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Estimation of Physicochemical Properties of Ionic Liquid $HPReO_4$ Using Surface Tension and Density[†]

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An ionic liquid (IL) $HPReO_4$ (*N*-hexylpyridine rheniumate) was prepared. The density and surface tension of the IL were determined in the temperature range of (293.15 to 343.15) K. The ionic volume and surface entropy of the IL were estimated by extrapolation. In terms of Glasser's theory, the standard molar entropy and lattice energy of the IL were estimated. Using Kabo's method and Rebelo's method, the molar enthalpy of vaporization of the IL, $\Delta_l^g H_m^0(298\ \mathrm{K})$, at 298 K and $\Delta_l^g H_m^0(T_b)$, at hypothetical normal boiling point, were estimated, respectively. According to the interstice model, the thermal expansion coefficient of IL $HPReO_4$, α, was calculated, and in comparison with experimental value, the magnitude order is in good agreement by 3.32 %.

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1. Introduction

The study of air and moisture stable ionic liquids has become the subject of an increasing number of scientific investigations. Most work has been invested in the elaboration of synthetic methods and applications of ionic liquids in catalytic processes. The physicochemical properties of ionic liquids are receiving increasing interest and are being studied more systematically.[1−7] Our interest in ionic liquids is focused on providing systematic data of phase equilibria, densities, and viscosities and other thermodynamic parameters. In continuation of our previous work,[8−12] we present new density data for the rhenium IL $HPReO_4$ (*N*-hexylpyridine rheniumate). In terms of Glasser's theory,[13] the volumetric and surface properties were discussed. Using Kabo's method[14] and Rebelo's method,[15] the molar enthalpy of vaporization, $\Delta_l^g H_m^0(298\ \mathrm{K})$, at 298 K and $\Delta_l^g H_m^0(T_b)$ at hypothetical normal boiling point were estimated, respectively. An interstice model was applied to calculate the thermal expansion coefficient of IL, α, and the magnitude order of its value calculated by the model was the same as the experimental one.

2. Experimental

2.1. Chemicals. NH_4ReO_4 (99.5 %) was purchased from Jiangxi Copper Corporation and was refined by recrystallization and dried under reduced pressure. Ethyl acetate (99.5 %), acetone (99.5 %), and acetonitrile (99.5 %) were all AR grade from Shanghai Reagent Co., Ltd. and after distillation stored in tightly sealed glass bottles, respectively. Pyridine (99.8 %) was AR grade from Shenyang Reagent Co., Ltd. and refined before use.

2.2. Preparation and Characterization of the Ionic Liquid. All glassware that contacted the IL were cleaned in hot dilution nitric acid and were washed by hot dense alkaline and rinsed repeatedly in double-distilled water. Then they were dried in a 393 K oven and stored in desiccators prior to use.

According to ref 16, *N*-hexylpyridine bromide (HPB) was synthesized. The product is a slightly snuff colored crystalloid. The reaction of synthesis of $HPReO_4$ carried out in acetone solvent is

$$NH_4ReO_4 + HPB \rightarrow NH_4Br\downarrow + HPReO_4$$

The solubility of NH_4ReO_4 and HPB in acetone is small, but NH_4Br is insoluble. As a result, NH_4Br is precipitated from liquid in reaction processes continually, so the reaction carries out toward the right. The procedure of the synthesis is as follows: in the glovebox filled with HPB and the equal molar amount of NH_4ReO_4, the acetone was added, removed from the glovebox, and stirred for 48 h, then filtrated by a Gooch funnel to remove the insoluble NH_4Br. After removing acetone, the IL $HPReO_4$ was obtained, then dried in vacuum desiccators under reduced pressure for 48 h and stored in desiccators prior to use.

The content of water in IL $HPReO_4$ measured using a Karl Fischer moisture titrator (ZSD-2 type) was 90 ppm. Analysis of ^1H NMR gave a spectrum identical to that for $HPReO_4$ with no imputiry apex.

The raman spectrum of ionic liquid $HPReO_4$ was measured on a Microscopic Confocal Raman Spectrometer (RM 2000) produced by Renishaw. Laser excitation was provided by a semiconductor laser (785 nm) and was passed through a line filter and a cylindrical lens and was focused onto the NMR tube containing the sample. The laser power at the sample was approximately 0.90 mW. Scattered light was collected at 90° from the excitation beam. The light was dispersed via an 1800 $\mathrm{line \cdot mm^{-1}}$ grating and detected via a liquid nitrogen cooled CCD. The Raman spectrum of the IL shows the special peaks of ReO_4^-: the symmetric and antisymmetric stretching models appear at 962 $\mathrm{cm^{-1}}$, the symmetric and antisymmetric deformation models appear at 332 $\mathrm{cm^{-1}}$, respectively. The results are similar to that at 971 $\mathrm{cm^{-1}}$ and 331 $\mathrm{cm^{-1}}$ of aqueous ReO_4^-.[18]

DSC trace of the product obtained with a differential scanning calorimeter DSC1 (Mettler-Toledo Co., Switzerland) shows that the IL has no melting point at (253.15 to 423.15) K. See the Supporting Information.

2.3. Measurement of Density and Surface Tension. The density of the sample was measured by a Westphal balance in the temperature range from (293.15 ± 0.05) K to (343.15 ± 0.05) K, and the uncertainties of the density values determined were ± 0.0002 $\mathrm{g \cdot cm^{-3}}$. The density of pure water was also determined by the same method and in good agreement with that in the literature[17] within the experimental error ± 0.0002 $\mathrm{g \cdot cm^{-3}}$.

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Table 1. Values of Density, ρ, and Surface Tension, γ, of $HPReO_4$ at (293.15 to 343.15) K

T/K	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15	338.15	343.15
ρ/g·cm^{-3}	1.7946	1.7870	1.7790	1.7713	1.7650	1.7590	1.7514	1.7439	1.7380	1.7323	1.7269
$10^3\gamma$/mJ·m^{-2}	34.4	34.0	33.6	33.2	33.0	32.6	32.3	32.0	31.8	31.5	31.1

Using the tensiometer of the forced bubble method (DP-AW type produced by Sang Li Electronic Co.), the surface tension of water was measured at [(293.15 ± 0.05) to (343.15 ± 0.05)] K and was in good agreement with that in the literature[18] within the experimental error $\pm (0.1 \cdot 10^{-3})$ N·m^{-1}. The surface tension of ionic liquid $HPReO_4$ was measured by the same method in the same temperature range.

3. Results and Discussion

The values of density and surface tension of ionic liquid $HPReO_4$ are listed in Table 1. Each value in Table 1 is the average of three determinations.

3.1. Estimation of Volumetric Properties for the IL. The experimental values of ln ρ against $(T - 298.15)$ were fitted by the method of the least-squares, and an empirical equation $\ln \rho = 0.5801 - 7.74 \cdot 10^{-4}(T - 298.15)$ was obtained (see Figure 1). The correlation coefficient is 0.99, and standard deviation $s = 6.15 \cdot 10^{-4}$. The coefficient of thermal expansion of $HPReO_4$, α, is defined by the following equation

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

then $\alpha = 7.74 \cdot 10^{-4}$ K^{-1} was calculated. In eq 1, V is molar volume of ionic liquid $HPReO_4$.

From the experimental density, the molecular volume, V_m, of $HPReO_4$ was calculated using the following equation

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

where M is molar mass (414.48 g·mol^{-1}); N is Avogadro's constant; and V_m=0.3851 nm^3 for $HPReO_4$.

According to Glasser's theory, the empirical equation[13] of calculation of the standard entropy for ionic liquids is

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

so that $S^0(298)$/J·K^{-1}·mol^{-1} = 509.52 for $HPReO_4$.

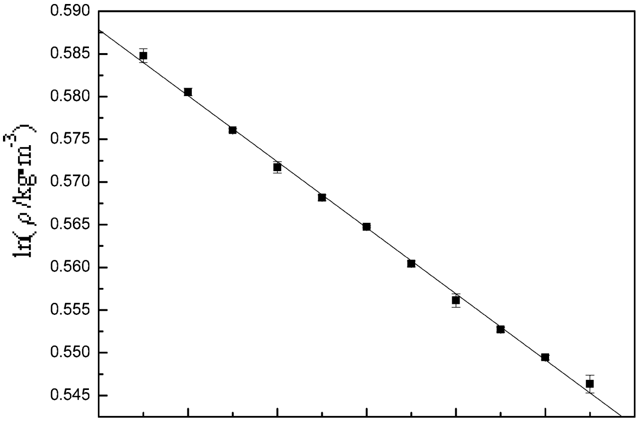

Figure 1. Plot of ln ρ vs T (■, experimental point; T, deviation).

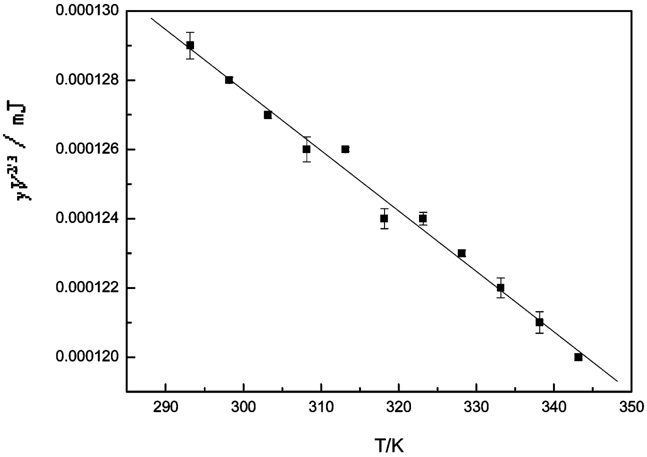

Figure 2. Plot of $\gamma V^{2/3}$ vs T (■, experimental point; T, deviation).

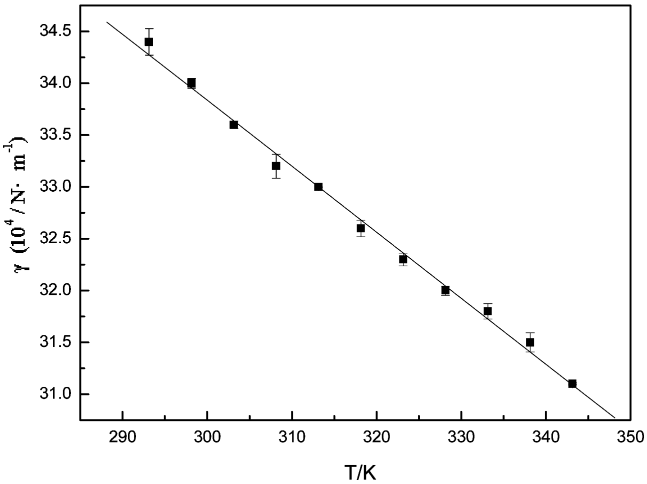

Figure 3. Plot of γ vs T (■, experimental point; T, deviation).

3.2. Estimation of Surface Properties for the IL. In general, surface tension, γ, of many liquids almost linearly decreases while temperature elevates and the relationship is expressed in the Eötvös equation[21]

$$\gamma V^{2/3} = k(T_c - T) \qquad (4)$$

where V is molar volume of the liquid; T_c is critical temperature; and k is an empirical constant. The linear regression of the product of γ and $V^{2/3}$ obtained from this experiment against absolute temperature T was made, and a good straight line was obtained (see Figure 2). From the slope of the straight line the value of $k = 1.78 \cdot 10^{-7}$ J·K^{-1} and from the intercept T_c = 1018 K were obtained, respectively. For the majority of organic liquids k is about $2.1 \cdot 10^{-7}$ J·K^{-1}, but for fused salts with large polarity, it is rather small, for example, $k = 0.4 \cdot 10^{-7}$ J·K^{-1} for fused NaCl;[21] therefore, the magnitude of k can represent the polarity of the ionic liquid. The value of $k = 1.783 \cdot 10^{-7}$ J·K^{-1} implies that $HPReO_4$ has medium polarity between an organic liquid and fused salt.

The values of γ obtained at different temperature have been fitted against T by least-squares to a linear equation (see Figure 3), and the correlation coefficient is 0.997. From the slope of the fitted line, the surface excess entropy, S_a, could be obtained; that is $S_a = -(\partial\gamma/\partial T)_p = 63.6 \cdot 10^{-6}$ J·K^{-1}·m^2. In addition, the surface excess energy at 298.15 K likewise may be obtained from the surface tension measured in this work: E_a(298.15 K) $= \gamma - T(\partial\gamma/\partial T)_p = 52.94$ mJ·m^{-2}. In comparison with fused salts, for example, E_a(298.15 K) = 146 mJ·m^{-2} (for fused $NaNO_3$), the value of E_a for $HPReO_4$ is much lower and is close to organic liquid, for example, 67 mJ·m^{-2} (for benzene) and 51.1 mJ·m^{-2} (for *n*-octane).[21] This fact shows that interaction energy between ions in $HPReO_4$ is less than that in fused salts. By Glasser's method,[13] the crystal energy, U_{POT}, may be estimated using the following equation

$$U_{\mathrm{POT}}/\mathrm{kJ{\cdot}mol^{-1}} = 1981.2(M/\rho)^{1/3} + 103.8 \qquad (5)$$

so that $U_{\mathrm{POT}} = 426.3$ kJ·mol^{-1} for $HPReO_4$ was obtained and the value is much less than that of fused salts, for example, $U_{\mathrm{POT}} = 613$ kJ·mol^{-1} for fused CsI[18] which is the lowest crystal energy among alkali-chlorides. The low crystal energy is the underlying reason for forming ionic liquid at room temperature.

3.3. Estimation of Vaporization Enthalpies for the IL. Kabo et al.[14] put forward an empirical equation for estimation of the enthalpy of vaporization, $\Delta_l{}^gH_m{}^0(298\ \mathrm{K})$, of ionic liquids

$$\Delta_l{}^gH_m{}^0(298\ \mathrm{K}) = A(\gamma V^{2/3}N^{1/3}) + B \qquad (6)$$

where N is Avogadro's constant; A and B are empirical parameters; and their values are $A = 0.01121$ and $B = 2.4$ kJ·mol^{-1}, respectively. The molar enthalpy of vaporization for ionic liquid $HPReO_4$ calculated from eq 6 was found to be 124 kJ·mol^{-1} at 298 K.

Rebelo et al.[15] put forward a method of estimating the hypothetical temperature of the normal boiling point (TNBP) of ionic liquid, T_b, in terms of critical temperature, T_c, obtained from the Eötvös equation. They thought that the relationship between T_b and T_c was $T_b \approx 0.6\ T_c$ for ionic liquid, and the T_b of ionic liquid $HPReO_4$ is 611 K approximately. The molar enthalpy of vaporization for ionic liquid $HPReO_4$ at TNBP, $\Delta_l{}^gH_m{}^0(T_b)$, can be estimated by a Trouton constant (≈ 90 J·mol^{-1}·K^{-1}). In this case, $\Delta_l{}^gH_m{}^0(652\ \mathrm{K}) = 61.1$ kJ·mol^{-1} at TNBP. The difference between $\Delta_l{}^gH_m{}^0(T_b)$ estimated in terms of Rebelo's method and $\Delta_l{}^gH_m{}^0(298\ \mathrm{K})$ estimated in terms of Kabo's method is caused by the heat capacity difference between the liquid and gas phases at different temperatures.[19,20]

3.4. Interstice Theory for Ionic Liquid. For the pure ionic liquid, a new theoretic model,[8] the expression of calculation of interstice volume, v, was obtained on the classical statistical mechanics

$$v = 0.6791(k_BT/\gamma)^{3/2} \qquad (7)$$

where k_B is the Boltzmann constant; T is thermodynamic temperature; and γ is the surface tension of ionic liquid. According to eq 7, the values of average volume of the interstices of ionic liquids at different temperatures are obtained. From Table 1, if the surface tension of $HPReO_4$ is $\gamma = 34.0$ mJ·m^{-2} at 298.15 K and the average volume of interstice is $v = 28.62 \cdot 10^{-24}$ cm^3, then the total volume of the interstice is $\Sigma v = 2Nv = 34.46$ cm^3 (formula unit)$^{-1}$. The volume fraction of interstice, $\Sigma v/V$, is about 14.86 % for ionic liquid $HPReO_4$. This most closely approaches that of the majority of materials which exhibit (10∼15) % volume expansion in the process from the solid to the liquid state.

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

$$V = V_i + 2Nv \qquad (8)$$

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 model

$$\alpha = (1/V)(\partial V/\partial T)_p = 3Nv/VT \qquad (9)$$

The value of α(calculated) = $7.48 \cdot 10^{-4}$ K^{-1} at 298.15 K, and α(experimental) = $7.74 \cdot 10^{-4}$ K^{-1}. The magnitude order of thermal expansion coefficient α(calculated) is in good agreement with α(experimental) with a deviation of 3.32 %, which means that the interstice model is reasonable.[22]

Supporting Information Available:

^{1}H NMR of $HPReO_4$ and DSC trace of IL $HPReO_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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