t, J = 6.8 Hz, 3H), 1.23 to 1.36 (m, 22H), 1.67 to 1.79 (m, 2H), 3.34 (s, 3H), 3.54 (t, J = 7.6 Hz, 2H), 3.68 to 3.82 (m, 4H), 4.11 to 4.18 (m, 4H), 4.46 to 4.57 (m, 2H). IR (KBr): ν (3294, 2920, 2852, 1466, 1444, 1085, 1050, 911, 728, 630) cm^{-1}; Elemental analysis results for $C_{19}H_{42}NO_2Br$ in mass %: N, 3.51; C, 58.11; H, 10.92. Calculated: N, 3.53; C, 57.56; H, 10.68.

C_{16}DHAB. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ: 0.86 (t, J = 6.8 Hz, 3H), 1.22 to 1.3 (m, 26H), 1.66 to 1.80 (m, 2H), 3.31 (s, 3H), 3.52 (t, J = 8.0 Hz, 2H), 3.69 to 3.79 (m, 4H), 4.04 to 4.10 (m, 4H), 4.93 to 5.04 (m, 2H). IR (KBr): ν (3293, 2919, 2851, 1465, 1380, 1086, 1051, 917, 728, 629) cm^{-1}. Elemental analysis results for $C_{21}H_{46}NO_2Br$ in mass %: N, 3.56; C, 60.04; H, 11.45. Calculated: N, 3.30; C, 59.42; H, 10.92.

Data from ITC Measurements. As an example, Figure 1 shows the representative isothermal titration curve obtained from the dilution of a concentrated solution of CTAB into water at 298.15 K. The enthalpy of dilution of CTAB as a function of the CTAB concentration is given in Figure 2, which can be described in three different concentration regions. In the first region, at surfactant concentrations up to $0.8 \cdot 10^{-3}$ mol·L^{-1}, below the CMC value, the relatively large and constant enthalpies are due to the dilution of micelles, demicellization of micelles, and dilution of the resultant monomers. The second region, in which the endothermic effect decreases sharply, indicates that the CMC value of the surfactant is reached. The enthalpic effect in the third concentration range from approximately $1.2 \cdot 10^{-3}$ mol·L^{-1} becomes small and keeps almost constant. It is because the system is concentrated enough and the surfactant molecules mainly exist in the form of micelles. The small enthalpic effects result from the dilution of micelles and no demicellization of micelles. The difference in enthalpy between the first and the third concentration region should be

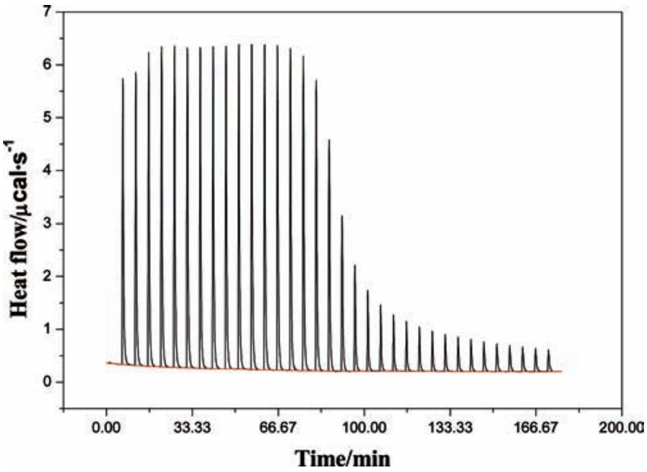


Figure 1. Curve of heat flow as a function of CTAB at 298.15 K.

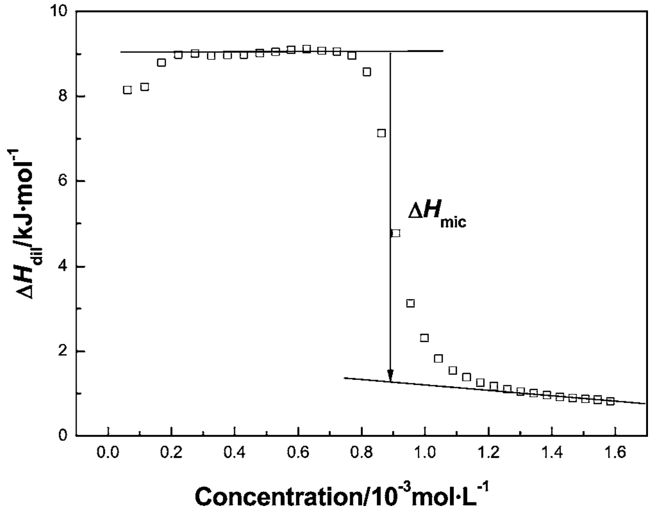


Figure 2. Enthalpy of dilution of CTAB in water at 298.15 K.

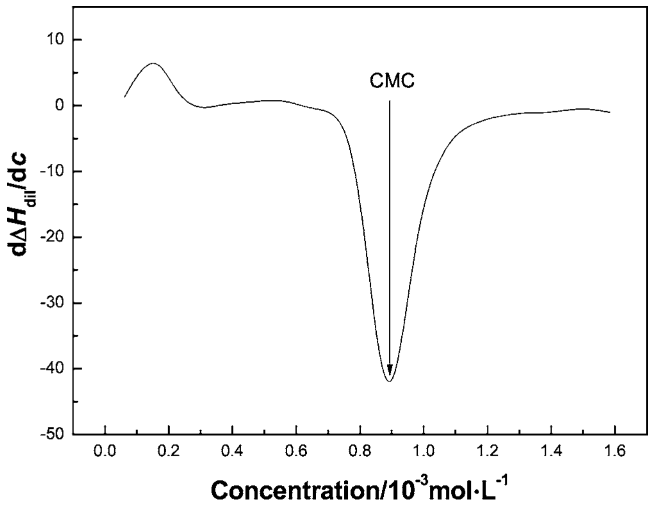


Figure 3. First derivative of enthalpy curve calculated from interpolated values for CTAB at 298.15 K.

the enthalpy of micellization, ΔH_{mic}.[15] The CMC value is obtained as the midpoint of the second range and determined from the first-order differential of the enthalpy profile curve as shown in Figure 3.

The enthalpies of dilution at different temperatures versus concentration for eight surfactants are shown in detail in Figures 4 to 11. It can be seen that all the dilution processes of the surfactant solutions are endothermic and the dilution enthalpies have positive values. Not all of the enthalpy plateaus before the CMC values stay flat because of the complicated interactions in the surfactant solutions.[16,17] Table 2 presents the determined CMC and ΔH_{mic} values at different temperatures for eight surfactants, along with the literature values of DTAB and CTAB.[17] The deviations for CMC are less than 5 %, and those for ΔH_{mic} are less than 8 % from the corresponding literature values. It follows that they are in satisfactory agreement. The calculated values of ΔG_{mic} and ΔS_{mic} from the pseudo-phase separation model are also summarized in Table 2. In all the cases, negative values of ΔH_{mic} and ΔG_{mic} and positive values of ΔS_{mic} are observed, which indicates that the formation of the micelles has been driven by both the increase in entropy and the loss in enthalpy. The positive ΔS_{mic} values result from that the ordered water molecules are excluded from the micellar interior during the micelle formation from monomers. The structures of the water molecules surrounding the hydrocarbon chains in aqueous medium are destroyed when the hydrocarbon chains are removed from the aqueous medium to the interior of the micelles.

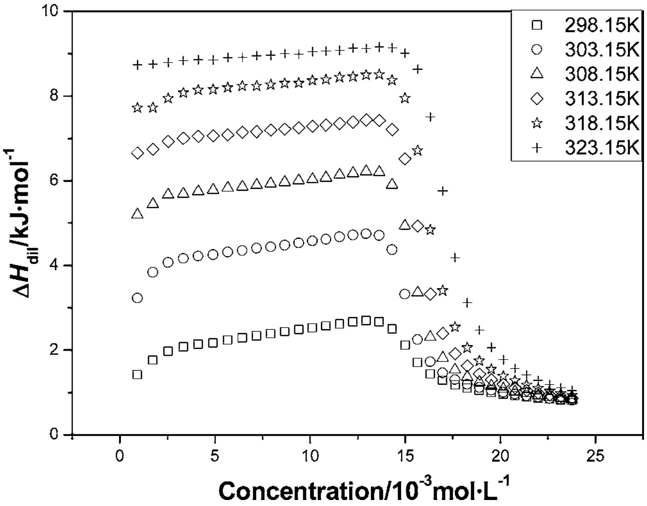


Figure 4. Enthalpies of dilution of DTAB as a function of surfactant concentration at different temperatures.

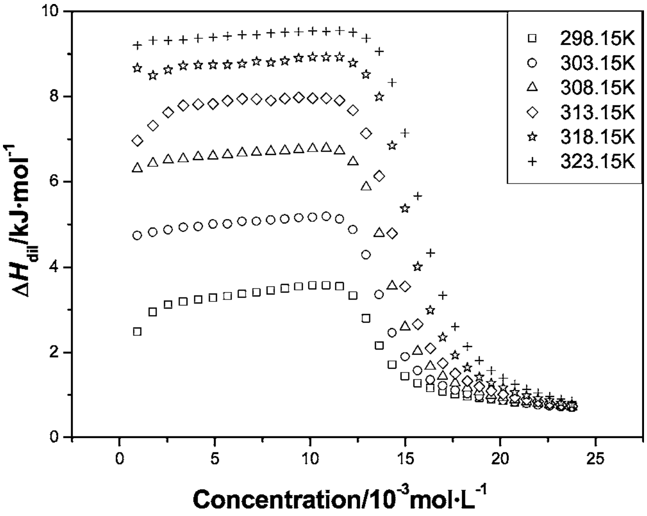


Figure 5. Enthalpies of dilution of C_{12}HDAB as a function of surfactant concentration at different temperatures.

Effects of the Temperature. Table 2 indicates that the increase in temperature causes a slight increase of the CMC value. This phenomenon has already been reported in the literature.[10] However, ΔH_{mic} changes clearly when the temperature increases. In the case of C_{12}HDAB, ΔH_{mic} gradually becomes more negative from (-2.723 to -7.955) $\mathrm{kJ \cdot mol^{-1}}$ with the temperature increasing from (298.15 to 323.15) K. It is because the increasing temperature causes the decrease in the amount of water molecules bound to the surfactant headgroups, which makes the dehydration heat decrease when the micelles form. ΔS_{mic} for C_{12}HDAB is 129.6 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ at 298.15 K and decreases to 119.4 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ at 308.15 K and 111.5 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ at 323.15 K. The positive values of ΔS_{mic} result from the destruction of the iceberg structure of the ordered water molecules around the hydrophobic alkane chains during the formation process of the micelles. The temperature-dependent trend is ascribed to the decrease in the amount of ordered water molecules around the hydrophobic alkane chains and water molecules bound to the surfactant headgroups when increasing the temperature. More negative values of ΔG_{mic} can be observed as the temperature increases, for example, -41.37 $\mathrm{kJ \cdot mol^{-1}}$ at

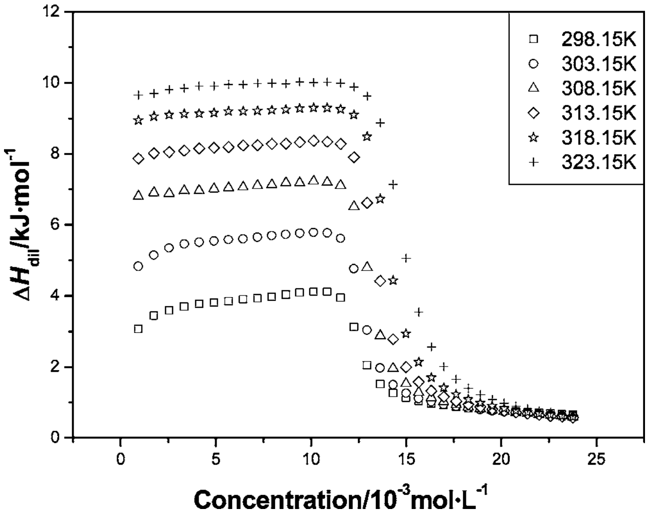


Figure 6. Enthalpies of dilution of C_{12}DHAB as a function of surfactant concentration at different temperatures.

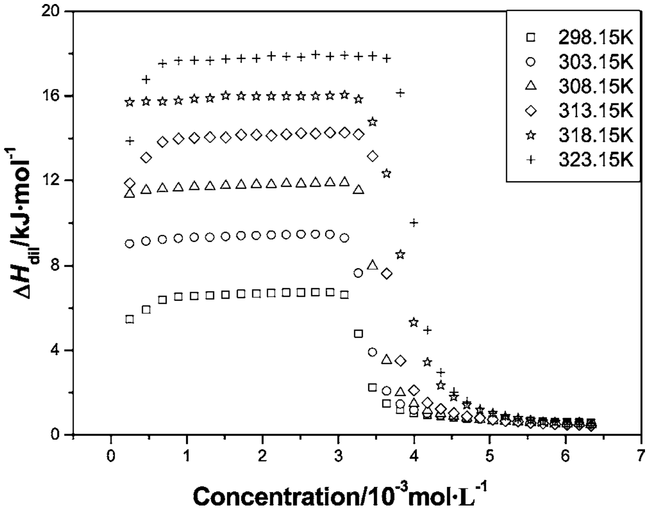


Figure 7. Enthalpies of dilution of C_{14}HDAB as a function of surfactant concentration at different temperatures.

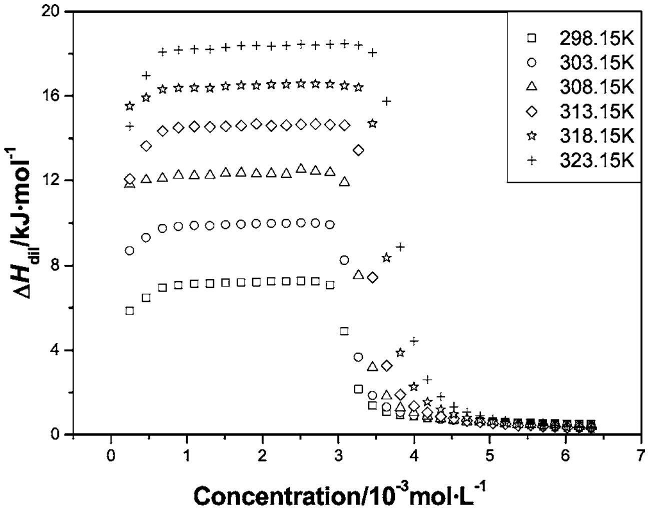


Figure 8. Enthalpies of dilution of C_{14}DHAB as a function of surfactant concentration at different temperatures.

298.15 K, $-42.48\ \mathrm{kJ\cdot mol^{-1}}$ at 308.15 K, and $-44.00\ \mathrm{kJ\cdot mol^{-1}}$ at 323.15 K for C_{12}HDAB. It indicates that the decrease in ΔS_{mic} or in ΔH_{mic} has opposite effects on the change of ΔG_{mic} with the increase of the temperature. The decrease in ΔS_{mic} has a smaller effect on ΔG_{mic} than the change in ΔH_{mic}.

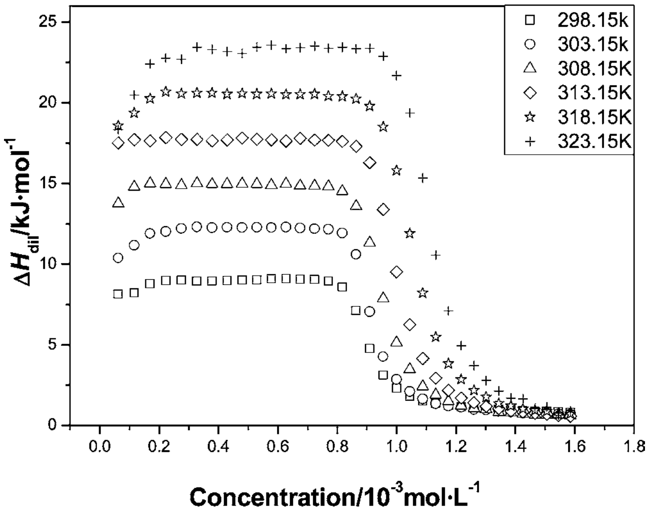


Figure 9. Enthalpies of dilution of CTAB as a function of surfactant concentration at different temperatures.

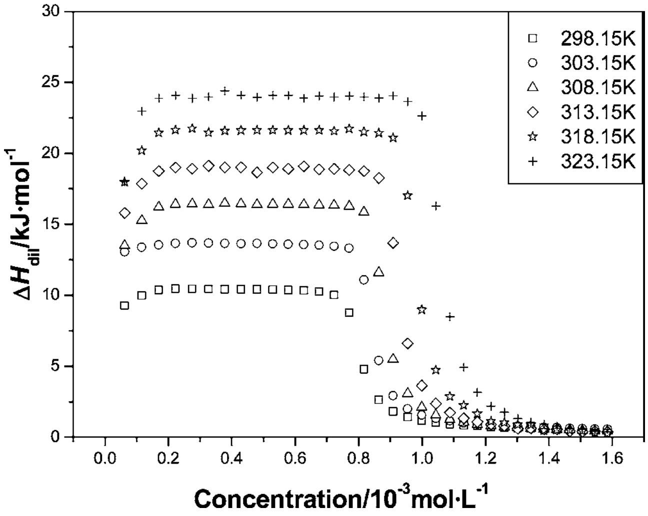


Figure 10. Enthalpies of dilution of C_{16}HDAB as a function of surfactant concentration at different temperatures.

Effects of the Length of the Alkane Chain. As the tail length in the surfactant molecule increases, the CMC value at a given temperature decreases. The similar phenomenon was also observed in some works reported in the literature.[10,18] Taking ΔH_{mic} at 298.15 K as an example, it is $-2.723\ \mathrm{kJ\cdot mol^{-1}}$ for C_{12}HDAB, $-5.967\ \mathrm{kJ\cdot mol^{-1}}$ for C_{14}HDAB, and $-9.678\ \mathrm{kJ\cdot mol^{-1}}$ for C_{16}HDAB. More negative values of ΔH_{mic} result from the stronger hydrophobic interaction between the alkane chains with the increase of the length of the alkane chains. However, ΔS_{mic} increases with the change of the hydrophobic segment in surfactants from *n*-dodecyl to *n*-cetyl chain. It is observed that ΔS_{mic} at 298.15 K is (128.5, 140.3, and 153.2) $\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ for C_{12}DHAB, CH_{14}DHAB, and C_{16}DHAB, respectively. This is the consequence of the increase in the amount of ordered water surrounding the alkane chain. With the increase in the length of the alkane chain, the changes in ΔH_{mic} and ΔS_{mic} have the same effects on ΔG_{mic}. At constant temperature, the ΔG_{mic} decreases of approximately $7.0\ \mathrm{kJ\cdot mol^{-1}}$ are observed for each addition of two $-CH_2-$ groups.

Effects of the Number of Hydroxyethyl Substituent. It is noted that the CMC value decreases with the increase of the

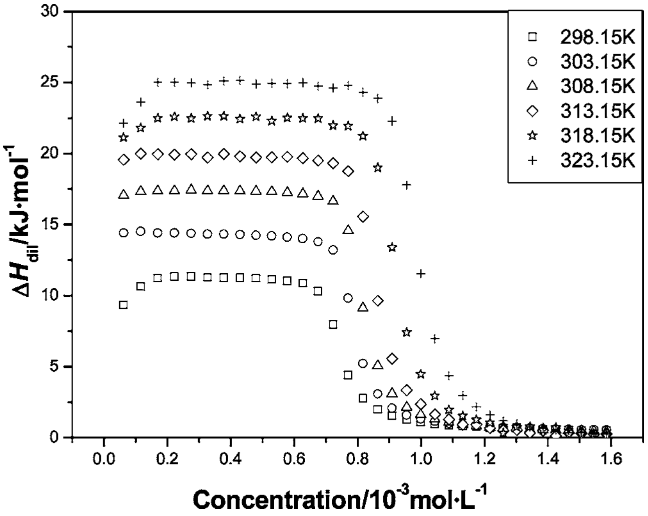


Figure 11. Enthalpies of dilution of C_{16}DHAB as a function of surfactant concentration at different temperatures.

number of the hydroxyethyl substituents on the quaternary ammonium headgroup. The formation of hydrogen bonds between hydroxyethyl groups in micelles weakens the repulsion between the charged headgroups. As a result, the micellization process occurs at a relatively low surfactant concentration. With the increase in the hydroxyethyl substituent number, ΔH_{mic} becomes more and more negative from DTAB to C_{12}DHAB (-1.824 kJ·mol^{-1} for DTAB, -2.723 kJ·mol^{-1} for C_{12}HDAB, and -3.343 kJ·mol^{-1} for C_{12}DHAB at 298.15 K, respectively). In these systems, more hydrogen bonds form among the hydroxyl groups in the micelles with the increase of the hydroxyethyl substituent number, and more energies are released. In the case of ΔS_{mic} at 298.15 K, the values are 130.5 J·mol^{-1}·K^{-1} for DTAB, 129.6 J·mol^{-1}·K^{-1} for C_{12}HDAB, and 128.5 J·mol^{-1}·K^{-1} for C_{12}DHAB, respectively. ΔS_{mic} progressively decreases with the increase in the hydroxyethyl substituent number. As mentioned above, more hydroxyethyl substituents on a surfactant headgroup cause more water molecules to be excluded from the micellar interior. It leads to an increase in the entropy of the system. However, the hydrogen bonds formed between hydroxyl groups and water molecules cause the decrease of the disorder degree. From the obtained results, the conclusion can be drawn that the formation of hydrogen bonds makes a larger contribution to the change in ΔS_{mic}. With increasing number of hydroxyethyl substituents, the decreases in both ΔH_{mic} and ΔS_{mic} make opposite contributions to ΔG_{mic}. It is noted that ΔG_{mic} at 298.15 K becomes more and more negative from -40.73 kJ·mol^{-1} for DTAB and -41.37 kJ·mol^{-1} for C_{12}HDAB to -41.65 kJ·mol^{-1} for C_{12}DHAB. Thus, the influence results on ΔG_{mic} of the increasing amount of the hydroxyethyl substituents are similar to those of the increasing temperature.

Table 2. CMC Values and Thermodynamic Parameters of Micellization of the Surfactants, DTAB, CTAB, C_nHDAB (n = 12, 14, 16), and C_nDHAB (n = 12, 14, 16), in Aqueous Solution Obtained from the ITC Measurements[a]

	T	CMC	ΔH_{mic}	ΔG_{mic}	ΔS_{mic}
compound	K	10^{-3} mol·L^{-1}	kJ·mol^{-1}	kJ·mol^{-1}	J·mol^{-1}·K^{-1}
DTAB	298.15	15.00	−1.824	−40.73	130.5
	303.15	15.07	−3.709	−41.39	124.3
		15.51[b]	−3.461[b]		
	308.15	15.24	−5.168	−42.02	119.6
		15.83[b]	−5.321[b]		
	313.15	15.67	−6.172	−42.56	116.2
	318.15	15.98	−6.987	−43.13	113.6
	323.15	16.92	−7.563	−43.50	111.2
C_{12}HDAB	298.15	13.20	−2.723	−41.37	129.6
	303.15	13.43	−4.195	−41.97	124.6
	308.15	13.92	−5.698	−42.48	119.4
	313.15	14.22	−6.726	−43.06	116.0
	318.15	14.83	−7.507	−43.52	113.2
	323.15	15.43	−7.955	−44.00	111.5
C_{12}DHAB	298.15	12.46	−3.343	−41.65	128.5
	303.15	12.62	−4.934	−42.29	123.2
	308.15	13.09	−6.315	−42.80	118.4
	313.15	13.36	−7.507	−43.39	114.6
	318.15	13.89	−8.221	−43.87	112.1
	323.15	14.56	−8.935	−44.31	109.5
C_{14}HDAB	298.15	3.318	−5.967	−48.21	141.7
	303.15	3.356	−8.645	−48.96	133.0
	308.15	3.505	−11.19	−49.55	124.5
	313.15	3.636	−13.58	−50.16	116.8
	318.15	3.742	−15.51	−50.81	111.0
	323.15	3.998	−17.22	−51.25	105.3
C_{14}DHAB	298.15	3.118	−6.686	−48.52	140.3
	303.15	3.165	−9.366	−49.26	131.6
	308.15	3.269	−11.89	−49.91	123.4
	313.15	3.376	−14.04	−50.55	116.6
	318.15	3.580	−15.86	−51.04	110.6
	323.15	3.731	−17.57	−51.62	105.4
CTAB	298.15	0.888	−7.894	−54.75	157.1
	303.15	0.907	−11.08	−55.56	146.7
		0.950[b]	−11.10[b]		
	308.15	0.929	−14.00	−56.35	137.4
		0.975[b]	−14.37[b]		
	313.15	0.977	−16.78	−57.00	128.5
	318.15	1.041	−19.67	−57.58	119.2
	323.15	1.104	−22.15	−58.17	111.5
C_{16}HDAB	298.15	0.797	−9.678	−55.28	153.0
	303.15	0.839	−12.44	−55.95	143.5
	308.15	0.879	−15.52	−56.64	133.4
	313.15	0.925	−18.01	−57.29	125.4
	318.15	0.975	−20.89	−57.93	116.4
	323.15	1.055	−22.88	−58.41	110.0
C_{16}DHAB	298.15	0.738	−9.999	−55.66	153.2
	303.15	0.786	−12.91	−56.28	143.1
	308.15	0.799	−16.40	−57.12	132.2
	313.15	0.838	−19.29	−57.80	123.0
	318.15	0.909	−21.63	−58.30	115.2
	323.15	0.974	−23.77	−58.84	108.5

[a] Experimental precisions for CMC and ΔH_{mic} are estimated to be ± 4 % and ± 5 %, respectively. [b] Ref 17.

Conclusions

The thermodynamics of the micellization process for eight quaternary ammonium surfactants, *N*-alkyl-*N*-2-hydroxyethyl-*N*,*N*-dimethyl ammonium bromide (C_nHDAB, n = 12, 14, and 16), *N*-alkyl-*N*,*N*-2-dihydroxyethyl-*N*-methyl ammonium bromide (C_nDHAB, n = 12, 14, and 16), along with *N*-dodecyl-*N*,*N*,*N*-trimethyl ammonium bromide (DTAB) and *N*-cetyl-*N*,*N*,*N*-trimethyl ammonium bromide (CTAB), were investigated. The values of the critical micellar concentration (CMC) and the enthalpies of micellization, ΔH_{mic}, of the surfactants at different temperatures were determined directly by using isothermal titration calorimetry (ITC), and the corresponding Gibbs free energy, ΔG_{mic}, and entropy, ΔS_{mic}, of the micellization were calculated. The CMC value decreases as the amount of the hydroxyethyl substituent on the surfactant headgroup increases and the alkane chain lengthens. The increase in temperature causes a slight increase in the CMC value. The increase in temperature, length of the hydrophobic alkane chain, and the decrease in the number of hydroxyethyl substituents make the ΔH_{mic} values more negative, respectively. Both the increases in temperature and the number of hydroxyethyl substituents make ΔS_{mic} decrease.

However, ΔS_{mic} increases with the lengthening of the alkane chain. ΔG_{mic} becomes more negative with the increase in temperature, length of the alkane chain, and the hydroxyethyl substituent number, respectively.

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