Available online at www.sciencedirect.com
ScienceDirect
J. Chem. Thermodynamics 40 (2008) 640–644
JCT
www.elsevier.com/locate/jct

Study on properties of ionic liquid based on $ZnCl_2$ with 1-butyl-3-methylimidazolium chloride

Qing-Guo Zhang *, Ying Wei

College of Chemistry and Chemical Engineering, Bohai University, Jinzhou 121013, PR China

Received 29 August 2007; received in revised form 4 November 2007; accepted 6 November 2007
Available online 17 November 2007

Abstract

An ionic liquid (IL) $BMIZnCl_3$ has been synthesized by directly mixing zinc chloride ($ZnCl_2$) and 1-butyl-3-methylimidazolium chloride (BMIC) with molar ratio 1/1 under a dry argon atmosphere. The density and surface tension of the IL in temperature range from 313.2 K to 343.2 K were determined. The value of thermal expansion coefficient and surface entropy were estimated by extrapolation. In terms of Glasser's theory, the standard molar entropy and lattice energy of the IL were estimated. Using the methods of Kabo and Rebelo, the molar enthalpy of vaporization of the IL, $\Delta_l^g H_m^\circ$ at $T = 298$ K and $\Delta_l^g H_m^\circ$ at the hypothetical normal boiling point were estimated. The thermal expansion coefficient, α, calculated by the interstice model is of the same order of magnitude as the experimental value.

Keywords: Ionic liquid; Density; Surface tension; Interstice model; Enthalpy of vaporization

1. Introduction

An ionic liquid (IL) is an ionic compound, which exhibits ionic conductivity, and it is a liquid below $T = 373$ K [1]. Because of the great potential as "green" solvents, ionic liquids (ILs) have been attracting great interest in the last decade and have received extensive attention from the academic and industrial communities [1–5]. Though the ILs based on $AlCl_3$ have been most widely studied, they were infrequently used as solvent systems due to their sensitivity to moisture and air [6,7]. Recently, it is found that the ILs based on $ZnCl_2$ constitute a new type of ionic liquid, air- and moisture-stable, friendly to the environment and with catalytic activity in many reactions [4,8–10]. In addition, it can be very useful for the electro-deposition of pure metals and alloys [11,12] and in other specialized fields [13–15]. As a continuation of our previous investigations of ionic liquids [16–18], this paper reports the synthesis of the ionic liquid $BMIZnCl_3$ by directly mixing $ZnCl_2$ and 1-butyl-3-methylimidazolium chloride (BMIC) with a molar ratio 1/1 under a dry argon atmosphere. In this paper, we adopted Lecocq's viewpoint [19] *viz.*: IL compounds with molar ratio BMIC/$ZnCl_2 = 1/1$ is $BMIZnCl_3$. The density and surface tension of $BMIZnCl_3$ were determined over the temperature range of 313.2 K to 343.2 K. The value of the thermal expansion coefficient and surface entropy were estimated by extrapolation. In terms of Glasser's theory, the standard molar entropy and crystal energy of $BMIZnCl_3$ were estimated [20]. Using the methods of Kabo [21] and Rebelo [22], the molar enthalpy of vaporization of the IL, $\Delta_l^g H_m^\circ$ at $T = 298$ K and $\Delta_l^g H_m^\circ$ at the hypothetical normal boiling point were obtained. In order to compare with experimental values, the thermal expansion coefficient was calculated by the interstice model [23], and their magnitude is of the same order.

2. Experimental

2.1. Chemicals

The 1-methylimidazole (AR grade reagent), obtained from ACROS, and chlorobutane of AR grade reagent,

* Corresponding author. Fax: +86 416 3400292.
E-mail address: zhangqguo23@yahoo.com.cn (Q.-G. Zhang).

0021-9614/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jct.2007.11.003

obtained from Beijing Chemicals Co., were distilled under a nitrogen atmosphere before use. Ethyl acetate and acetonitrile were distilled and then stored over molecular sieves in tightly sealed glass bottles. Anhydrous $ZnCl_2$ (mass fraction purity 0.9999) was purchased from Aldrich, opened in the glove box filled with dry argon, and used without further purification.

2.2. Preparation of BMIC/$ZnCl_2$ ionic liquids

The BMIC (1-butyl-3-methylimidazolium chloride) was synthesized by Wilkes' method [24]. The melting point of the product is $T = (339$ to $341)$ K. Its n.m.r. spectrum is in good agreement with that in the literature. The $ZnCl_2$ was added slowly with stirring to a small glass vial containing BMIC (molar ratio of BMIC/$ZnCl_2 = 1/1$) in a glovebox filled with dry argon, then heated to $T = 363$ K for 48 h. The colourless and transparent ionic liquid compound, $BMIZnCl_3$, was obtained.

2.3. Measurement of density and surface tension

First, the densities of water were measured by Westphal balance and were in good agreement with those in the literature [25] within experimental error ± 0.0001 g · cm^{-3} at $T =$ 313.2 K to (343.2 ± 0.1) K. Then the density of $BMIZnCl_3$ was measured by the same method under dry argon at the same temperatures.

After the surface tension of water was measured by the forced bubble method, the results were in good agreement with that in the literature [25] within experimental error ± 0.1 mJ · m^{-2} at $T = 313.2$ K to $T = (343.2 \pm 0.1)$ K. The values of surface tension of $BMIZnCl_3$ were measured by the same method under dry argon at the same temperatures.

3. Results and discussion

3.1. Density and surface tension measurements

The values of density, ρ, and surface tension, γ, of $BMIZnCl_3$ are listed in table 1. Each value in table 1 is the average of three determinations. The experimental values of ln ρ against T were fitted by the method of least-squares and empirical equations $\ln \rho = 0.5271$ to $5.36 \cdot 10^4$ (T/K) was obtained. See figure 1. The correlation coefficient, $r =$ 0.999, and standard deviation, $s = 1.8 \cdot 10^4$, of the linear fit were obtained. The slope of the fitting equation is the thermal expansion coefficient of $BMIZnCl_3$ at $T = 298.2$ K, α, as it is defined by the following equation:

$$\alpha = -(\partial \ln \rho / \partial T)_p. \quad (1)$$

The value of α (exp) obtained from the slope of the linear fit was $5.36 \cdot 10^4$ K^{-1}.

TABLE 1
The values of surface tension, γ, and density, ρ, of the ionic liquid $BMIZnCl_3$

T/K	ρ/(g · cm^{-3})	γ/(mJ · m^{-2})
313.2	1.4319	57.49
318.2	1.4281	56.90
323.2	1.4248	56.62
328.2	1.4207	56.16
333.2	1.4165	55.70
338.2	1.4128	55.40
343.2	1.4093	54.79

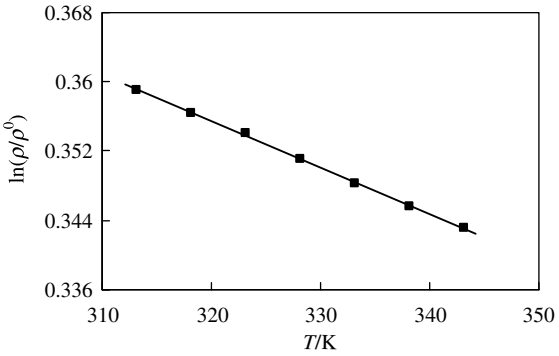

FIGURE 1. Plot of ln ρ against temperature for IL $BMIZnCl_3$: (■) experimental values; line, linear fit.

3.2. Estimation of the crystal energy and standard entropy of $BMIZnCl_3$

From the experimental values of density, the molar volume, V_m, of $BMIZnCl_3$ was calculated using the following equation:

$$V_m = M/(N \cdot \rho), \quad (2)$$

where M is average molar mass and N is Avogadro's constant. The value of ρ at $T = 298.2$ K, 1.4322 g · cm^{-3}, was obtained by extrapolation of the experimental data. The calculated value of V_m for $BMIZnCl_3$ is 0.3545 nm^3. According to the previous work [26], the volume of the cation is 0.2751 nm^3, so that the volume of the anion is 0.0794 nm^3. Compared with the previous study of IL based on aluminium [27], it is found that the V_m of $BMIZnCl_3$ is less than the V_m of the $BMIAlCl_4$, 0.4133 nm^3, because of the smaller volume of the anion $ZnCl_3^-$.

In terms of Glasser's theory [20], the standard molar entropy, S^0/J · K^{-1} · mol^{-1}, and the crystal energy, U_{POT}/kJ · mol^{-1} of the IL can be estimated by the following equations:

$$S^0/\mathrm{J \cdot K^{-1} \cdot mol^{-1}} = 1246.5(V_m/\mathrm{nm^3 \text{ per formula}}) + 29.5, \quad (3)$$

and

$$U_{POT}/\mathrm{kJ \cdot mol^{-1}} = 234.6/V_m^{1/3} + 103.8. \quad (4)$$

The value of the standard molar entropy of $BMIZnCl_3$ calculated by equation (3), $S^0(298.2\ \mathrm{K})/\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, is 471.4 and the crystal energy of $BMIZnCl_3$ calculated by equation. (4), $U_{pot}(298.2\ \mathrm{K})/\mathrm{kJ \cdot mol^{-1}}$, is 435.3. The calculated value of the crystal energy of $BMIZnCl_3$ is very close