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RESEARCH ARTICLE

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Studies on the properties of ionic liquid BMIInCl$_4$

Abstract An ionic liquid (IL) was prepared by directly mixing InCl$_3$ and 1-methyl-3-butylimidazolium chloride(BMIC) with molar ratio 1:1 under dry argon atmosphere. The densities, and surface tension of pure IL were determined at temperature range of (278.15 to 343.15±0.1K). The properties for ionic liquid based on group III were discussed using Glasser's theory. The standard entropy, the surface energy and the crystal energy of ionic liquid were calculated, respectively. The crystal energy of ionic liquid is much lower than ionic solid and this is the underlying reason for forming ionic liquid at room temperature. In addition, a new theoretical model of IL, that is interstice model, was applied to calculate the thermal expansion coefficient of BMIInCl$_4$. The order of magnitude for the thermal expansion coefficient, α, calculated by the theoretical model is in good agreement with experimental value. The result shows that there is much reasonableness for the interstice model of ionic liquid.

Keywords ionic liquid (IL), density, surface tension, InCl$_3$, interstice model

1 Introduction

Ionic liquids (ILs) or room temperature ionic liquids (RTILs) are composed solely of ions and are liquid at ambient temperature. Recently, RTILs have received more attention from both industrial and academic communities because of their unusual properties. Thus, they are viewed as a novel class of green, benign solvents, which promise widespread application in industry, possibly replacing currently used organic solvents [1]. In particular, the RTILs based on AlCl$_3$ have been most widely studied [2,3]. However, there is a limited number of reports of ILs based on elements of group III other than aluminum [4–6].

To expand our knowledge of RTIL chemistry, and as a continuation of our previous investigations [7–10], this paper reports that an IL was prepared by directly mixing InCl$_3$ and 1-methyl-3-butylimidazolium chloride with molar ratio 1:1 under dry argon atmosphere. The densities and surface tension of the IL BMIInCl$_4$ were determined at the temperature range of 293.15 to 343.15±0.1 K. The properties for IL based on group III were discussed by Glasser's theory [10,11]. Yang's interstice model [7] was applied to calculate the thermal expansion coefficient of BMIInCl$_4$ and the magnitude order of the thermal expansion coefficient, α, calculated by the model is in good agreement with experimental value. The result shows that there is much reasonableness for the interstice model of IL.

2 Experimental

2.1 Chemicals

Anhydrous InCl$_3$ (purity 99.99%) was purchased from Aldrich, opened in the glove box filled with dry argon, and used without further purification. 1-Methyl-3-butylimidazolium chloride (BMIC) was prepared using previous method [12] and the rough product was recrystallized twice from acetonitrile/ethyl acetate. Deionized water was distilled in a quartz still and its conductivity was (0.9 to 1.2)×10^{-4} S·m^{-1}.

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2.2 Preparation of $BMIInCl_4$

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

$InCl_3$ was added slowly with stirring to a glass vial containing the equal molar BMIC in a glove box filled with dry argon, and then the colorless and transparent IL compound $BMIInCl_4$ was obtained.

2.3 Measurement of density and surface tension

First, the densities of water were measured by a Westphal balance and were in good agreement with that in literature [14] within experimental error ± 0.0001 g·cm^{-3} at 293.15 to 343.15±0.1 K. Then densities of IL $BMIInCl_4$ was measured by the same method under dry argon in the same temperature range and the sample to be measured was placed in a cell with a jacket that was thermostated at each temperature with an accuracy ± 0.1 K.

After the surface tension of water was measured by the forced bubble method at 293.15 to 343.15± 0.1 K and was in agreement with that in literature [13] within experimental error $\pm 0.1\times10^{-3}$ N·m^{-1}. The surface tension of IL $BMIInCl_4$ was measured by the same method under dry argon in the same temperature range.

3 Results and discussion

The values of density, ρ, and surface tension, γ, of IL $BMIInCl_4$ measured experimentally are listed in Table 1. Each one in Table 1 is the average value of three determinations.

3.1 The volumetric properties for the IL $BMIInCl_4$

The experimental values of ln ρ against (T–298.15) were fitted by the method of the least-square and an empirical equation (1) was obtained:

$$\ln\rho = 0.45822 - 6.497\times10^{-4}(T - 298.15) \qquad (1)$$

The correlation coefficient is 0.999, standard deviation is 1.7×10^{-4}. The coefficient of thermal expansion of $BMIInCl_4$, α, is defined as $\alpha = (\partial\ln V/\partial T)_p = -(\partial\ln\rho/\partial T)_p$, where V is the molar volume of IL $BMIInCl_4$. Then $\alpha = 6.50\times10^{-4}$ K^{-1} for the IL was obtained from the slope of the linear fitting. In comparison with $\alpha = 6.53\times10^{-4}$ K^{-1} for IL $EMIInCl_4$ [15], the coefficients of thermal expansion for $EMIInCl_4$ and for $BMIInCl_4$ are almost the same within experimental error. However, experimental value of α for IL $BMIGaCl_4$ (which is 6.00×10^{-4} K^{-1} [16]) is obviously different. These facts imply that the magnitude of α is dependent on anion of IL. In order to compare, the density data of 1,3-dialkyl- imidazolium chloride-aluminum chloride ILs [17] are listed in Table 2. From the experimental density data, the molecular volume of IL $BMIInCl_4$ was calculated using following equation, $V_m = M/(N\cdot\rho)$, where M is molar mass (395.79 g/mol), N is Avogadro constant and V_m = 0.4321 nm^3 for $BMIInCl_4$ at 333.15 K. The values of molecular volume of other ILs having anion $AlCl_4^-$ are listed in Table 2. The molecular volume V_m= 0.4223 nm^3 for $BMIAlCl_4$ ($AlCl_3$/BMIC equals unity) at the same temperature. The increment of molecular volume ΔV_m =0.0098 nm^3 by replacing $AlCl_3$ with $InCl_3$ because of larger atomic volume of In than of Al. However, in terms of the data in Table 2, plot of V_m of [C_n-min][$AlCl_4$] (where C_n means 1,3-dialkyl) versus n (the number of methylene groups [treating methyl as methylene + H] in the varying alkane groups-methyl to butyl-with n = 2 to 8) yields a slope

Table 1 The values of surface tension γ and density ρ of the IL $BMIInCl_4$

T/K	278.15	283.15	288.15	293.15	298.15	303.15	308.15
ρ/(g·cm^{-3})	1.5766	1.5716	1.5666	1.5611	1.5557	1.5503	1.5453
$\gamma\times10^3$/(N/m)	45.95	44.95	44.74	44.41	43.90	43.89	43.60
T/K	313.15	318.15	323.15	328.15	333.15	338.15	343.15
ρ/(g·cm^{-3})	1.5406	1.5355	1.5307	1.5258	1.5211	1.5155	1.5123
$\gamma\times10^3$/(N/m)	43.04	43.05	42.78	42.66	42.54	42.43	42.31

Table 2 The values of molecular volume of IL based on aluminum (V_m/ nm^3) at 333.15 K

IL	M/g·mol^{-1}	M_+/g·mol^{-1}	ρ/g·cm^{-3}	V_m/nm^3	V_+/nm^3	r_+/nm
$MMIAlCl_4$	266.0	97.2	1.3053	0.3384	0.1976	0.361
$EMIAlCl_4$	280.0	111.2	1.2660	0.3673	0.2258	0.378
$PrMIAlCl_4$	294.0	125.2	1.2348	0.3954	0.2541	0.393
$BMIAlCl_4$	308.1	139.2	1.2113	0.4223	0.2806	0.406
$BBIAlCl_4$	350.1	181.2	1.1391	0.5103	0.3686	0.445

Note: $MMIAlCl_4$ means IL of mixing of 1,3-dimethylimidazolium chloride and $AlCl_3$ with molar ratio 1:1; $EMIAlCl_4$ is of 1-methyl-3-ethylimidazolium chloride and $AlCl_3$ with 1:1; $PrMIAlCl_4$ is of 1-methyl-3-propylimidazolium chloride and $AlCl_3$ with 1:1; $BMIAlCl_4$ is of 1-methyl-3-butylimidazolium chloride and $AlCl_3$ with 1:1; $BBIAlCl_4$ is of 1, 3-dibutylimidazolium chloride and $AlCl_3$ with 1:1

of 0.0278 nm^3 per methylene group (R^2 = 0.998). This is in agreement with methylene contributions of 0.0280 nm^3 for *n*-alcohols, 0.0272 nm^3 for n-amines, and 0.0267 nm^3 for *n*-paraffins [11].

As seen in Table 2, there is linear relationship between molecular volume V_m/nm^3 and molar mass of positive ions, M_+/g • mol^{-1}. Then the linear regression of V_m against M_+ was carried out and the correlation coefficient R^2 is 0.9998. The intercept of the linear regression may be regarded as the volume of anion $AlCl_4^-$, that is 0.141 0 nm^3. Then, all values of cation volume calculated are listed in Table 2 so that the volume of anion $InCl_4^-$ is 0.151 1 nm^3 obtained from the cation volume of BMI$^+$. We have noted that the value of the anion volume of $AlCl_4^-$ reported by Jenkins *et al.* [12] is 0.156 nm^3 and is much larger than ours. But Jenkins *et al.* used the Goldschmidt radii of alkali metal cations, r_+, to define the corresponding effective cation volumes, V_+, taking them to be equal to $(4/3)\pi r_+^3$. The volume of the anion is then estimated by subtracting the appropriate number of cation volumes from the molecular volume, V, of the solid salt containing an alkali metal cation. This approach assigns any 'free space' in the crystal structure to the anion volumes, $V-$. For this reason, the larger Jenkins' value of the anion volume of $AlCl_4^-$ can be understood.

Glasser *et al.* [10,11] have established good linear relationship between standard entropy and molecular volume for both ionic solid and organic liquid. Recently, the relationship was applied to IL and the empirical equation [11] of calculation of the standard entropy for IL is

$$S^0(298)/\mathrm{J\cdot K\cdot mol^{-1}}$$
$$=1246.5(V_m/\mathrm{nm^3 per\ formular}) + 29.5 \qquad (2)$$

and $S^0(298)$/J·K^{-1}·mol^{-1}=555.7 for BMIInCl$_4$. Similarly, $S^0(298)$/J·K^{-1}·mol^{-1}=544.4 for BMIAlCl$_4$. [17] This result shows that the standard entropy increased by replacing $AlCl_3$ with $InCl_3$. The values of the standard entropy for IL [C$_n$-min][AlCl$_4$] calculated by Eq. (2) are listed in Table 2. As may be seen in Table 2, the mean entropy contribution per methylene group, from a graph of S^0 versus n, is 35.2 J K^{-1} mol^{-1}. This value is in excellent agreement with the value of 33.9 J·K^{-1}·mol^{-1} for [C$_n$-min][BF$_4$] and 35.1 J·K^{-1}·mol^{-1} for [C$_n$-min][NTf$_2$] calculated by Glasser [11].

3.2 The properties of surface for IL BMIInCl$_4$

In general, surface tension, γ, of many liquids almost linearly decreases while temperature elevates and the relationship is expressed in Eötvös equation [17]:

$$\gamma V_m^{2/3} = k(T_C - T) \qquad (3)$$

where V_m is molecular volume of the liquid, T_C is critical temperature, k is empirical constant. The linear regression of product of γ and $V_m^{2/3}$ obtained from this experiment against absolute temperature T was made and the value of k = 1.28 × 10^{-7} J/K. For majority of organic liquids k is about 2.1 × 10^{-7} J/K [17], but rather small for fused salts with large polarity, for example, k = 0.4×10^{-7} J/K for fused NaCl [17]. This implies that BMIInCl$_4$ has medium polarity between organic liquids and fused salts. Therefore, the magnitude of k can represent the polarity of ILs.

The values of γ obtained at various temperatures have been fitted against T by the least square to a linear equation. The correlation coefficient R^2 is 0.99 and the slope $(\partial\gamma/\partial T)_p = -0.05077$, so that the surface excess entropy, $S_a = -(\partial\gamma/\partial T)_p$ =50.77×10^{-6} J·K^{-1}·m^{-2}. In addition, the surface excess energy likewise may be obtained from the surface tensions measured in this work: $E_a = \gamma - T(\partial\gamma/\partial T)_p$ =59.38×10^{-3} J m^{-2} for BMIInCl$_4$ at 298.15 K. In comparison with fused salts, for example, E_a= 146 × 10^{-3} J m^{-2} (for fused NaNO$_3$), the value of E_a for EMIInCl$_4$ is much lower and is close to organic liquids, for example, 67 ×10^{-3} J m^{-2} for benzene and 51.1×10^{-3} J m^{-2} for *n*-octane [18]. This fact shows that interaction energy between ions in BMIInCl$_4$ is much less than ones in fused salts. By Glasser's theory [11,12], which is used to estimate crystal energy U_{POT} for IL. U_{POT} = 416 kJ/mol for BMIInCl$_4$ was obtained, and similarly, U_{POT}=419 kJ/mol for BMIGaCl$_4$ and U_{POT}=418 kJ/mol for BMIAlCl$_4$. This fact shows that crystal energies of IL based on group III are almost the same and the values are much less than that of fused salts, for example, U_{POT}=602.5 kJ/mol for fused CsI [19]. The low crystal energy is the underlying reason for forming IL at room temperature.

3.3 The interstice theory for IL

If the hole model of molten salt [20] was transplanted to pure IL, it yields a new theoretical model, which was called interstice model [8,21]. It was built on the basis of the following assumptions: (a) Because of its large size and asymmetric shape, the ions may not be closely packed and lots of interstices between ions come into existence; (b) In order to calculate the volume easily, the interstice is regarded as a bubble; (c) There are 2N interstices for 1 mole 1-1 IL, where N is Avogadro constant；(d) The interstice in BMIInCl$_4$ can move around like an ion or another particle. In the movement the interstice does not vanish, but can be compressed and expanded, which has an extra feature of motion of an interstice called the breathing motion.

According to the same procedure of the hole model of molten salt, the expression of calculation of interstice volume, v, was obtained on the classical statistical mechanics:

$$v = 0.6791(k_b T/\gamma)^{3/2} \qquad (4)$$

where k_b is Boltzmann constant, T thermodynamic temperature, γ surface tension of IL. According to equation (4), the values of average volume of the interstices of IL BMIInCl$_4$ at different temperatures are obtained. From Table 1, the surface tension of BMIInCl$_4$ γ =43.90×10^{-3} N/m at 298.15 K, and the average volume of interstice, v=19.26×10^{-24} cm^3, then total volume of the interstice: $\Sigma v = 2Nv = 23.20$

$\text{cm}^3(\text{formula unit})^{-1}$. The volume fraction of interstice, $\Sigma v/V$, is about 0.091 for IL BMIInCl_4 and this is closest approach to that of majority of materials which exhibit 10%–15% volume expansion in process from the solid to liquid state.

The volume of IL, V, consists of the inherent volume, V_i, and total volume of the all interstices, $\Sigma v = 2Nv$, that is

$$V = V_i + 2Nv \qquad (5)$$

If the expansion of IL volume only results from the expansion of the interstices when temperature increases, then calculation expression of α was derived from the interstice theory:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{3}{2}\cdot\frac{2Nv}{VT} = \frac{3Nv}{VT} \qquad (6)$$

The values of α (calculated)$=4.58\times10^{-4}$ K^{-1} at 298.15 K and α (experimental)$=6.50\times10^{-4}$ K^{-1}. The order of magnitude of thermal expansion coefficient α (calculated) is in agreement with α (experimental) so that this result means that the interstice theory is reasonable.

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