

Short Articles

Solution Enthalpies of Ionic Liquid 1-Hexyl-3-methylimidazolium Chloride

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The molar enthalpies of solution of ionic liquid (IL) [C₆mim][Cl] (1-hexyl-3-methylimidazolium chloride) at various molalities in water were measured by a solution–reaction isoperibol calorimeter at 298.15 K. According to Pitzer's electrolyte solution theory, the molar standard enthalpy of solution of [C₆mim][Cl], $\Delta_{\text{sol}}H_m^0$ and Pitzer's parameters, $\beta_{\text{MX}}^{(0)\text{L}}$, $\beta_{\text{MX}}^{(1)\text{L}}$, and C_{MX}^{L} , were obtained. In terms of the experimental data in literature, the mean contribution per methylene (–CH₂–) group to the standard molar enthalpies of solution of [C_xmim][Cl] is discussed.

Introduction

Ionic liquids (ILs) are composed of ions and their melting temperatures are below 100 °C. According to this definition, [C₆mim][Cl] (1-hexyl-3-methylimidazolium chloride) is not only an intermediate but also an ionic liquid.^{1–5} Detailed knowledge of the solution enthalpy of [C_xmim][Cl] in water is very important for many technological processes with ILs incorporating the imidazolium cation. Recently, there have been several papers available in the literature that give enthalpies of solution of ILs.^{6–10} In this paper, we report the molar enthalpies of solution of ionic liquids [C₆mim][Cl] (1-hexyl-3-methylimidazolium chloride) at various molalities in water determined by solution–reaction isoperibol calorimeter^{11,12} at 298.15 K. The standard molar enthalpies of solution of [C₆mim][Cl], $\Delta_{\text{sol}}H_m^0$, and Pitzer's parameters, $\beta_{\text{MX}}^{(0)\text{L}}$, $\beta_{\text{MX}}^{(1)\text{L}}$, and C_{MX}^{L} , were obtained. Comparing the experimental data in literature, the mean contribution per methylene (–CH₂–) group to the standard molar solution enthalpies of [C_xmim][Cl] is discussed.

Experimental Section

Chemicals. 1-Methylimidazole was obtained from ACROS and was distilled at reduced pressure prior to being used. 1-Chlorohexane, ethyl acetate, and acetonitrile were distilled and then stored over molecular sieves in tightly sealed glass bottles, respectively. KCl with a purity more than 99.99 % was dried in a vacuum oven at 408 K for 6 h. THAM (Tris-(hydroxymethyl)aminomethane), GR grade reagent, was dried in a vacuum oven before use. Double-distilled water was used.

Preparation of [C₆mim][Cl]. According to Huddleston's method,¹³ [C₆mim][Cl] was synthesized by refluxing the 1-methylimidazole with a large excess of the chlorohexane at 60 °C for 48 h. The excess 1-chlorohexane was removed by evaporation, and the crude product was recrystallized triply from acetonitrile + ethyl acetate. The product was a slightly yellow

liquid and then was dried in vacuo for 24 h. The yield was approximately 80 %. Analysis of [C₆mim][Cl] by ¹H NMR resulting in a spectrum is in good agreement with the literature.¹³ The purity of the IL was 99.6 %, and 0.4 % H₂O was found.

Determination of the Molar Enthalpies of Solution. On the basis of other calorimetric apparatus,^{11,12} an online solution–reaction isoperibol calorimeter was constructed. It consists of a water thermostat, a 200 mL pyrex glass-plated silver Dewar, a 4 mL glass sample cell, a calibration heater, a glass-sheathed thermistor probe, an amplifier, a circuit used as an A/D converter, and a personal computer for data acquisition and processing. A 150 g sample of solvent (water) was placed in the Dewar and (0.1 to 2) g of solute (KCl, THAM, or [C₆mim][Cl]) in the sample cell. The inevitable heat transfer and heat generation owing to friction were compensated, and the corrected temperature change (the adiabatic temperature change) ΔT^* was obtained according to conventional method (the equal area method).⁶ The enthalpies of solution were calculated from the equation

$$Q_s / \Delta T_s^* = Q_E / \Delta T_E^*$$

where Q_s is the enthalpy of solution of the sample; ΔT_s^* is the adiabatic temperature change of the solution process; Q_E is the electric energy calibration; and ΔT_E^* is the adiabatic temperature change of electric calibration.

The performance and accuracy of the calorimetric system was tested by measuring the molar enthalpy of solution of KCl in water and THAM [tris-(hydroxymethyl) aminomethane] in 0.1 mol·dm^{–3} HCl(aq) at 298.15 K. The results are listed in Table 1 and Table 2. From both tables, the mean molar solution enthalpies are $\Delta_{\text{sol}}H_m = (17542 \pm 31) \text{ J}\cdot\text{mol}^{-1}$ for KCl and $(-29794 \pm 28) \text{ J}\cdot\text{mol}^{-1}$ for THAM, which are in good agreement with the published data $(17536 \pm 9) \text{ J}\cdot\text{mol}^{-1}$ for KCl^{14,15} and $(-29766 \pm 31.5) \text{ J}\cdot\text{mol}^{-1}$ for THAM.¹⁶ Then, the molar enthalpies of solution in water of the ionic liquid [C₆mim][Cl] were measured at different molalities.

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Table 1. Values of Molar Enthalpy of Solution in Water of KCl, $\Delta_{\text{sol}}H_{\text{m}}/\text{J}\cdot\text{mol}^{-1}$ at 298.15 K^a

W_{KCl}/g	$\Delta_{\text{sol}}H_{\text{m}}/\text{kJ}\cdot\text{mol}^{-1}$	$\delta/\text{J}\cdot\text{mol}^{-1}$
0.5556	17.56	14
0.5552	17.55	4
0.5570	17.55	4
0.5563	17.56	20
0.5532	17.51	-37
0.5528	17.56	15
0.5515	17.50	-46
0.5524	17.57	23
0.5512	17.55	4

^a The molar mass of KCl, $M_{\text{KCl}} = 74.551 \text{ g}\cdot\text{mol}^{-1}$; $W_{\text{KCl}} (\text{g})$, the mass of KCl; $\Delta_{\text{sol}}H_{\text{m}} (\text{J}\cdot\text{mol}^{-1})$, molar enthalpy of solution; δ , deviation of $\Delta_{\text{sol}}H_{\text{m}} (\text{J}\cdot\text{mol}^{-1})$ from average.

Table 2. Enthalpy of the Reaction of THAM in 0.1 Mol·dm⁻³ of HCl(aq) at 298.15 K^a

W_{THAM}/g	$\Delta_{\text{sol}}H_{\text{m}}/\text{kJ}\cdot\text{mol}^{-1}$	$\delta/\text{J}\cdot\text{mol}^{-1}$
0.7504	-29.76	7
0.7506	-29.76	7
0.7502	-29.74	25
0.7510	-29.75	11.3
0.7522	-29.79	-25
0.7515	-29.78	-22
0.7534	-29.76	7
0.7519	-29.74	25
0.7525	-29.75	11
0.7500	-29.78	-15
0.7535	-29.79	-32

^a The molar mass of THAM, $M_{\text{THAM}} = 121.14 \text{ g}\cdot\text{mol}^{-1}$; $W_{\text{THAM}} (\text{g})$, the mass of THAM; $\Delta_{\text{sol}}H_{\text{m}} (\text{J}\cdot\text{mol}^{-1})$, molar enthalpy of solution; δ , deviation of $\Delta_{\text{sol}}H_{\text{m}} (\text{J}\cdot\text{mol}^{-1})$ from average.

Table 3. Values of Molar Enthalpy of Solution in Water of [C₆mim][Cl] with Various Molalities at 298.15 K

$m/\text{mol}\cdot\text{kg}^{-1}$	$\Delta_{\text{sol}}H_{\text{m}}/\text{kJ}\cdot\text{mol}^{-1}$	$\Phi_{\text{L}}/\text{kJ}\cdot\text{mol}^{-1}$
0.003142	-13.08	4.22
0.003639	-12.73	4.57
0.004105	-12.25	5.05
0.004544	-11.74	5.56
0.005569	-11.06	6.24
0.006869	-10.07	7.23
0.01632	-9.541	7.76
0.03048	-7.849	9.56
0.04173	-7.612	9.45
0.05082	-7.417	9.69
0.05507	-7.246	9.88
0.06142	-7.050	10.05
0.06689	-6.833	10.25
0.07011	-6.631	10.47
0.07617	-6.493	10.67
0.08033	-6.272	10.81
0.09049	-6.065	11.03
0.1081	-5.843	11.24

Results and Discussion

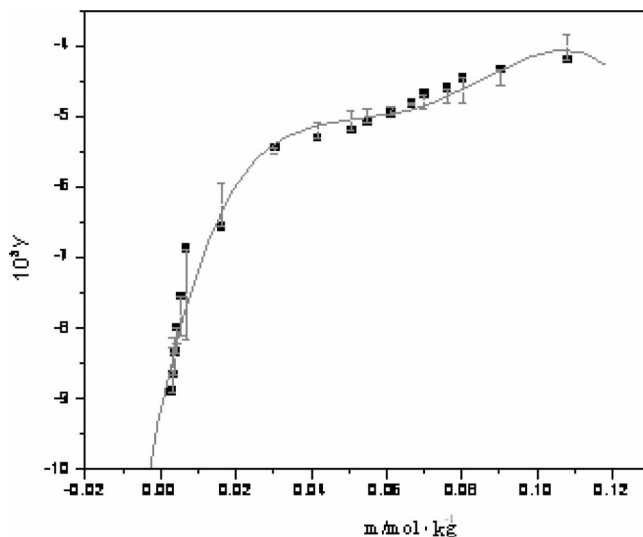
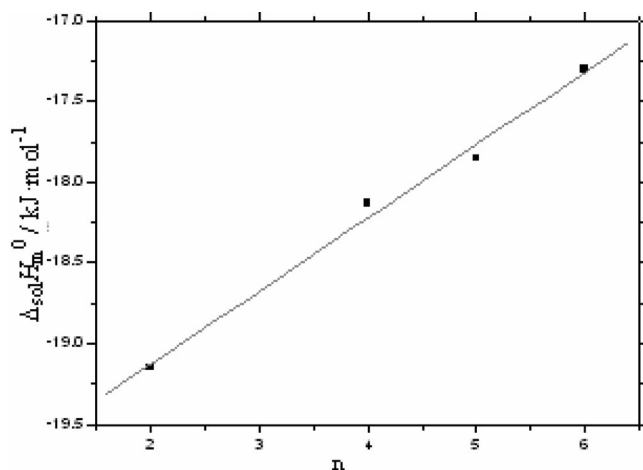
The values of molar enthalpies of solution in water of [C₆mim][Cl] with various molalities at 298.15 K are listed in Table 3.

From Table 3, the solution processes of the ionic liquids are exothermic; also, the solution enthalpy of [C₆mim][Cl] increases with decreasing molality.

The molar solution enthalpy of [C₆mim][Cl] is expressed as

$$\Delta_{\text{sol}}H_{\text{m}} = \Delta_{\text{sol}}H_{\text{m}}^0 + \Phi_{\text{L}} \quad (1)$$

where $\Delta_{\text{sol}}H_{\text{m}}^0$ is the standard molar solution enthalpy at infinite dilution, and Φ_{L} is the apparent relative molar enthalpy. According to Pitzer's theory,¹⁷ we have

**Figure 1.** Plot of extrapolating function, Y , against molality, m . ■, Y values of extrapolating function; —, values of fitting to Pitzer's equation; | (vertical line), deviation of the fitting.**Figure 2.** Plot of $\Delta_{\text{sol}}H_{\text{m}}^0$ vs carbon number n in alkyl imidazole.

$$\Phi_{\text{L}} = 2(A_{\text{H}}/2.4) \ln(1 + 1.2I^{1/2}) - 2RT^2(mB'_{\text{MX}} + m^2C'_{\text{MX}}) \quad (2)$$

where I means ionic strength; m is molality; R is gas constant; and other symbols are defined by the following equations:

$$B'_{\text{MX}} = (\partial B_{\text{MX}}/\partial T)_{P,I} = 2\beta^{(0)\text{L}}_{\text{MX}} + 2[1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2})]\beta^{(1)\text{L}}_{\text{MX}}/\alpha^2 I \quad (3)$$

$$\beta^{(0)\text{L}}_{\text{MX}} = (\partial \beta^{(0)}_{\text{MX}}/\partial T)_P \quad (4)$$

$$\beta^{(1)\text{L}}_{\text{MX}} = (\partial \beta^{(1)}_{\text{MX}}/\partial T)_P \quad (5)$$

$$C'_{\text{MX}} = (1/2)(\nu_{\text{M}}\nu_{\text{X}})^{1/2}C^{\varphi\text{L}}_{\text{MX}} \quad (6)$$

$$C^{\varphi\text{L}}_{\text{MX}} = (\partial C^{\varphi}_{\text{MX}}/\partial T)_P \quad (7)$$

where subscripts M and X mean cation and anion, respectively; ν_{M} and ν_{X} are the numbers of cation and anion in the formula MX; $\beta^{(0)}_{\text{MX}}$ and $\beta^{(1)}_{\text{MX}}$ show different kinds of reactions of short-distance among ions; C^{φ}_{MX} is the triple-ionic action term, which indicates the important interaction in higher molalities; for [C₆mim][Cl], $\alpha = 2.0$. The values of Pitzer's parameters, $\beta^{(0)}_{\text{MX}}$, $\beta^{(1)}_{\text{MX}}$, and C^{φ}_{MX} , were obtained from the experimental data of osmotic coefficient by the least-squares method. The

value of Debye–Hückel parameter of enthalpy, A_H , was taken from the literature.¹⁷

From eqs 3 and 4, the working equation to determine the standard molar solution enthalpy and Pitzer's parameters was obtained as

$$Y = [\Delta_{\text{sol}} H_m - 2(A_H/2.4) \ln(1 + 1.2I^{1/2})]/2RT^2 \\ = a_0 - m\beta_{\text{MX}}^{(0)\text{L}} - my'\beta_{\text{MX}}^{(1)\text{L}} - m^2C_{\text{MX}}^{\text{qL}}/2 \quad (8)$$

where Y is the extrapolating function, which can be obtained with the experimental data. Figure 1 is a plot of the extrapolating function, Y , against molality, m . Parameters a_0 and y' in eq 8 are defined by following equations, respectively:

$$a_0 = \Delta_{\text{sol}} H_m^0/2RT^2 \quad (9)$$

$$y' = [1 - (1 + 2I^{1/2}) \exp(-2I^{1/2})]/2I \quad (10)$$

Molar enthalpies of solution of $[\text{C}_6\text{mim}][\text{Cl}]$ were fitted to eq 8. The values of the parameters are: $a_0 = -1.1704 \cdot 10^{-2}$, $\beta_{\text{MX}}^{(0)\text{L}} = 8.0219 \cdot 10^{-2}$, $\beta_{\text{MX}}^{(1)\text{L}} = 6.7132 \cdot 10^{-2}$, and $C_{\text{MX}}^{\text{qL}} = -0.4211$ with a standard deviation of the fitting $s = 2.5 \cdot 10^{-4}$. The standard molar enthalpy of solution of $[\text{C}_6\text{mim}][\text{Cl}]$ was calculated from the parameter a_0 , and its value was $\Delta_{\text{s}} H_m^0 = -17.30 \text{ kJ} \cdot \text{mol}^{-1}$. Comparing the standard molar solution enthalpies of $[\text{C}_6\text{mim}][\text{Cl}]$ with $-19.15 \text{ kJ} \cdot \text{mol}^{-1}$ for $[\text{C}_2\text{mim}][\text{Cl}]$ (1-ethyl-3-methylimidazolium chloride),⁹ $-18.13 \text{ kJ} \cdot \text{mol}^{-1}$ for $[\text{C}_4\text{mim}][\text{Cl}]$ (1-butyl-3-methylimidazolium chloride),¹⁰ and $-17.85 \text{ kJ} \cdot \text{mol}^{-1}$ for $[\text{C}_5\text{mim}][\text{Cl}]$ (1-pentyl-3-methylimidazolium chloride),¹⁸ we can see that the standard molar enthalpies of solution of $[\text{C}_x\text{mim}][\text{Cl}]$ ($x = 2, 4, 5, 6$) decreases with increasing alkyl chain length. When we make a plot with the standard molar enthalpy of solution versus carbon number in alkyl chains of the ionic liquid, a straight line was obtained with a correlation coefficient 0.99 and a slope of 0.45 (see Figure 2). We can draw the conclusion that each mole of methylene group contributes to the standard molar enthalpy of solution of $[\text{C}_x\text{mim}][\text{Cl}]$ ($x = 2, 4, 5, 6$) is about $0.45 \text{ kJ} \cdot \text{mol}^{-1}$.

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