JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

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Surface Tension and Density of Ionic Liquid *n*-Butylpyridinium Heptachlorodialuminate

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Supporting Information

ABSTRACT: An ionic liquid (IL), $[C_4Py][Al_2Cl_7]$ (*n*-butylpyridinium heptachlorodialuminate), was prepared, and its density and surface tension were measured under dry argon in the temperature range from (298.15 to 333.15) K. The experimental data showed that the Eötvös equation was applicable to the IL and the experimental parachor value was larger than that calculated from neutral parachor contribution which did not consider the Coulomb interaction in IL. In terms of Glasser's theory, the molar entropy, S^0, and the lattice energy, U_{POT}, were estimated. Using Kabo's method the molar enthalpy of vaporization $\Delta_l^g H_m^0$ (298 K) and using the interstice model the thermal expansion coefficient, α, for $[C_4Py][Al_2Cl_7]$ were predicted, respectively.

INTRODUCTION

The rapid growth in ionic liquid (IL) literature indicates that they continue to attract much attention from both industrial and academic community as green solvents[1−5] with their special physical and chemical properties, such as low vapor pressure, low inflammability, high inherent conductivities, thermal stability, liquidity over a wide temperature range, easy recycling, and being a good solvent for a wide variety of organic and inorganic chemical compounds. As the first generation of ionic liquids, $[C_4Py][Al_2Cl_7]$ (*n*-butylpyridinium heptachlorodialuminate) has been in-depth studied by Osteryoung and co-workers.[6−10] But, the ILs based on $AlCl_3$ have a disadvantage of being reactive with water, and they were restricted in application due to their moisture- and air-sensitivity. Nevertheless, $AlCl_3$-based ILs, especially aluminum halide-alkylpyridinium halides, have wider and variable Lewis acidity so they can still be very useful for many other specialized fields.[11,12]

Recently, there is a developing trend in the literature toward the estimation of physicochemical properties for ILs, which is to be commended because it provides valuable insight into the origins of the behavior of materials.[13−17] As a continuation of our previous investigation,[18,19] in this paper we report the following: (1) the density and surface tension of the IL $[C_4Py][Al_2Cl_7]$ were measured under dry argon in the temperature range from (298.15 to 338.15) K; (2) Eötvös equation was applied to the IL, and the experimental parachor was obtained; (3) in terms of the semiempirical method the standard entropy, lattice energy, the molar enthalpy of vaporization, and the thermal expansion coefficients for $[C_4Py][Al_2Cl_7]$ were estimated.

EXPERIMENTAL SECTION

Chemicals. All reagents were of commercial origin with purities > 99.5 %. 1-Chlorobutane (CAS Registry No.: 109-69-3, analytical reagent (AR) grade, Sinopharm Chemical Regent Co., China) and pyridine (CAS Registry No.: 110-86-1) were distilled before use. After removing the water by molecular sieves, ethyl acetate (CAS Registry No.: 141-78-6, AR grade, Tianjin Kermel Chemical Reagent Co., China) and acetonitrile (CAS Registry No.: 75-05-8, AR grade, Tianjin Fengchuan Chemical Reagent Co., China) were distilled.

Anhydrous $AlCl_3$ (purity of 99.99 %) was purchased from Aldrich. It was opened in the glovebox filled with dry argon and used without further purification.

Preparation of Ionic Liquids. According to the method in the literature,[7] $[C_4Py]Cl$ was synthesized and purified. The IL $[C_4Py][Al_2Cl_7]$ was prepared by simple addition of $AlC1_3$ to $[C_4Py]Cl$ with molar ratio of 2:1 in a glovebox filled with dry argon. $[C_4Py]Cl$ was placed in a small glass vial with a glass-coated magnetic stirring bar, and the $AlCl_3$ was then very slowly added with stirring. The reaction of $AlC1_3$ with $[C_4Py]Cl$ was highly exothermic, and the temperature of the mixture was not permitted to rise above about 100 °C. The resulting product was the colorless and transparent IL compound $[C_4Py][Al_2Cl_7]$. The analysis of the product by H NMR gave a spectrum identical to that of literature[8] (see Figure S1 in the Supporting Information). The onset of thermal decomposition, T_d = 520 K, for the IL (see Figure S2 in the Supporting Information) was determined by thermogravimetric analysis using a TA Instruments (SDT) model Q600 thermogravimetric analyzer.

Measurement of Density and Surface Tension. The density of the sample was measured with Anton Paar DMA 4500 oscillating U-tube densitometer, provided with automatic viscosity correction, under dry argon in the temperature range from (298.15 to 333.15) K. The temperature in the cell was regulated to ± 0.01 K with a solid state thermostat. The apparatus was calibrated daily with dry air and double-distilled freshly degassed water and cleaned with absolute ethyl alcohol, followed by drying using air.

Received: February 18, 2011
Accepted: August 3, 2011
Published: September 08, 2011

Table 1. Values of Density, ρ, and Surface Tension, γ, of $[C_4Py][Al_2Cl_7]$ at T= (298.15 to 333.15 ± 0.05) K

T /K	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 323.15	T/K = 328.15	T/K = 333.15
ρ/g·cm^{-3}	1.34066 ± 0.00001	1.33622 ± 0.00001	1.33179 ± 0.00001	1.32738 ± 0.00001	1.32290 ± 0.00001	1.31830 ± 0.00001	1.31370 ± 0.00001	1.30960 ± 0.00001
10^3 γ/mJ·m^{-2}	40.3 ± 0.2	40.1 ± 0.2	39.9 ± 0.2	39.6 ± 0.1	39.2 ± 0.2	38.9 ± 0.2	38.5 ± 0.1	38.2 ± 0.2

Using the tensiometer of the forced bubble method (DP-AW type produced by Sang Li Electronic Co.), the surface tension of water was measured in the temperature range from (298.15 to 333.15) ± 0.05 K and was in good agreement with literature[20] within the experimental error, ± 0.1 mJ·m^{-2}. After the tensiometer was dried in an oven, the surface tension of IL $[C_4Py][Al_2Cl_7]$ was measured by the same method under dry argon in the same temperature range.

RESULTS AND DISCUSSION

The measured density and surface tension values of IL $[C_4Py][Al_2Cl_7]$ are listed in Table 1. Each value in Table 1 is the average of three measurements.

Volumetric Properties of $[C_4Py][Al_2Cl_7]$. The experimental values of $\ln(\rho/\rho_0)$ against $(T/K - 298.15)$ were fitted by the method of the least-squares, and an empirical equation, $\ln(\rho/\rho_0) = 0.2932 - 6.74\cdot10^{-4}\ (T/K - 298.15)$ was obtained (see Figure S3 in Supporting Information), where $\rho_0 = 1$ g·cm^{-3}. The correlation coefficient of the fitting is 0.9999, with a standard deviation of $s = 9.5\cdot10^{-5}$. According to the definition of the coefficient of thermal expansion, α:

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

From the slope of the empirical equation the experimental value of α for IL $[C_4Py][Al_2Cl_7]$ was obtained, that is, $\alpha(\exp) = 6.74\cdot10^{-4}$ K^{-1}.

The molecular volume, V_m, is the sum of cation and anion volume and may be calculated using the eq 2:

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

where M is molar mass (438.35 g·mol^{-1}) and N is Avogadro's constant. Using eq 2, $V_m = 0.5429$ nm^3 for $[C_4Py][Al_2Cl_7]$ was obtained from the density value at 298.15 K.

According to Glasser's empirical relation,[21] the standard entropy for ILs, S^0, can be calculated according to the following equation:

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

Using eq 3, the calculated value of $S^0 = 706.2$ J·K^{-1}·mol^{-1} for $[C_4Py][Al_2Cl_7]$ was fitted.

The value of lattice energy for $[C_4Py][Al_2Cl_7]$, $U_{POT} = 391$ kJ·mol^{-1}, may be estimated using eq 4:[21]

$$U_{POT}/kJ\cdot mol^{-1} = 1981.2(\rho/M)^{1/3} + 103.8 \quad (4)$$

U_{POT} of $[C_4Py][Al_2Cl_7]$ is much smaller than that of fused salts, for example, $U_{POT} = 613$ kJ·mol^{-1} for the fused CsI,[20] which possesses the lowest lattice energy among alkali halides. The low lattice energy is the underlying reason for forming an IL at room temperature.

Properties of Surface for $[C_4Py][Al_2Cl_7]$. In general, surface tension, γ, of many liquids almost linearly decreases, while temperature elevates and the relationship is expressed using the Eötvös equation:[25]

$$\gamma V^{2/3} = k(T_c - T) \quad (5)$$

where V is the molar volume of the IL, T_c is the critical temperature, and k is an empirical constant. The linear regression of the product of γ and $V^{2/3}$ for $[C_4Py][Al_2Cl_7]$ against absolute temperature T was made, and a straight line was obtained (see Figure 1; the two lowest temperature data points are omitted from the fit, but not from the graph) with a correlation coefficient of 0.99. From the slope of the straight line, the values of $k = 2.249\cdot10^{-7}$ J·K^{-1} were obtained. It can be seen from Figure 1 that the Eötvös equation is applicable to the IL $[C_4Py][Al_2Cl_7]$.

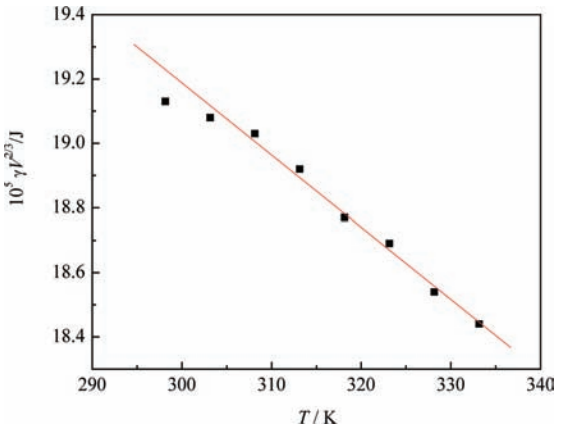

Figure 1. Fitting of $\gamma V^{2/3}$ vs T for $[C_4Py][Al_2Cl_7]$ ($\gamma V^{2/3} = 2.5398\cdot10^{-4}$ to $2.0819\cdot10^{-7}T$, $r = 0.99$, $s = 3.9\cdot10^{-7}$).

Another semiempirical relationship for surface tension is the parachor, P, which is a relatively old concept that relates the surface tension (γ) and density (ρ) of a substance.[15,22] The parachor as a tool to predict physical properties of substances was defined by Sugden:[23]

$$P = (M\gamma^{1/4})/\rho = V\gamma^{1/4} \quad (6)$$

where M is molar mass and V is molar volume. According to eq 6, $P = 823.9$ for IL $[C_4Py][Al_2Cl_7]$ was obtained at 298.15 K. In comparison with $P = 646.5$ for IL $[C_4mim][AlCl_4]$,[11] the value of parachor for $[C_4Py][Al_2Cl_7]$ was larger because of its larger molar mass.

Recently, in the absence of sufficient data of parachor contribution values for ions, Deetlefs et al.[15] considered that the parachor of ILs may be calculated using neutral parachor contribution values[22] so that the parachor can be a tool to predict physical properties of ILs. Using Deetlefs's method,[15] parachor values of $[C_4Py][Al_2Cl_7]$, $P' = 770.0$, were calculated. However, the difference between the experimental and the corresponding calculated value, $\Delta P = 53.9$, is remarkably large. Coulomb interaction was not considered in Deetlefs's method in the IL.

Predicting Vaporization Enthalpies for $[C_4Py][Al_2Cl_7]$. The enthalpy of vaporization ($\Delta_l^g H_m^0$) forms an important measure for molecular interactions in the liquid state. To gain the value of

dx.doi.org/10.1021/je200471w |J. Chem. Eng. Data 2011, 56, 3722–3724

$\Delta_l{}^g H_m{}^0$ for $[C_4Py][Al_2Cl_7]$, we have used Kabo's empirical equation:[24]

$$\Delta_l{}^g H_m{}^0(298\ \mathrm{K}) = A(\gamma V^{2/3} N^{1/3}) + B \quad (7)$$

where V is molar volume, N is Avogadro's constant, A and B are empirical parameters, their values are A = 0.01121 and B = 2.4 kJ·mol^{-1}, respectively. $\Delta_l{}^g H_m{}^0$ (298 K) = 183.5 kJ·mol^{-1} for $[C_4Py][Al_2Cl_7]$ was calculated from eq 7. The value is close to 182.4 kJ·mol^{-1} for IL $[C_2mim][AlCl_4]$,[11] which means that $[C_4Py][Al_2Cl_7]$ has a very low vapor pressure at room temperature like the IL $[C_2mim][AlCl_4]$.

Predicting the Thermal Expansion Coefficient of $[C_4Py][Al_2Cl_7]$ Using the Interstice Model. According to the interstice model,[26] the expression of the calculation of interstice volume, v, was obtained by the classical statistical mechanics:

$$v = 0.6791(k_b T/\gamma)^{3/2} \quad (8)$$

where k_b is the Boltzmann constant, T the thermodynamic temperature, and γ the surface tension of IL.

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

$$V = V_i + 2Nv \quad (9)$$

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

$$\alpha = (1/V)(\partial V/\partial T)_p = 3Nv/VT \quad (10)$$

The value of α(cal) = 4.11·10^{-4} K^{-1} for the IL $[C_4Py][Al_2Cl_7]$ was calculated from eq 10. In comparison of the calculated value with the corresponding experimental value, α(exp) = 6.74·10^{-4} K^{-1}, for $[C_4Py][Al_2Cl_7]$, they were in good agreement within the magnitude order. This result implies that predicting surface tension in our work is somewhat reasonable.

■ ASSOCIATED CONTENT

Supporting Information. ^{1}H NMR spectrum (Figure S1), thermogravimetric trace (Figure S2), and fitting of $\ln(\rho/\rho_0)$ vs $(T - 298.15)$ (Figure S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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Funding Sources

This project was supported by NSFC (20903053), the Education Bureau of Liaoning Province (LS2010069, LS2010068) P. R. China, and Liaoning University research funding.

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