Journal of Thermal Analysis and Calorimetry, Vol. 94 (2008) 2, 507–510

STUDIES ON THERMOCHEMICAL PROPERTIES OF IONIC LIQUIDS BASED ON TRANSITION METAL

W. Guan, L. Li, H. Wang, J. Tong and J.-Z. Yang[*]

Department of Chemistry, Laboratory of Green Chemistry, Liaoning University, Shenyang, 110036, P.R. China

A brown and transparent ionic liquid (IL), $[C_4mim][FeCl_4]$, was prepared by mixing anhydrous $FeCl_3$ with 1-butyl-3-methylimidazolium chloride ($[C_4mim][Cl]$), with molar ratio 1/1 under stirring in a glove box filled with dry argon. The molar enthalpies of solution, Δ_sH_m, of $[C_4mim][FeCl_4]$, in water with various molalities were determined by a solution-reaction isoperibol calorimeter at 298.15 K. Considering the hydrolyzation of anion $[FeCl_4]^-$ in dissolution process of the IL, a new method of determining the standard molar enthalpy of solution, $\Delta_sH_m^0$, was put forward on the bases of Pitzer solution theory of mixed electrolytes. The values of $\Delta_sH_m^0$ and the sum of Pitzer parameters: $(4\beta^{(0)L}_{Fe,Cl}+4\beta^{(0)L}_{C_4mim,Cl}+\Phi^{L}_{Fe,C_4mim})$ and $(\beta^{(1)L}_{Fe,Cl}+\beta^{(1)L}_{C_4mim,Cl})$ were obtained, respectively. In terms of thermodynamic cycle and the lattice energy of IL calculated by Glasser's lattice energy theory of ILs, the dissociation enthalpy of anion $[FeCl_4]^-$, $\Delta H_{dis}\approx5650$ kJ mol^{-1}, for the reaction: $[FeCl_4]^-(g)\rightarrow Fe^{3+}(g)+4Cl^-(g)$, was estimated. It is shown that large hydration enthalpies of ions have been compensated by large the dissociation enthalpy of $[FeCl_4]^-$ anion, Δ_dH_m, in dissolution process of the IL.

Keywords: *enthalpy of solution, ionic liquid, isoperibol calorimeter, Pitzer's theory*

Introduction

Since Wilkes *et al.* [1] synthesized the air- and water-stable ionic liquid (IL) $[Emim][BF_4]$ (1-methyl-3-ethylimidazolium tetrafluoroborate), ILs are receiving increased attention from industrial and academic communities as a novel class of green benign solvents, which promise possibly replacing currently used organic solvents industrially [2–6]. However, air- and water-sensitive ILs based on $AlCl_3$ and $FeCl_3$ are still very attractive for basic electrochemical research, and for especial catalytic reaction and for nanotechnology because their acidity can be varied over wide ranges [7]. Recently, Sitze *et al.* [8] and Zhang *et al.* [9] also prepared ILs based on $FeCl_3$. They pointed out that $[FeCl_4]^-$ was main anion in the ILs.

Most study on ILs has been investigated in elaboration of the synthetic methods, application in catalytic processes, electrochemistry and other more specialized fields. However, the physico-chemical properties of ILs have not been studied systematically, this holds in particular for thermochemical properties. The solution enthalpy of hydrophilic ILs in water is employed in many thermodynamic calculations, from thermochemistry to solution chemistry and is important for designing chemical engineering processes. However, only a very restricted number of research on solution enthalpy of hydrophilic ILs in water is available in the literature [10–12]. As a continuation of our previous investigations on ILs, this paper reports that (1) A brown and transparent IL, $[C_4mim][FeCl_4]$, was prepared by mixing $FeCl_3$ with 1-methyl-3-butylimidazolium chloride ($[C_4mim][Cl]$), and the molar solution enthalpies of the ILs, Δ_sH_m, in water with various molalities were determined using the on-line solution-reaction isoperibol calorimeter at T=298.15 K; (2) Since the hydrolyzation of anion $[FeCl_4]^-$ in dissolution process of the IL, a new method of determining the standard molar enthalpy of solution, $\Delta_sH_m^0$, was put forward on the basis of Pitzer electrolyte solution theory [13]. The values of $\Delta_sH_m^0$ and the sum of Pitzer parameters: $(4\beta^{(0)L}_{Fe,Cl}+4\beta^{(0)L}_{C_4mim,Cl}+\Phi^{L}_{Fe,C_4mim})$ and $(\beta^{(1)L}_{Fe,Cl}+\beta^{(1)L}_{C_4mim,Cl})$ were obtained, respectively. (3) According to thermodynamic cycle and the lattice energy of IL calculated by Glasser's theory [14], the dissociation enthalpy of $[FeCl_4]^-$ anion, that is heat for the reaction $[FeCl_4]^-(g)\rightarrow Fe^{3+}(g)+4Cl^-(g)$, was estimated.

Experimental

Materials

Chemicals

Anhydrous $FeCl_3$ was purchased from Aldrich, opened in the glove box filled with dry argon, and used without further purification. 1-Methylimidazole (AR reagents) was distilled under reduced pressure. Acetonitrile, chlorobutane and ethyl acetate were AR reagents and distilled. KCl, with purity more than 99.99%, was dried

---

[*] Author for correspondence: jzyanglnu@yahoo.com.cn

1388–6150/$20.00

© 2008 Akadémiai Kiadó, Budapest

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

in a vacuum oven at 130°C for 6 h prior to use. THAM (tris-(hydroxymethy)aminomethane), GR grade reagent, was dried in a vacuum oven before use. Double-distilled water was used.

Preparation of 1-methyl-3-butylimidazolium chloride [15]

1-methyl-3-butylimidazolium chloride ($[C_4mim][Cl]$) was synthesized by refluxing the 1-methylimidazole with a large excess of the chlorobutane for 24 h. The excess chlorobutane was removed by evaporation and crude product was recrystallized from the mixed solvent of (acetonitrile+ethyl acetate). The resulting white precipitate was isolated by filtration and then dried *in vacuo* for 24 h. The melting point is 66–68°C. Analysis of $[C_4mim][Cl]$ by ^{1}H-NMR resulting in a spectrum is in good agreement with the literature [15].

Preparation of IL $[C_4mim][FeCl_4]$

All glasswares that contacted the IL were cleaned in hot dilution nitric acid and rinsed repeatedly in doubly deionized water, then were baked dry in 393 K oven and stored in desiccators before use.

$FeCl_3$ was added slowly with stirring to a small glass vial containing the equal molar $[C_4mim][Cl]$ in a glove-box filled with dry argon, then the brown and transparent ionic liquid compounds, $[C_4mim][FeCl_4]$, was obtained [8]. Analysis of the product by Raman scattering gave a spectrum identical to that for $[C_4mim][FeCl_4]$ in literature [8].

Determination of the molar enthalpies of solution of ILs

On the basis of other calorimetric apparatus [16, 17] and our previous work [18], an isoperibol calorimeter was constructed. The construction of the calorimeter and the detailed experimental procedure have been described elsewhere [12, 18].

The performance and accuracy of the calorimetric system was tested by measuring the molar enthalpy of solution of KCl in water and THAM in 0.1 mol dm^{-3} HCl(*aq*) at 298.15 K. The mean molar enthalpies solution are 17542±31 J mol^{-1} for KCl and –29794±21 J mol^{-1} for THAM which are good in conformity with the corresponding published data: 17536±9 J mol^{-1} for KCl [19, 20] and –29765±10 J mol^{-1} for THAM [20, 21]. Then, using the tested isoperibol calorimeter the molar enthalpies of solution of $[C_4mim][FeCl_4]$ with various molalities in water were measured.

Results and discussion

The molar enthalpy of solution

The values of molar solution enthalpy of $[C_4mim][FeCl_4]$ with various molalities in water at 298.15 K are listed in Table 1. From Table 1, the dissolution process of ionic liquid $[C_4mim][FeCl_4]$ is exothermic. The molar enthalpies of solution of the IL increase with the decrease of molalities.

The standard molar solution enthalpy, $\Delta_s H_m^0$, of the IL

The solution reaction of IL, $[C_4mim][FeCl_4]$, is

$$[C_4mim][FeCl_4](l)+W H_2O(l)\rightarrow [C_4mim]^+(aq)+Fe^{3+}(aq)+4Cl^-(aq)$$

where W is number of kilogram of water. The solution enthalpies of IL $[C_4mim][FeCl_4]$, $\Delta_s H$, may be expressed:

$$\Delta_s H = n_1 H_1 + n_2 (H_{Fe^+} + H_{[C_4mim]^+} + 4H_{Cl^-}) - n_1 H_1^0 - n_2 H^0_{[C_4mim][FeCl_4](l)} \qquad (1)$$

where H_i and n_i are partial molar enthalpy and mole number of component i, subscripts 1 and 2 mean solvent and solute, respectively, H_1^0 and $H^0_{BMIFeCl_4(l)}$ mean enthalpy of pure solvent and pure IL $[C_4mim][FeCl_4]$, respectively. Equation (1) may be rewritten as

$$\Delta_s H = L + n_2 (H^0_{Fe^+} + H^0_{[C_4mim]^+} + 4H^0_{Cl^-}) - n_2 H^0_{[C_4mim][FeCl_4](l)} \qquad (2)$$

where $L=H-H^0$ is relative thermodynamic function of solution. As the concentration m approaches zero, we have

$$\lim_{m\to 0} (\Delta_s H/n_2) = (H^0_{Fe^+} + H^0_{[C_4mim]^+} + 4H^0_{Cl^-}) - H^0_{[C_4mim][FeCl_4](l)} = \Delta_s H_m^0 \qquad (3)$$

where $\Delta_s H_m^0$ is the molar enthalpy of solution of IL at infinite dilution, that is, standard molar enthalpy of solution. At finite concentrations we therefore have

$$\Delta_s H_m = \Delta_s H/n_2 = \Delta_s H_m^0 + L/n_2 \qquad (4)$$

Table 1 Values of molar solution enthalpy of $[C_4mim][FeCl_4]$ with various molalities at 298.15 K

$10^2 m$/mol kg^{-1}	0.2784	0.2995	0. 3393	0. 4001	0. 4017	0. 5010
$\Delta_s H_m$/J mol^{-1}	–62.06	–61.01	–60.47	–59.93	–59.79	–59.41
$10^2 m$/mol kg^{-1}	0. 5970	0. 6044	0.8042	0. 9999	1.500	2.998
$\Delta_s H_m$/J mol^{-1}	–59.07	–58.42	–58.50	–58.00	–57.51	–57.30

According to thermodynamics, the relationship between the relative enthalpy, L, and excess Gibbs free energy, G^{ex}, is

$$L=-T^2[\partial(G^{ex}/T)/\partial T]_{p,m} \qquad (5)$$

where the subscript m and p indicate constancy of composition and pressure for the partial derivatives, respectively. It is useful to recall that the excess Gibbs free energy for a mixed electrolytes by Pitzer equations [13]. We shall write out for the mixture system of $\{BMI^+(aq)+Fe^{3+}(aq)+4Cl^-(aq)\}$ without the terms of triple-ionic interaction:

$$G^{ex}/WRT=f(I)+2\Sigma_c\Sigma_a m_c m_a B_{ca}+2\Sigma_c\Sigma_{c'} m_c m_{c'}\Phi_{cc'} \qquad (6)$$

where subscripts, c and a, mean cation and anion, respectively, other symbols are defined by following Eqs.

$$f(I)=-(4IA_\Phi/1.2)\ln(1+1.2I^{1/2}) \qquad (7)$$

$$B_{ca}=\beta^{(0)}_{ca}+\beta^{(1)}_{ca}g(x) \qquad (8)$$

$$g(x)=2[1-(1+x)\exp(-x)]/x^2 \qquad (9)$$

$$x=2I^{1/2} \qquad (10)$$

For a mixture of $\{[C_4mim]^+(aq)+Fe^{3+}(aq)+4Cl^-(aq)\}$, Eq. (6) may be simplified. Because $m_{Fe^{3+}}=m_{[C_4mim]^+}=m$, $m_{Cl^-}=4m$, Eq. (6) changed to Eq. (11)

$$\begin{aligned}G^{ex}/WRT=&-(4IA_\Phi/1.2)\ln(1+1.2I^{1/2})+\\&2m^2(4\beta^{(0)}_{Fe,Cl}+4\beta^{(0)}_{[C_4mim],Cl}+\Phi_{Fe,[C_4mim]})+\\&8m^2(\beta^{(1)}_{Fe,Cl}+\beta^{(1)}_{[C_4mim],Cl})g(x)\end{aligned} \qquad (11)$$

One may now proceed to obtain L by differentiation of (G^{ex}/WRT)

$$\begin{aligned}L=-(WRT^2)[&-(4IA_H/1.2)\ln(1+1.2I^{1/2})+\\&2m^2(4\beta^{(0)L}_{Fe,Cl}+4\beta^{(0)L}_{[C_4mim],Cl}+\Phi^L_{Fe,[C_4mim]})+\\&8m^2(\beta^{(1)L}_{Fe,Cl}+\beta^{(1)}_{[C_4mim],Cl})g(x)\end{aligned} \qquad (12)$$

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

$$\beta^{(0)L}_{MX}=(\partial\beta^{(0)}_{MX}/\partial T)_P \qquad (13)$$

$$\beta^{(1)L}_{MX}=(\partial\beta^{(1)}_{MX}/\partial T)_P \qquad (14)$$

$$\Phi^L_{Fe,[C_4mim]}=(\partial\Phi_{Fe,[C_4mim]}/\partial T)_P \qquad (15)$$

$$A_H=(\partial A_\Phi/\partial T)_P \qquad (16)$$

where A_H is Debye-Hückel parameter of enthalpy and its value was taken from literature [13]. Substituting Eq. (12) into (4) and rearranging, the working equation to determine Pitzer's parameters was obtained:

$$\begin{aligned}Y=\Delta_s H_m/2RT^2-(1/2m)(4IA_H/1.2)\ln(1+1.2I^{1/2})=&\\a_0-m(4\beta^{(0)}_{Fe,Cl}+4\beta^{(0)}_{[C_4mim],Cl}+\Phi_{Fe,[C_4mim]})-&\\4m(\beta^{(1)L}_{Fe,Cl}+\beta^{(1)L}_{[C_4mim],Cl})g(x)&\end{aligned} \qquad (17)$$

where Y is the extrapolate function, which can be obtained by experimental data. a_0 in the Eq. (17) is defined by following equations, respectively.

$$a_0=\Delta_s H^0_m/2RT^2 \qquad (18)$$

The experimental data of molar solution enthalpies of $[C_4mim][FeCl_4]$ was fitted to Eq. (17), and the values of $a_0=-0.047042$, $(4\beta^{(0)}_{Fe,Cl}+4\beta^{(0)}_{C_4mim,Cl}+\Phi_{Fe,C_4mim})=0.063383$ and $(\beta^{(1)L}_{Fe,Cl}+\beta^{(1)L}_{C_4mim,Cl})=0.096257$ and standard deviation of the fit, $s=2.8\cdot10^{-4}$, and correlation coefficient, $r=0.97$, for $[C_4mim][FeCl_4]$ are obtained, respectively. The value of standard molar solution enthalpy, $\Delta_s H^0_m=-69.5$ kJ mol^{-1} was calculated using Eq. (18). In comparison with $\Delta_s H^0_m=-76.6$ kJ mol^{-1} of $[C_2mim][FeCl_4]$ in [22], we can draw a conclusion that each mole of methylene group contributes to the standard molar enthalpy of solution of $[C_xmim][FeCl_4]$ (x=2, 4) is about 3.55 kJ mol^{-1} since the hydrophobicity of hydrocarbonic chain.

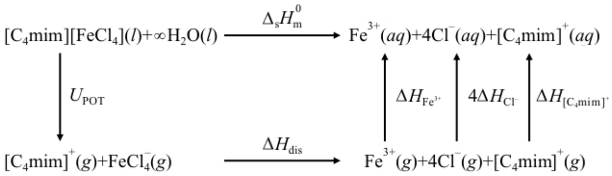

Fig. 1 The schematic diagram of thermodynamic cycle for hydration process of $[C_4mim][FeCl_4]$

Dissociation enthalpy of $[FeCl_4]^-(g)$, $\Delta_d H_m$

Figure 1 is the thermodynamic cycle for the reaction of solution of $[C_4mim][FeCl_4](l)$ in water at infinite dilution. In Fig. 1, $\Delta_s H^0_m$ is standard molar solution enthalpy of $[C_4mim][FeCl_4](l)$, $\Delta H_{Fe^{3+}}=-4435$ kJ mol^{-1} [23] is hydration enthalpy of Fe^{3+}, $\Delta H_{[C_4mim]^+}=-201$ kJ mol^{-1} [11] is hydration enthalpy of $[C_4mim]^+$ and $\Delta H_{Cl^-}=-376$ kJ mol^{-1} [23] is hydration enthalpy of Cl^-, U_{POT} is crystal energy, 420 kJ mol^{-1}, which was calculated by Glasser's theory [14]:

$$U_{POT}=1981.2(\rho/M)^{1/3}+103.8\ \text{kJ mol}^{-1} \qquad (19)$$

where M and ρ are molar mass and density of ionic liquid $[C_4mim][FeCl_4]$, respectively, $\Delta_d H_m$ is the dissociation enthalpy of anion $[FeCl_4]^-(g)$ and may be calculated in terms of the thermodynamic cycle in Fig. 1:

$$\Delta_d H_m=\Delta_s H^0_m-U_{POT}-\Delta H_{[C_4mim]^+}-\Delta H_{Fe^{3+}}-4\Delta H_{Cl^-}\approx 5650\ \text{kJ mol}^{-1}$$

The result shows the cause of low solution enthalpy of the IL, that is, the large hydration enthalpies of ions are made compensation [24, 25] for the large dissociation enthalpy of anion $[FeCl_4]^-(g)$. In comparison of Δ_dH_m (5650 kJ mol^{-1}) in this work with 5659 kJ mol^{-1} obtained by Zhang *et al.* [22], they are in good agreement within experimental error.

Acknowledgements

This project was supported by NSFC (20773056).

References

1 J. S. Wilkes and M. J. Zaworotko, J. Chem. Soc., Chem. Commun., (1992) 965.
2 R. D. Rogers and K. S. Seddon, Ionic Liquids as Green Solvents: ACS Symposium series, Vol. 856, Amer. Chem. Soc., Washington DC 2003.
3 R. D. Rogers and K. S. Seddon, Ionic Liquids Industrial Applications for Green Chemistry, ACS Symposium series, Vol. 818, Amer. Chem. Soc., Washington DC 2002.
4 J.-Z. Yang, J. Tong and J.-B. Li, J. Solution Chem., 36 (2007) 573.
5 J.-Z. Yang, X.-M. Lu, J.-S. Gui and W.-G. Xu, Green Chem., 6 (2004) 541.
6 P. Wasserscheid and T. Welton, Ionic Liquid in Synthesis, Wiley-VCH, Weinheim 2003.
7 F. Endres, Chem. Phys. Chem., 3 (2002) 144.
8 M. S. Sitze, E. R. Schreiter, E. V. Patterson and R. G. Freedman, Inorg. Chem., 40 (2001) 2298.
9 Q.-G. Zhang, W. Guan, J. Tong and X.-H. Jin, Chem. J. Chin. Univ., 27 (2006) 925 (in Chinese).
10 D. G. Archer, J. A. Widegren, D. R. Kirklin and J. W. Magee, J. Chem. Eng. Data, 50 (2005) 1484.
11 W. Guan, H. Wang, L. Li and J.-Z. Yang, Thermochim. Acta, 437 (2005) 196.
12 J.-Z. Yang, W. Guan, J. Tong, H. Wang and L. Li, J. Solution Chem., 35 (2006) 845.
13 K. S. Pitzer, Activity Coefficients in Electrolyte Solutions, Revised Ed., Ch. 3., CRC, Boca Raton 1991.
14 L. Glasser, Thermochim. Acta., 421 (2004) 87.
15 J. S. Wilkes, J. A. Levisky and R. A. Wilson, Inorg. Chem., 21 (1982) 1263.
16 Y. Y. Di, S. S. Qu, Y. Liu, Y. D. Wen, C. H. Tang and L. W. Li, Thermochim. Acta, 387 (2002) 115.
17 H.-G. Yu, Y. Liu, Z. C. Tan, J. X. Dong, T. J Zou, X. M. Huang and S. S. Qu, Thermochim. Acta, 401 (2003) 217.
18 W. Guan, L. Lei, H. Wang, W.-G. Xu and J.-Z. Yang, Chem. J. Chin. Univ., 27 (2006) 310 (in Chinese).
19 R. Rychly and V. Pekarek, J. Chem. Thermodyn., 9 (1977) 391.
20 R. L. Montgomery, R. A. Melaugh, C. C. Lau, G. H. Meier, H. H. Chan and F. D. Rossini, J. Chem. Thermodyn., 9 (1977) 915.
21 C. Wang, S. Song, W. Xiong and S. Qu, Acta Physico-Chimica Sinica, 7 (1991) 586 (in Chinese).
22 Z.-F. Zhang, H. Wang, D.-W. Fang and J.-Z. Yang, Chin. Univ., 28 (2006) 1310 (in Chinese).
23 Y. Marcus, Ion Solvation John Wiley, Chichester 1985, p. 107.
24 M. H. Hamedi and J.-P. E. Grolier, J. Therm. Anal. Cal., 89 (2007) 87.
25 M. Fernandez-Tarrio, C. Alvarez-Lorenzo and A. Concheiro, J. Therm. Anal. Cal., 87 (2007) 171.

Received: June 6, 2006
Accepted: January 4, 2008
OnlineFirst: September 20, 2008

DOI: 10.1007/s10973-008-7743-x