J. Chem. Eng. Data **2010,** *55,* 147–151

Micelle Formation of Long-Chain Imidazolium Ionic Liquids in Aqueous Solution Measured by Isothermal Titration Microcalorimetry

Fei Geng,[†] Jie Liu,[‡] Liqiang Zheng,[†] Li Yu,*[,†] Zhen Li,[†] Ganzuo Li,[†] and Chenho Tung[§]

Key Laboratory of Colloid and Interface Chemistry, Shandong University, Ministry of Education, Jinan, 250100, PR China, Department of Chemistry, Liaocheng University, Liaocheng, 252059, PR China, and Technical Institute of Physics and Chemistry, The Chinese Academy of Sciences, Beijing, 100190, PR China

Self-association of three long-chain imidazolium ionic liquids (ILs), [C$_{12}$mim]Br, [C$_{14}$mim]Br, and [C$_{16}$mim]Br, in aqueous solution was studied by surface tension measurements over a temperature range from (278.15 to 328.15) K. Effects of temperature and hydrocarbon chain length of the three long-chain ILs on the critical micelle concentration (CMC) were examined. Thermodynamic parameters, $\Delta_{mic}G$, $\Delta_{mic}H$, and $\Delta_{mic}S$, of micellization were determined by applying a mass-action model equation. Isothermal titration microcalorimetry was used to obtain the enthalpy change upon micellization of the three long-chain ILs at 298.15 K. Moreover, the CMCs and the thermodynamic parameters ($\Delta_{mic}G$, $\Delta_{mic}H$, and $\Delta_{mic}S$) were determined based on the isothermal titration microcalorimetry results. These CMC values are approximately equal to the CMCs obtained by surface tension measurement.

Introduction

Ionic liquids (ILs) are a class of organic molten electrolytes which are liquid around room temperature.[1] They have specific properties such as insignificant vapor pressures, high ion conductivity, outstanding catalytic properties, nonflammability, and stability from room temperature up to 300 °C or more.[2] Moreover, the physical and chemical properties of ILs can be adjusted by selection of the cation, anion, and substituent.[3] ILs are environmentally friendly solvents since their nonvolatile nature can prevent environmental pollution. ILs have been used for many applications, ranging from media for organic synthesis and catalysis to lubricants.[4−6]

Long-chain ILs consist of a charged hydrophilic headgroup and one or more hydrophobic tails. Due to their structure and inherent charge, they can self-assemble. In some ways, long-chain ILs resemble conventional surfactants and can form aggregates.[7] Knowledge of their aggregation behavior is an important part of understanding how ILs participate in a mixed solvent system.

ILs composed of the 1-alkyl-3-methylimidazolium cation, [C$_n$mim]$^+$, have been extensively studied in the field of colloid and interface science. Micellar aggregates formed by three different long-chain ILs based on [C$_n$mim]$^+$ have been presented previously.[8] Micellization of a homologous series of *N*-alkyl-*N*-methylpyrrolidinium bromides in aqueous solution has been studied by Baker's group.[9]

Thermodynamic parameters play important roles in understanding the self-assembly of surfactants. The effects of temperature and the structure of surfactants, in particular the hydrocarbon chain length on molecular self-assembly, can be observed by thermodynamic parameters. The thermodynamic properties of surfactants have been widely studied by applying different techniques such as surface tension,[10] light scattering,[11] and densitometry.[12] In recent years, calorimetry, especially microcalorimetry, has been used to offer a direct and precise determination of the enthalpy change upon micellization.[13] Recently, isothermal titration microcalorimetry has been introduced as a promising method for the quantitative study of amphiphile self-aggregation or micellization. Bai et. al used isothermal titration calorimetry along with conductivity to determine the thermodynamics of aggregation of 1-alkyl-3-methylimidazolium chlorides ([C$_n$mim]Cl, $n = 8$, 10, 12, and 14) in aqueous solution.[14]

Previously, our group reported the effects of the hydrocarbon chain length of long-chain ILs and the type of halide counterion present on micelle formation and surface activity of long-chain ILs.[10] It was found that the CMC values of the long-chain ILs were lower than those of typical cationic surfactants, the alkyltrimethylammonium bromides. These results demonstrated that the surface activity of the long-chain imidazolium ILs is somewhat superior to that of conventional ionic surfactants. As an extension of these previous studies, here we report the micelle formation of a homologous series of 1-alkyl-3-methylimidazolium derivatives, [C$_{12}$mim]Br, [C$_{14}$mim]Br, and [C$_{16}$mim]Br. The three long-chain ILs have the same hydrophilic portion but differ in their hydrophobic groups. Isothermal titration microcalorimetry provided information about their thermodynamic parameters and CMCs.

Experimental Section

Materials. The long-chain imidazolium IL samples, 1-dodecyl-3-methylimidazolium bromide ([C$_{12}$mim]Br), 1-tetradecyl-3-methylimidazolium bromide ([C$_{14}$mim]Br), and 1-hexadecyl-3-methylimidazolium bromide ([C$_{16}$mim]Br) were prepared as described earlier.[15] The purity of the samples was checked by ^{1}H NMR spectroscopy. The chemical structure of the long-chain IL is displayed in Figure 1. Triply distilled water was used to prepare the solutions.

---

* Corresponding author. Phone number: +86-531-88364807. Fax number: +86-531-88564750. E-mail address: ylmlt@sdu.edu.cn.
[†] Shandong University.
[‡] Liaocheng University.
[§] The Chinese Academy of Sciences.

10.1021/je900290w CCC: $40.75

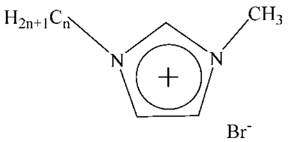

Figure 1. Chemical structure of 1-alkyl-3-methylimidazolium bromide, [$C_n$mim]Br. n = 12, 14, and 16.

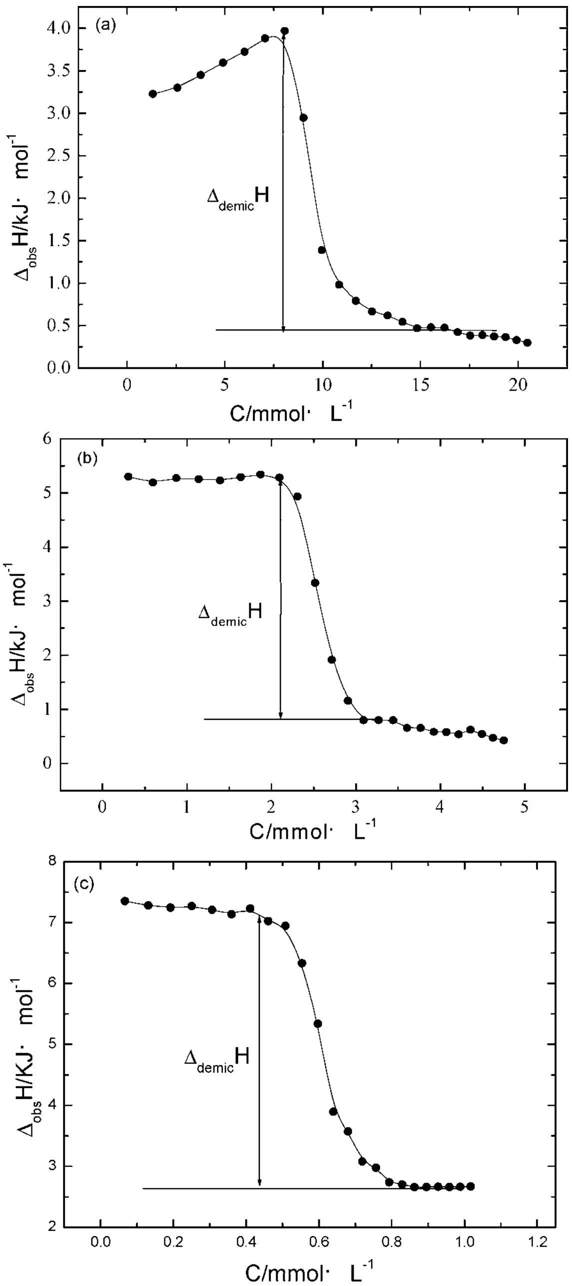

Figure 2. Enthalpograms for each titration as a function of total long-chain IL concentration: (a) [C_{12}mim]Br; (b) [C_{14}mim]Br; (c) [C_{16}mim]Br.

Surface Tension Measurements. Surface tension was measured on a K_{12} Processor Tensionmeter (Krüss Co., Germany) using the ring method. The precision of the measurement is ±0.01 mN·m^{-1}. Temperature was controlled with a HAAKE DC 30 thermostatic bath (Switzerland, accuracy ±0.1 K). The density is 0.9986 g·mL^{-1} for water and is 0.0013 g·mL^{-1} for air. Long-chain IL solutions were kept in sample cells for 30 min until the surface tension did not change with time. The average values of equilibrium surface tension were obtained by repeating three times, and the difference of the three values is less than 0.2 mN·m^{-1}. The surface tension value of water measured is 72.36 mN·m^{-1}, which is consistent with that reported previously.[16] The values of the critical micelle concentration (CMC) and the surface tension at the CMC (γ_{CMC}) were determined from the intersection of the two straight lines drawn in low and high concentration regions in surface tension curves (γ−log C curves) using a linear regression analysis method.[17]

Isothermal Titration Microcalorimetry Measurements. A 2277 TAM isothermal titration microcalorimeter (Thermometric Co., Sweden) controlled by Digitam 4.1 software was used for direct measurement of enthalpy. The temperature sensitivity is 10^{-4} K over 24 h, and the temperature stability of the thermostat is better than 0.01 K. The relative mean deviation of thermal powers determined three times was 0.3 %, and at last the uncertainties of measurement for the molar enthalpies of micellization were estimated to be < 1 %.[18] The 1 mL stainless steel sample and reference cells of the calorimeter were initially filled with (0.5 and 0.74) mL of triply distilled water, respectively. A 500 μL injection syringe controlled by a 612 Thermometric Lund pump was used for all studies. Concentrations of [C_{12}mim]Br, [C_{14}mim]Br, and [C_{16}mim]Br in the titration syringe were chosen to be approximately 5 times the CMC: (54, 13, and 2.86) mmol·L^{-1}, respectively. Injections of 24 × 12 μL of long-chain IL solutions were made into the sample cell with a 45 min interval between each injection. To ensure stability, the samples were stirred at 30 rpm.

Results and Discussion

Surface Tension Measurements. Surface Tension Measurements at Various Temperatures. The effect of temperature on the surface tension of the three long-chain ILs was investigated from (278.15 to 328.15) K. The surface tension experimental values are listed in Table 1. The CMC and γ_{CMC} values of the three long-chain ILs are listed in Table 2. The CMC values are only slightly affected by temperature because two opposite processes counteract one another. A temperature increase weakens the hydration of the hydrophilic group, which favors micelle formation and decreases the CMC. However, increasing temperature also breaks the orderly structure of the water surrounding the hydrophobic group, which is disadvantageous to micelle formation and increases the CMC.[19] It is found that the γ_{CMC} values of each long-chain IL at different temperatures are not distinctly different. Therefore, we can conclude that the effect of temperature on γ_{CMC} is relatively weak, which is consistent with the behavior of conventional ionic surfactants.[20]

The CMC vs temperature plot of a conventional ionic surfactant displays a minimum at a certain temperature.[21] The CMC of the three long-chain ILs vs temperature exhibits the same trend, and there is a minimum in the vicinity of 298.15 K.

Effect of Hydrocarbon Chain Length on CMC. The relationship between the CMC values and the hydrocarbon chain length of the three long-chain ILs ranging from (278.15 to 328.15) K is investigated. The logarithm of x_{CMC} (the CMC expressed as mol fraction) decreases almost linearly with the increase in N_{C} (hydrocarbon chain). The slopes of the straight lines (−0.322, −0.319, −0.320, −0.322, −0.322, and −0.320) are in the range reported for conventional ionic surfactants (−0.27 to −0.33).[21] The intercept of the lines, 3.192, expresses the effect of the hydrophilic headgroup on micelle formation. A remarkable decrease in the CMC values going from [C_{12}mim]Br to [C_{16}mim]Br shows that increasing the hydrocarbon chain length leads to stronger hydrophobic interactions

Table 1. Surface Tension Experimental Values of Long-Chain ILs over a Temperature Range

c	T/K					
mmol·L^{-1}	278.15	288.15	298.15	308.15	318.15	328.15
			γ/mN·m^{-1}			
			[C$_{12}$mim]Br			
0.1	64.79	62.93	62.21	60.48	58.84	57.61
0.5	61.21	60.86	59.84	58.62	56.56	55.07
1.5	56.82	56.68	55.19	55.18	53.88	50.63
5.0	45.33	44.27	43.81	44.47	43.89	42.36
10.0	37.64	37.52	37.45	37.18	36.92	37.64
20.0	37.72	37.63	37.41	37.55	37.12	37.03
30.0	37.73	37.41	37.15	37.38	37.47	37.16
40.0	37.53	37.77	37.23	37.42	37.3	37.06
50.0	37.59	37.61	37.26	37.23	37.06	37.09
			[C$_{14}$mim]Br			
0.05	64.69	62.69	61.26	59.5	57.16	54.16
0.1	64.07	62.07	60.88	58.59	55.92	52.7
0.3	61.72	59.72	57.1	54.93	52.9	50.17
0.5	55.17	53.17	52.79	51.51	49.56	46.39
1.0	50.32	48.32	47.37	45.26	43.88	42.75
2.0	41.28	40.28	39.48	39.15	39.15	38.28
4.0	38.44	37.94	37.81	37.81	37.12	36.2
6.0	38.68	38.18	37.73	37.51	37.13	36.32
8.0	38.88	38.38	37.57	37.67	37.12	36.58
10.0	38.88	38.38	37.57	37.6	37.13	36.45
			[C$_{16}$mim]Br			
0.005	69.16	66.26	63.93	61.53	58.5	55.05
0.02	63.91	61.84	60	58.48	54.53	51.85
0.1	56.17	52.62	51.14	49.46	47.36	45.42
0.2	50.9	48.63	46.77	45.39	42.7	42.13
0.3	46.66	43.95	43.38	41.17	39.84	39.44
0.4	42.78	41.32	39.38	38.02	37.93	38
0.5	39.25	37.45	37.26	36.21	36.75	37.07
0.8	38.25	37.54	37.37	36.14	36.11	36.2
1.1	38.38	37.4	37.09	36.28	36.18	36.25
2.0	38.11	37.87	37.19	36.97	36.12	36.15
4.0	37.61	37.33	37.21	36.37	36.04	35.98

between the hydrocarbon chains. Hence, the micelles can form easily and the CMC values decrease. As reported for conventional surfactants, the CMC is approximately halved with each addition of one carbon atom to the hydrocarbon chain.[16] The results accord well with this rule.

Thermodynamic Parameters of Micellization. According to the mass-action model of micellization, the thermodynamic parameters of micellization for an ionic surfactant in aqueous solution can be obtained by the following equations[22]

$$\Delta_{\mathrm{mic}}G = (1 + \beta)RT \ln x \tag{1}$$

$$\Delta_{\mathrm{mic}}H = -(1 + \beta)RT^2\frac{d \ln x}{dT} \tag{2}$$

$$\Delta_{\mathrm{mic}}S = \frac{\Delta_{\mathrm{mic}}H - \Delta_{\mathrm{mic}}G}{T} \tag{3}$$

where β is the degree of counterion dissociation. In the previous work,[23] the β values of the three long-chain ILs at (288.15, 298.15, and 308.15) K by the electrical conductivity method were reported. These data are listed in Table 2. R is the gas constant; T is the absolute temperature; and x is the CMC expressed as mol fraction. The calculated parameters are listed in Table 2.

From Table 2, we can see that $\Delta_{\mathrm{mic}}H$ changes from positive to negative as the temperature rises, which means the micelle formation process changes from endothermic to exothermic. The change of sign occurs between (288.15 and 298.15) K. The free energy of micelle formation, $\Delta_{\mathrm{mic}}G$, becomes more negative as the hydrocarbon chain length increases. The entropy term ($-T\Delta_{\mathrm{mic}}S$) plays the dominant role in the negative free energy. In other words, the micelle formation process for long-chain imidazolium ILs is entropy driven, which is consistent with the micelle formation of conventional surfactants.[16]

Enthalpy−Entropy Compensation Phenomenon for Micelle Formation. The so-called enthalpy−entropy compensation phenomenon has been observed in several processes, including the micellization of surfactants.[24] In general, the compensation phenomenon between $\Delta_{\mathrm{mic}}H$ and $\Delta_{\mathrm{mic}}S$ can be described as follows

$$\Delta_{\mathrm{mic}}H = \Delta_{\mathrm{mic}}H^* + T_{\mathrm{c}}\Delta_{\mathrm{mic}}S \tag{4}$$

According to Lumry and Rafender,[24] in the compensation phenomenon, the micellization of a surfactant can be described by two processes: (a) the “desolvation” part, i.e., the dehydration of the hydrocarbon chain, and (b) the “chemical” part, i.e., aggregation of the hydrocarbon chain to form a micelle. The slope of the compensation plot, T_{c}, named the compensation temperature, can be explained as a characteristic of solute−solvent interactions, i.e., considered as a measure of the “desolvation” part. The intercept of that plot, $\Delta_{\mathrm{mic}}H^*$, characterizes the solute−solute interactions, i.e., is considered to represent the “chemical” part.

The slopes of the enthalpy−entropy compensation plots for the three long-chain ILs are (256.68, 296.25, and 304.81) K for [C$_{12}$mim]Br, [C$_{14}$mim]Br, and [C$_{16}$mim]Br, respectively, which means the compensation temperatures are (256.68, 296.25, and 304.81) K for [C$_{12}$mim]Br, [C$_{14}$mim]Br, and [C$_{16}$mim]Br, respectively. The micellization process at this temperature only depends on enthalpic factors. The absolute value of the intercept, $\Delta_{\mathrm{mic}}H^*$, increases as the hydrocarbon chain length increases, which means that the effect of the chemical part strengthens. It is interesting that the intercept, $\Delta_{\mathrm{mic}}H^*$, is a linear function of the hydrocarbon chain length of the three long-chain ILs.

Isothermal Titration Microcalorimetry Measurements. The beginning injections of long-chain IL result in large energy flows because of dissociation of micelles when the concentration in the sample cell is below the CMC. Once the concentration exceeds the CMC, the energy flows reduce significantly and approach a constant value. These reduced energy flows are the result of dilution of micelles in the sample cell.[24] Figure 2 is the demicellization enthalpy plot at 298.15 K. The difference in the enthalpy between the two horizontal parts of the S-shaped curve is equal to $\Delta_{\mathrm{demic}}H$. Obviously, the demicellization is endothermic, while the micelle formation is exothermic, in agreement with the surface tension results at 298.15 K (see Table 2). The graph in Figure 2 exhibits two plateaus. The first plateau represents the dilution of a micellar solution into a monomeric solution. The second plateau is representative of a micellar solution being injected into another micellar solution and is far less endothermic than the first plateau.[22] Since micellization is a reversible process, the enthalpy of demicellization ($\Delta_{\mathrm{demic}}H$) is directly correlated to the enthalpy of micellization ($\Delta_{\mathrm{mic}}H$). Thus the values of $\Delta_{\mathrm{mic}}H$ are (−3.51, −4.18, and −4.43) kJ·mol^{-1} for [C$_{12}$mim]Br, [C$_{14}$mim]Br, and [C$_{16}$mim]Br, respectively (see Table 3).

It is interesting to note that the first plateau in the enthalpogram of [C$_{12}$mim]Br is sloped, whereas the enthalpograms for [C$_{14}$mim]Br and [C$_{16}$mim]Br are relatively flat. Higher concentrations of shorter-chain ILs are used in the injected solution because the CMC increases at low hydrocarbon chain lengths. The high concentration used for [C$_{12}$mim]Br means that the behavior of the solution being injected and the solution in the sample cell cannot be assumed to be ideal.[24]

Table 2. Interfacial Properties and Thermodynamic Parameters of Long-Chain ILs over a Temperature Range Measured by Surface Tension

	T	CMC	γ_{CMC}		$\Delta_{\mathrm{mic}}G$	$\Delta_{\mathrm{mic}}H$	$-T\Delta_{\mathrm{mic}}S$
	K	$\mathrm{mmol \cdot L^{-1}}$	$\mathrm{mN \cdot m^{-1}}$	β	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$
[C_{12}mim]Br	278.15	10.30 ± 0.05	37.76 ± 0.1	−			
	288.15	9.84 ± 0.05	37.62 ± 0.1	0.77	−36.63 ± 0.18	7.94 ± 0.04	−44.57 ± 0. 22
	298.15	9.68 ± 0.05	37.40 ± 0.1	0.76	−37.76 ± 0.19	−5.21 ± 0.03	−32.53 ± 0.22
	308.15	10.10 ± 0.05	37.32 ± 0.1	0.74	−38.39 ± 0.19	−8.24 ± 0.04	−30.15 ± 0.23
	318.15	10.50 ± 0.05	37.26 ± 0.1	−			
	328.15	10.90 ± 0.06	37.12 ± 0.1	−			
[C_{14}mim]Br	278.15	2.79 ± 0.01	38.66 ± 0.1	−			
	288.15	2.71 ± 0.01	38.30 ± 0.1	0.79	−42.58 ± 0.21	4.94 ± 0.03	−47.52 ± 0.24
	298.15	2.69 ± 0.01	37.70 ± 0.1	0.78	−43.84 ± 0.22	−1.98 ± 0.01	−41.86 ± 0.23
	308.15	2.74 ± 0.01	37.47 ± 0.1	0.76	−44.72 ± 0.22	−6.26 ± 0.03	−38.46 ± 0.25
	318.15	2.82 ± 0.01	37.12 ± 0.1	−			
	328.15	2.89 ± 0.01	36.31 ± 0.1	−			
[C_{16}mim]Br	278.15	0.53 ± 0.01	37.80 ± 0.1	−			
	288.15	0.52 ± 0.01	37.44 ± 0.1	0.78	−49.38 ± 0.25	2.46 ± 0.01	−51.84 ± 0.26
	298.15	0.51 ± 0.01	37.41 ± 0.1	0.77	−50.89 ± 0.25	0	−50.84 ± 0.17
	308.15	0.52 ± 0.01	36.16 ± 0.1	0.76	−52.21 ± 0.26	−4.17 ± 0.02	−48.04 ± 0.28
	318.15	0.54 ± 0.01	36.18 ± 0.1	−			
	328.15	0.57 ± 0.01	36.14 ± 0.1	−			

Table 3. CMC and Thermodynamic Parameters of Long-Chain ILs at 298.15 K Measured by Isothermal Titration Microcalorimetry

	T	CMC	$\Delta_{\mathrm{mic}}G$	$\Delta_{\mathrm{mic}}H$	$-T\Delta_{\mathrm{mic}}S$
	K	$\mathrm{mmol \cdot L^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$
[C_{12}mim]Br	298.15	9.56 ± 0.03	−42.97 ± 0.13	−3.51 ± 0.01	−39.46 ± 0.11
[C_{14}mim]Br	298.15	2.52 ± 0.01	−49.58 ± 0.15	−4.18 ± 0.01	−45.4 ± 0.14
[C_{16}mim]Br	298.15	0.64 ± 0.01	−56.38 ± 0.17	−4.43 ± 0.01	−51.95 ± 0.16

Bijma et. al[25] proposed that the calorimetric titration plots for deaggregation of micelles formed by alkyltrimethylammonium and alkylpyridinium cationic surfactants could be classified into types A, B, and C, depending on the shape of the dilution enthalpy plot as a function of surfactant concentration. For type A plots, the recorded heat changes sharply between two parts of the titration curve over which the recorded heats are effectively independent of the composition of the solution in the sample cell. In cases classified as type B, the change is less sharp, and both parts of the plot show dependences of heat on solution composition. Type C plots are complicated, in that no sharp change of heat is recorded. According to the classification standards above, the enthalpograms for [C_{14}mim]Br and [C_{16}mim]Br would be classified as “textbook” examples of type A. Surfactants of type A behave ideally and do not demonstrate micelle−micelle interactions. However, the enthalpogram of [C_{12}mim]Br would be classified as type B in which the micelle−micelle interactions begin to impact the enthalpy change.

Additionally, the CMC can be determined by plotting the first-order differential curve of the isothermal titration microcalorimetry thermogram, as shown in Figure 2.[26] As can be seen in Figure 3 (only gives a demonstration of [C_{12}mim]Br), the curve can be subdivided into two concentration ranges with an intermediate transition region indicating micelle formation, corresponding to the CMC. The enthalpy change results from the breakup of the added micelles and the further dilution of the monomers when the concentration is below the CMC. When the concentration is above the CMC, only the added micelles are diluted, and finally $d\Delta H/d\mathrm{C}$ drops toward zero. The maximum enthalpy changes, $d\Delta H/d\mathrm{C}$, are observed at (9.26, 2.52, and 0.64) $\mathrm{mmol \cdot L^{-1}}$, respectively. So the CMC values determined by isothermal titration microcalorimetry of [C_{12}mim]Br, [C_{14}mim]Br, and [C_{16}mim]Br are (9.26, 2.52, and 0.64) $\mathrm{mmol \cdot L^{-1}}$, respectively, at 298.15 K (Table 3). These CMC values are approximately equal to the CMCs obtained by surface tension measurement and the values reported by Vanyúr et. al ([C_{12}mim]Br: 9.8 $\mathrm{mmol \cdot L^{-1}}$; [$C_{14}$mim]Br: 2.5 $\mathrm{mmol \cdot L^{-1}}$ and [C_{16}mim]Br: 0.61 $\mathrm{mmol \cdot L^{-1}}$).[27] Compared with the CMC values reported for traditional cationic surfactants with the same hydrocarbon chain length, alkyltrimethylammonium bromides, 14.1 (dodecyltrimethylammonium bromide), 3.68 (tetradecyltrimethylammonium bromide), 0.79 $\mathrm{mmol \cdot L^{-1}}$ (hexadecyltrimethylammonium bromide),[28] and alkylpyridinium bromides, 10.0 (dodecylpyridinium bromide), 2.7 (tetradecylpyridinium bromide), 0.64 $\mathrm{mmol \cdot L^{-1}}$ (hexadecylpyridinium bromide),[29] the CMCs for the three long-chain ILs are somewhat lower. This indicates that the long-chain imidazolium ILs are better surfactants than conventional cationic surfactants.

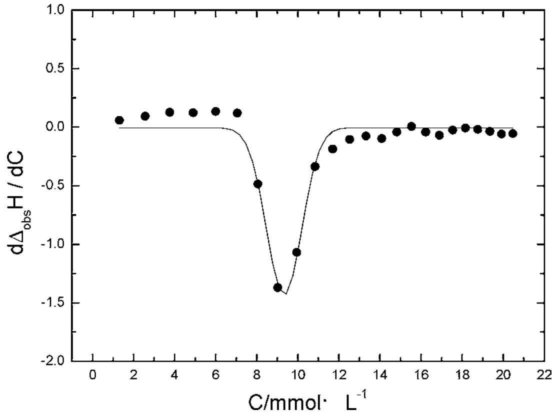

Figure 3. First-order differential plots of enthalpy value vs total [C_{12}mim]Br concentration.

Conclusions

Micelle formation of [C_{12}mim]Br, [C_{14}mim]Br, and [C_{16}mim]Br in aqueous solution was investigated. The process of micellization is entropy driven. The enthalpy−entropy compensation study reveals the effect of hydrocarbon chain length on micellization; i.e., the longer the hydrocarbon chain, the easier it is to form aggregates. Isothermal titration microcalorimetry measurements showed that [C_{14}mim]Br and [C_{16}mim]Br act as ideal surfactants in the micellization process because there are no micelle−micelle interactions, whereas $[C_{12}mim]Br$ does not behave ideally because of micelle−micelle interactions in the high concentration solutions. The CMC values of the three long-chain ILs are lower than those reported for conventional cationic surfactants with the same hydrocarbon chain lengths. In conclusion, this study shows that the long-chain imidazolium ILs can act as ionic surfactants and are superior to traditional ionic surfactants. This paper shows the potential for application of long-chain ILs in colloidal systems.

Literature Cited

(1) Welton, T. Room-temperature Ionic Liquids. Solvents for Synthesis and Catalysis. *Chem. Rev.* **1999**, *99*, 2071–2084.
(2) Rogers, R. D.; Seddon, K. R. Ionic Liquids-Solvents of the Future. *Science* **2003**, *302*, 792–793.
(3) Li, R. X. *Green Solvent: Synthesis and Application of Ionic Liquids*; Chemistry Technology Press: Beijing, 2004.
(4) Earle, M. J. *Ionic Liquids: Industrial Applications for Green Chemistry*; American Chemical Society: Washington DC, 2002.
(5) Wasserscheid, P.; Keim, W. Ionic Liquids-New “Solutions” for Transition Metal Catalysis. *Angew Chem., Int. Ed.* **2000**, *39*, 3772–3789.
(6) Ye, C. F.; Liu, W. M.; Chen, Y. X.; Yu, L. G. Room-Temperature Ionic Liquids: A Novel Versatile Lubricant. *Chem. Commun.* **2001**, *21*, 2244–2245.
(7) £uczak, J.; Hupka, J.; Thöming, J.; Jungnickel, C. Self-Organization of Imidazolium Ionic Liquids in Aqueous Solution. *Colloids Surf., A Physicochem. Eng. Aspects* **2008**, *329*, 125–133.
(8) Bowers, J.; Butts, C. P.; Martin, P. J.; Vergara-Gutierrez, M. C. Aggregation Behavior of Aqueous Solutions of Ionic Liquids. *Langmuir* **2004**, *20*, 2191–2198.
(9) Baker, G. A.; Pandey, S.; Pandey, S.; Baker, S. N. A New Class of Cationic Surfactants Inspired by *N*-alkyl-*N*-methyl Pyrrolidinium Ionic Liquids. *Analyst* **2004**, *129*, 890–892.
(10) Dong, B.; Li, N.; Zheng, L. Q.; Yu, L.; Inoue, T. Surface Adsorption and Micelle Formation of Surface Active Ionic Liquids in Aqueous Solution. *Langmuir* **2007**, *23*, 4178–4182.
(11) Ruso, J. M.; Attwood, D.; Rey, C.; Taboada, P.; Mosquera, V.; Sarmiento, F. Light Scattering and NMR Studies of the Self-Association of the Amphiphilic Molecule Propranolol Hydrochloride in Aqueous Electrolyte Solutions. *J. Phys. Chem. B* **1999**, *103*, 7092–7096.
(12) Steele, W. V.; Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A. Possible Precursors and Products of Deep Hydrodesulfurization of Gasoline and Distillate Fuels IV. Heat Capacities, Enthalpy Increments, Vapor Pressures, and Derived Thermodynamic Functions for Dicyclohexylsulfide between the Temperatures (5 and 520) K. *J. Chem. Thermodyn* **2004**, *3*, 845–855.
(13) McGinnis, T. P.; Woolley, E. M. Thermodynamic Properties of Aqueous 1-*n*-alkanepyridinium Chlorides at Temperatures from 283.15 to 343.15 K. *J. Chem. Thermodyn.* **1997**, *29*, 401–422.
(14) Bai, G. Y.; Lopes, A.; Bastos, M. Thermodynamics of Micellization of Alkylimidazolium Surfactants in Aqueous Solution. *J. Chem. Thermodyn.* **2008**, *40*, 1509–1516.
(15) Dupont, J.; Consorti, C. S.; Suarez, P. A. Z.; De Souza, R. F.; Fulmer, S. L.; Richardson, D. P.; Smith, T. E.; Wolff, S. Preparation of 1-Butyl-3-Methyl Imidazolium-Based Room Temperature Ionic Liquids. *Org. Synth.* **2002**, *79*, 236–243.
(16) Zhao, G. X. *Surfactant Physical Chemistry*; Beijing University Press: Beijing, 1984.
(17) Drapper, N. R.; Smith. H. *Applied Regression Analysis*; Wiley: New York, 1968.
(18) Yu, L.; Geng, F.; Lin, X. H.; Zhu, Y.; Zheng, L. Q.; Li, G. Z. Enthalpic Pairwise Interactions between Some Amino Acids and 2-Butanone in Aqueous Solutions at 298.15 K. *J. Chem. Eng. Data* **2007**, *52*, 1715–1719.
(19) 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.
(20) Rosen, M. J.; Dahanayake, M.; Cohen, A. W. Relationship of Structure to Properties in Surfactants. 11. Surface and Thermodynamic Properties of *N*-dodecyl-pyridinium Bromide and Chloride. *Colloids Surf.* **1982**, *5*, 159–172.
(21) Rosen, M. J. *Surfactants and Interfacial Phenomena*; Wiley: New York, 1989.
(22) Tanford, C. *Micellization, Solubilization, and Micromulsion*; Plenum Press: New York, 1997.
(23) Inoue, T.; Ebina, H.; Dong, B.; Zheng, L. Q. Electrical Conductivity Study on Micelle Formation of Long-chain Imidazolium Ionic Liquids in Aqueous Solution. *J. Colloid Interface Sci.* **2007**, *314*, 236–241.
(24) Lumry, R.; Rajender, S. Enthalpy-Entropy Compensation Phenomena in Water Solutions of Proteins and Small Molecules: A Ubiquitous Properly of Water. *Biopolymers* **1970**, *9*, 1125–1227.
(25) Bijma, K.; Engberts, J. B. F. N.; Blandamer, M. J.; Cullis, P. M.; Last, P. M.; Irlam, K. D.; Soldi, L. G. Classification of Calorimetric Titration Plots for Alkyltrimethylammonium and Alkylpyridinium Cationic Surfactants in Aqueous Solutions. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 1579–1584.
(26) Bijma, K.; Engberts, J. B. F. N.; Haandrikman, G.; Van Os, N. M.; Blandamer, M. J.; Butt, M. D.; Cullis, P. M. Thermodynamics of Micelle Formation by 1-methyl-4-alkylpyridinium Halides. *Langmuir* **1994**, *10*, 2578–2582.
(27) Vanyúr, R.; Biczók, L.; Miskolczy, Z. Micelle Formation of 1-alkyl-3-methylimidazolium Bromide Ionic Liquids in Aqueous Solution. *Colloids Surf., A Physicochem. Eng. Aspects* **2007**, *299*, 256–261.
(28) Kosaka, O.; Sehgal, P.; Doe, H. Behavior of Cationic Surfactants Micellar Solution Solubilizing An Endocrine Disruptor Bisphenol A. *Food Hydrocolloid* **2008**, *22*, 144–149.
(29) Škerjanc, J.; Kogej, K.; Cerar, J. Equilibrium and Transport Properties of Alkylpyridinium Bromides. *Langmuir* **1999**, *15*, 5023–5028.

Received for review March 22, 2009. Accepted May 26, 2009. This work was supported by the Natural Scientific Foundation of China (20773081), the Natural Scientific Foundation of Shandong Province of China (Z2007B03), and the doctoral fund of the Ministry of Education of China (070422047).

JE900290W