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Short communication

Enthalpy of solution of the ionic liquid $BMIBF_4$ in water

Wei Guan [a,b], Heng Wang [c], Lei Li [c], Qing-Guo Zhang [a,b], Jia-Zhen Yang [c,*]

[a] *The Institute of Salt Lakes, Chinese Academy of Science, Xining 810008, PR China*
[b] *The Graduate School of The Chinese Academy of Sciences, Beijing 100039, PR China*
[c] *Department of Chemistry, Liaoning University, 66 Chongshanzhonglu St., Shenyang 110036, PR China*

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Abstract

The molar enthalpies of solution of ionic liquid 1-methyl-3-butylimidazolium tetrafluoroborate ($BMIBF_4$) in water at various molalities were determined by calorimetry at 298.15 K. Pitzer's electrolyte solution theory was used to obtain the molar solution enthalpy of $BMIBF_4$ at infinite dilution, $\Delta_s H_m^0 = 26.82 \pm 0.26\,kJ/mol$.

Keywords: Room temperature ionic liquid; Isoperibol calorimeter; Solution enthalpy; Pitzer's theory; $BMIBF_4$

1. Introduction

As a continuation of our previous investigation on ionic liquids [1–4], the molar solution enthalpies of 1-methyl-3-butylimidazolium tetrafluoroborate ($BMIBF_4$) with various molalities were determined at $T = 298.15$ K in water by calorimetry [5,6].

2. Experimental

1-Methylimidazole and chlorobutane were AR reagents and distilled under reduced pressure. Acetonitrile and ethyl acetate were AR reagent and distilled. $NaBF_4$ and acetone were AR reagents and used as received. KCl, with a purity more than 99.99%, was dried in a vacuum oven at 408 K for 6 h prior to use. Deionized water was distilled in a quartz still. Its conductivity was $0.8–1.2 \times 10^{-4}\,S\,m^{-1}$.

1-Methyl-3-butylimidazolium chloride (BMIC) was synthesized according to the method of Wilkes et al. [9]. The product melting point is 339–341 K and the NMR spectrum agrees with that in literature [9].

BMIC and an equal molar amount of $NaBF_4$ were added into acetone in the glove box filled with dry argon, removed from glove box and stirred 48 h, and filtered to remove the insoluble NaCl [10]. After evaporating the acetone, colorless $BMIBF_4$ was obtained, dried in a vacuum desiccator for 20 h, and stored in desiccators prior to use. NMR spectrum agrees with that in literature [10].

On the basis of other calorimetric apparatus [11] and our previous work [12], an isoperibol calorimeter was constructed. The calorimeter 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. 150 g of water was placed in the Dewar and 0.1–4 g of $BMIBF_4$ in the sample cell. The glass sample cell was sealed by a plastic film and broken the film to initiate the measurement with stirring. The inevitable heat transfer and heat generations due 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 heat of solution was finally calculated from the equation:

$$\frac{Q_S}{\Delta T_S^*} = \frac{Q_E}{\Delta T_E^*}$$

* Corresponding author. Tel.: +86 248 6814524; fax: +86 248 6814527.
E-mail address: jzyanglnu@yahoo.com.cn (J.-Z. Yang).

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Table 1
Molar solution enthalpy of $BMIBF_4$

m (mol kg^{-1})	$\Delta_s H_m$(kJ mol^{-1})
0.002953	22.45
0.004020	21.56
0.005000	19.77
0.007077	19.25
0.007991	18.68
0.01000	17.47
0.01999	16.84
0.03999	17.09
0.04999	15.52
0.06002	16.73
0.07000	15.86
0.07999	15.90
0.09000	15.49
0.09998	15.64
0.1200	15.85
0.1402	15.38

where Q_S is the heat solution, ΔT_S^* the adiabatic temperature change of the solution process, Q_E the heat of electric calibration, and ΔT_E^* the adiabatic temperature change of electric calibration.

The accuracy of the calorimetric system was tested by measuring the enthalpy of solution of KCl at 0.05 mol kg^{-1}. $\Delta_s H_m = 17542 \pm 31$ J mol^{-1}, which was in agreement with 17536 J mol^{-1} at the same molality of KCl in literature [11–15]. The molar solution enthalpies of $BMIBF_4$ in water were measured from about 0.003 mol kg^{-1} to about 0.14 mol kg^{-1}.

3. Results and discussion

The values of molar solution enthalpy of $BMIBF_4$ in water at various molalities at 298.15 K are listed in Table 1.

The molar solution enthalpy of $BMIBF_4$ is expressed [7]:

$$\Delta_s H_m = \Delta_s H_m^0 + {}^{\Phi}L \tag{1}$$

$\Delta_s H_m^0$ is the molar solution enthalpy at infinite dilution, ${}^{\Phi}L$ is the apparent relative molar enthalpy. According to Pitzer' theory [8]:

$$\begin{aligned} {}^{\Phi}L = {} & 2\left(\frac{A_H}{2.4}\right)\ln(1+1.2I^{1/2}) \\ & -2RT^2\left(m\,\beta_{MX}^{(0)L} + my'\,\beta_{MX}^{(1)L} + \frac{m^2C_{MX}^{\Phi L}}{2}\right) \end{aligned} \tag{2}$$

where I is ionic strength, $\beta_{MX}^{(0)L}$, $\beta_{MX}^{(1)L}$, and $C_{MX}^{\Phi L}$ are Pitzer's parameters for enthalpies, and A_H is the Debye–Huckel parameter for enthalpy [8], 1986 J mol^{-1} at 298.150 K.

From equations (1) and (2), the working equation to determine Pitzer's parameters is:

$$\begin{aligned} Y &= \frac{\Delta_s H_m - 2(A_H/2.4)\ln(1+1.2I^{1/2})}{2RT^2} \\ &= a_0 - m\beta_{MX}^{(0)L} - my'\beta_{MX}^{(1)L} - \frac{m^2C_{MX}^{\Phi L}}{2} \end{aligned} \tag{3}$$

where Y is the extrapolate function, $a_0 = \Delta_s H_m^0/2RT^2$, and $y' = [1-(1+2I^{1/2})\exp(-2I^{1/2})]/2I$. Regression of Y against m, my', and $m^2/2$ was made by least-squares to obtain: $a_0 = 0.01814$, $\beta_{MX}^{(0)L} = -0.09474$, $\beta_{MX}^{(1)L} = -0.079977$, and $C_{MX}^{\Phi L} = 0.35569$, with a standard deviation of fit 1.8×10^{-4} and correlation coefficient 0.964. The molar solution enthalpy of $BMIBF_4$ at infinite dilution was $\Delta_s H_m^0 = 26.82 \pm 0.26$ kJ mol^{-1}.

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