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SHORT ARTICLE

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Property Estimation of Ionic Liquid *N*-Pentylpyridine Perrhenate

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Supporting Information

ABSTRACT: A new air and water stable metal ionic liquid (IL) $PPReO_4$ (*N*-pentylpyridine perrhenate) was synthesized. The density and surface tension of the IL were determined in the temperature range of (293.15 to 343.15) K. The surface entropy of the IL was obtained by extrapolation. In terms of Glasser's theory, the standard molar entropy and lattice energy of the IL were estimated, respectively. Using Kabo's method and Rebelo's method, the molar enthalpy of vaporization of the IL, $\Delta_l^g H_m^0$ (298 K), at 298 K and $\Delta_l^g H_m^0$ (T_b), at the hypothetical normal boiling point, $T_b = 697$ K, was estimated, respectively. According to the interstice model, the thermal expansion coefficient of the IL was calculated, and in comparison with experimental value, it is in good agreement by 4.2 %.

INTRODUCTION

Ionic liquids (ILs) have attracted increasing attention from industrial and academic communities since Wilkes et al. synthesized the first air and water stable IL, C_2MIBF_4 (1-ethyl-3-methylimidazolium tetrafluoroborate).[1] Nowadays, many new air and water stable ILs have been synthesized and viewed as novel class of green, benign solvents which promise widespread applications in industry, possibly replacing currently used organic solvents.[2−7] As a continuation of our previous investigation on metal ILs,[8−12] in this paper, we synthesized a new kind of air and water stable metal IL $PPReO_4$ (*N*-pentylpyridine perrhenate), then measured the density and surface tension in temperature range of (293.15 to 343.15) K, and estimated other properties of the IL using the experimental data.

EXPERIMENTAL SECTION

Chemicals. NH_4ReO_4 (99.5 %) (from Jiangxi Copper Co., Ltd.) was refined by recrystallization and dried under reduced pressure. Ethyl acetate, acetone, and acetonitrile (from Shanghai Reagent Co., Ltd.) were distilled and then stored over molecular sieves in tightly sealed glass bottles, respectively. Pyridine (99.8 %) and 1-bromopentane and 1-bromohexane (99.8 %) (all from Shanghai Reagent Co., Ltd.) were distilled before use.

Preparation of Ionic Liquids. All glasswares that contacted the IL were cleaned in hot dilute nitric acid and were washed with hot densely alkaline KOH and rinsed repeatedly in double-distilled water. Then they were dried at 393 K and stored in desiccators prior to use.

Following ref 13, *N*-pentylpyridine bromide (PPB) was synthesized. The product is a slightly yellow liquid. Analysis of PPB by ^1H NMR resulted in a spectrum in good agreement with the literature.[13]

The synthesis of $PPReO_4$ carried out in acetone solvent is:

$$NH_4ReO_4 + PPB \rightarrow NH_4Br\downarrow + PPReO_4$$

The molar ratio of NH_4ReO_4/PPB is 1.2:1. The solubility of NH_4ReO_4 and PPB in acetone is small, but NH_4Br is insoluble. As a result, NH_4Br is precipitated from a liquid in reaction processes continually, so the reaction carries out toward the right. The procedure of synthesis was as follows: in the glovebox PPB and the equal molar NH_4ReO_4 were added into the acetone, removed from glovebox, stirred for 48 h, and then filtrated by a Gooch funnel for removing the insoluble NH_4Br. After removing acetone, a brown color $PPReO_4$ was obtained, and it was then dried in vacuum desiccators under reduced pressure for 24 h and stored in desiccators prior to use. An analysis of the product by ^1H NMR gave a spectrum identical to that for PPB. The content of Br^- was examined by dripping the silver nitrate solution, that is, taking a small amount of the product to dissolve in water and then dripping aqueous silver nitrate; no white deposit appeared. The content of NH_4 was also determined as 55 ppm.

The Raman spectrum of the IL $PPReO_4$ was measured on a microscopic confocal Raman spectrometer (RM2000) produced by Renishaw. Laser excitation was provided by a semiconductor laser (785 nm), which was passed through a line filter and a cylindrical lens and 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 line/mm grating and detected via a liquid nitrogen cooled charge-coupled device. The Raman spectrum of the IL showed the special peaks of

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Table 1. Values of Density, ρ, and Surface Tension, γ, of $PPReO_4$ at (293.15 to 343.15) K

T/K	293.15	298.15	303.15	308.15	313.15	318.15
ρ/g·cm^{-3}	1.8526	1.8446	1.8361	1.8292	1.8230	1.8181
$10^3\ \gamma$/mJ·m^{-2}	37.9	37.5	37.3	36.9	36.4	36.3

T/K	323.15	328.15	333.15	338.15	343.15
ρ/g·cm^{-3}	1.8099	1.8029	1.7967	1.7929	1.7870
$10^3\ \gamma$/mJ·m^{-2}	35.9	35.6	35.2	34.9	34.6

ReO_4^-: the symmetric and antisymmitric stretching models at 962.04 cm^{-1}, the symmetric and antisymmetric deformation models at 332.68 cm^{-1}, respectively. The results are similar to that of ReO_4^-.[14]

Calorimetric data were obtained with a differential scanning calorimeter DSC1 (Mettler-Toledo Co., Switzerland). The temperature range was (−100 to 150) °C with a heating rate of 10 °C·min^{-1}. Then samples were incubated at −100 °C for 5 min and began to heat at a rate of 10 °C until 150 °C. The result shows that the IL has no melting point but a glass transition temperature at −65.4 °C, which bring forth the common sense of ILs. All of the figures are listed in the Supporting Information.

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 g·cm^{-3}. The density of pure water were also determined by the same method and in good agreement with that in the literature[15] within the experimental error ± 0.0002 g·cm^{-3}.

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 K to 343.15 ± 0.05 K and was in good agreement with that in literature[15] within the experimental error ± 0.1·10^{-3} N·m^{-1}. The surface tension of the IL $PPReO_4$ was measured by the same method in the same temperature range.

The content of water in IL $PPReO_4$ was measured using a Karl Fischer moisture titrator (ZSD-2 type, 500 ppm ∼100 %). The result shows zero before and after the experiment.

RESULTS AND DISCUSSION

The values of density and surface tension of the IL $PPReO_4$ are listed in Table 1, respectively. Each value in Table 1 is the average of three determinations.

Estimation of Standard Entropy and Lattice Energy 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 $\ln \rho = 0.8260 - 7.19 \cdot 10^{-4}(T - 298.15)$ was obtained (see Figure 1). The correlation coefficient is 0.998, standard deviation $s = 8.3 \cdot 10^{-4}$. The coefficient of thermal expansion of $PPReO_4$, α, is defined by following equation:

$$\alpha \equiv (1/V)(\partial V/\partial T)_p = (\partial \ln \rho/\partial T)_p \tag{1}$$

then $\alpha = 7.19 \cdot 10^{-4}\ K^{-1}$ was calculated. In eq 1 V is the molar volume of the IL $PPReO_4$.

From the experimental density, the molecular volume, V_m, of $PPReO_4$ was calculated using the following equation:

$$V_m = M/(N \cdot \rho) \tag{2}$$

where M is the molar mass (400.47 g·mol^{-1}), N is Avogadro's constant, and $V_m = 0.3605\ nm^3$ for $PPReO_4$.

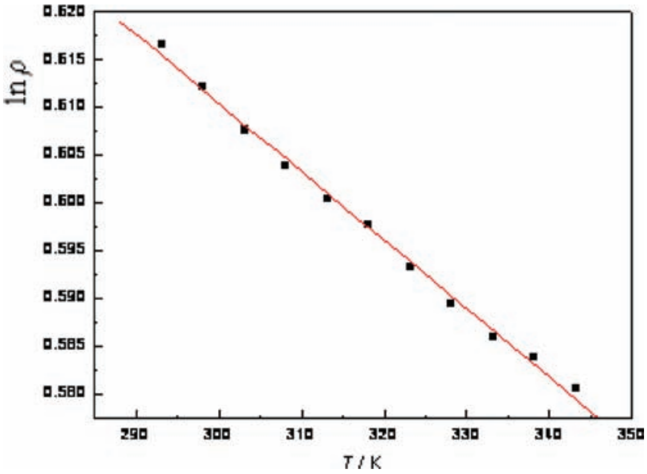

Figure 1. Plot of ln ρ vs T ($\ln \rho = 0.8260 - 7.19 \cdot 10^{-4}(T - 298.15)$, $r = 0.998$, $s = 8.3 \cdot 10^{-4}$).

According to Glasser's theory, the empirical equation[16] of the calculation of the standard entropy for an IL is:

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

so that $S^0(298)/J \cdot K^{-1} \cdot mol^{-1} = 479$ for $PPReO_4$.

By Glasser's method,[16] the lattice energy, U_{POT}, may be estimated using the following equation:

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

so that $U_{POT} = 443\ kJ \cdot mol^{-1}$ for $PPReO_4$ was obtained and the value is much less than that of fused salts, for example, $U_{POT} = 613\ kJ \cdot mol^{-1}$ for fused CsI[15] which is the lowest lattice energy among alkali halides. The low lattice energy is the underlying reason for forming an IL at room temperature.

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

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

where V is the molar volume of the liquid, T_c is the critical temperature, and k is an empirical constant. The linear regression of 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); the correlation coefficient is 0.995. From the slope of the straight line, the value of $k = 1.78 \cdot 10^{-7}\ J \cdot K^{-1}$, and from the intercept $T_c = 1060$ K were obtained, respectively. For the majority of organic liquids k is about $2.1 \cdot 10^{-7}\ J \cdot K^{-1}$ but for fused salts with large polarity is rather small, for example, $k = 0.4 \cdot 10^{-7}\ J \cdot K^{-1}$ for fused NaCl;[17] therefore, the magnitude of k can represent the polarity of an IL. The value of $k = 1.78 \cdot 10^{-7}\ J \cdot K^{-1}$ implies that $PPReO_4$ has a medium polarity between organic liquid and fused salt.

The values of γ against T have been fitted to a linear equation by least-squares (see Figure 3), and the correlation coefficient is 0.998. From the slope of the fitted line, the surface excess entropy, S_a, could be obtained, that is, $S_a = -(\partial \gamma/\partial T)_p = 66.22 \cdot 10^{-6}\ J \cdot K^{-1} \cdot m^2$. In addition, the surface excess energy, E_a, likewise may be obtained from the surface tension measured in this work: $E_a = \gamma - T(\partial \gamma/\partial T)_p = 57.26\ mJ \cdot m^{-2}$. In comparison with fused salts, for example, $E_a = 146\ mJ \cdot m^{-2}$

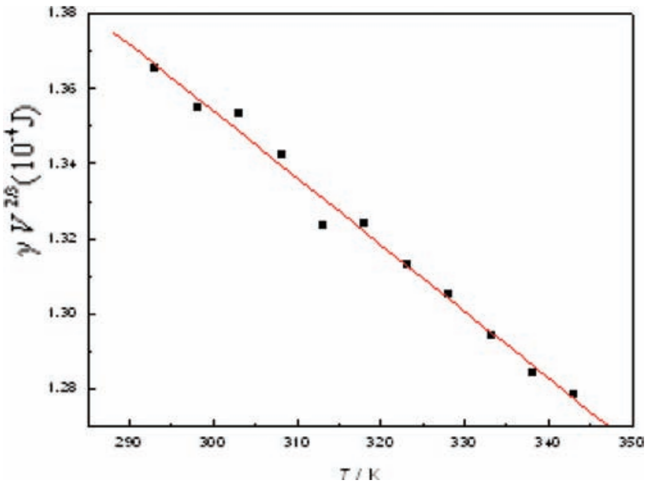

Figure 2. Plot of $\gamma V^{2/3}$ vs T ($\gamma V^{2/3} = -1.78 \cdot 10^{-7}(1060 - T)$, r = 0.995, $s = 3.3 \cdot 10^{-3}$).

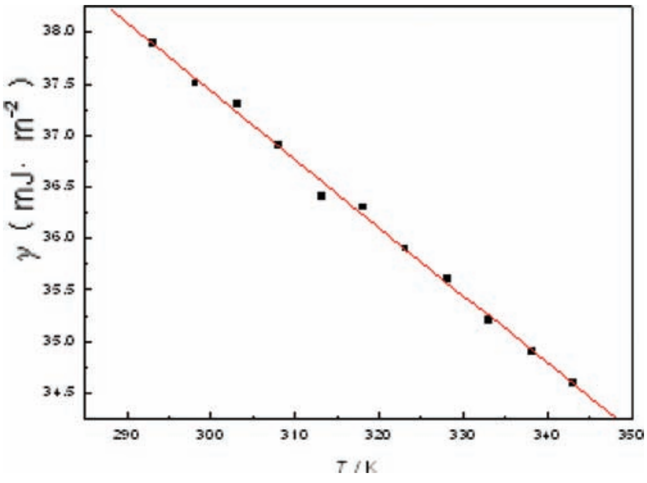

Figure 3. Plot of γ vs T ($\gamma = 57.2 - 0.066 \cdot T$, $r = 0.998$, $s = 0.069$).

(for fused $NaNO_3$), the value of E_a for $PPReO_4$ is much lower and is close to the organic liquid, for example, 67 $mJ \cdot m^{-2}$ (for benzene) and 51.1 $mJ \cdot m^{-2}$ (for *n*-octane).[17] In general, surface excess energy is dependent on interaction energy between ions. The value of E_a for $PPReO_4$ is smaller than one for fused salts, and this fact shows that interaction energy between ions of $PPReO_4$ is less than that in fused salts.

Estimation of Vaporization Enthalpies for the IL. Kabo and colleagues[18] put forward an empirical equation for estimation of the enthalpy of vaporization, $\Delta_l^g H_m^0$ (298 K), of ILs:

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

where N is Avogadro's constant, A and B are empirical parameters, and their values are $A = 0.01121$ and $B = 2.4$ $kJ \cdot mol^{-1}$, respectively. The molar enthalpy of vaporization for IL $PPReO_4$ calculated from eq 6 was found to be 130.7 $kJ \cdot mol^{-1}$ at 298 K.

Rebelo et al.[19] put forward a method of estimating the hypothetical temperature of normal boiling point (TNBP) of the IL, T_b, in terms of critical temperature, T_c, obtained from the Eötvös equation. They suggested that the relationship between T_b and T_c is $T_b \approx 0.6T_c$ for ILs so that T_b of the IL $PPReO_4$ is 636 K approximately. The molar enthalpy of vaporization for the IL $PPReO_4$ at TNBP, $\Delta_l^g H_m^0(T_b)$, can be estimated by a Trouton constant (≈ 90 $J \cdot mol^{-1} \cdot K^{-1}$). In the case $\Delta_l^g H_m^0$(636 K) = 57.2 $kJ \cdot mol^{-1}$ at TNBP. The difference between $\Delta_l^g H_m^0(T_b)$ estimated in terms of Rebelo's method and $\Delta_l^g H_m^0$(298 K) estimated in terms of Kabo's method is caused by the heat capacity difference between the liquid and the gas phases at different temperatures. If the linear change of $\Delta_l^g H_m^0$ with temperature in the range between 298 K and T_b was supposed, the hypothetical vapor pressures, p, of the IL at different temperatures may be estimated by the Clapeyron−Clausius equation.

Interstice Theory for Ionic Liquids. According to the interstice model,[9] the expression of calculation of interstice volume, ν, was obtained on the classical statistical mechanics:

$$\nu = 0.6791(k_b T/\gamma)^{3/2} \qquad (7)$$

where k_b is Boltzmann constant, T the thermodynamic temperature, and γ the surface tension of ILs. According to eq 7, the values of average volume of the interstices of ILs at different temperatures are obtained. From Table 1, the surface tension of $PPReO_4$ is $\gamma = 37.5$ $mJ \cdot m^{-2}$ at 298.15 K, and the average volume of interstice is $\nu = 19 \cdot 10^{-24}$ cm^3; then the total volume of the interstice is $\sum \nu = 2N\nu = 23$ cm^3 (formula unit)$^{-1}$. The volume fraction of interstice, $\sum \nu / V$, is about 12 % for the ionic liquid $PPReO_4$. They are closest approach to that of the majority of materials which exhibit (10 to 15) % volume expansion in process from the solid to liquid state.

The volume of ILs, V, consists of the inherent volume, V_i, and total volume of the all interstices, $\sum \nu = 2N\nu$, that is:

$$V = V_i + 2N\nu \qquad (8)$$

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:

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

The values of α(calculated) = $6.896 \cdot 10^{-4}$ K^{-1} at 298.15 K and α(experimental) = $7.19 \cdot 10^{-4}$ K^{-1}. The thermal expansion coefficient α(calculated) is in good agreement with α(experimental) by 4.2 %, so that this result means that the interstice model can estimate the thermal expansion coefficient of ILs.

■ ASSOCIATED CONTENT

S Supporting Information. ^{1}H NMR and Raman spectra and DSC characterization of $PPReO_4$.This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(1) Wilkes, J. S.; Zaworotko, J. J. Air and water stable 1-ethyl-3-methylimidazolium based ionic liquids. *J. Chem. Soc., Chem. Commun.* **1992**, 965.

(2) Rogers, R. D.; Seddon, K. S. *Ionic liquids: Industrial applications for green chemistry*; ACS Symposium Series 818; ACS: Washington, DC, 2002.

(3) Yang, J.-Z.; Zhang, Q.-G.; Wang, B.; Tong, J. Study on the Properties of Amino Acid Ionic Liquid EMIGly. *J. Phys. Chem. B* **2006**, *110*, 22521–22524.

(4) Wang, J.; Pei, Y.; Zhao, Y.; Hu, Z. Recovery of amino acids by imidazolium based ionic liquids from aqueous media. *Green Chem.* **2005**, *7*, 196–202.

(5) Seddon, K. S. Ionic liquids for clean technology. *J. Chem. Technol. Biotechnol.* **1997**, *68*, 351–356.

(6) Endure, F. Ionic Liquids: Solvents for the Electrodeposition of Metals and Semiconductors. *ChemPhysChem* **2002**, *3*, 144–154.

(7) Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. Ionic Liquid (Molten Salt) Phase Organometallic Catalysis. *Chem. Rev.* **2002**, *102*, 3667–3692.

(8) Yang, J.-Z.; Jin, Y.; Xu, W.-G.; Zhang, Q.-G.; Zang, S.-L. Studies on mixture of ionic liquid EMIGaCl$_4$ and EMIC. *Fluid Phase Equilib.* **2005**, *227*, 41–46.

(9) Yang, J.-Z.; Lu, X.-M.; Gui, J.-S.; Xu, W.-G. A new theory for ionic liquids—the Interstice Model Part 1. The density and surface tension of ionic liquid EMISE. *Green Chem.* **2004**, *6*, 541–543.

(10) Tong, J.; Hong, M.; Guan, W.; Yang, J.-Z. Studies on the thermodynamic properties of new ionic liquids: 1-Methyl-3-pentylimidazolium salts containing metal of group III. *J. Chem. Thermodyn.* **2006**, *38*, 1416–1421.

(11) Yang, J.-Z.; Tian, P.; He, L.-L.; Xu, W.-G. Studies on room temperature ionic liquid InCl$_3$—EMIC . *Fluid Phase Equilib.* **2003**, *204*, 295–302.

(12) Xu, W. G.; Lu, X.-M.; Gui, J.-S.; Zhang, Q.-G.; Yang, J. Z. Studies on the Thermodynamic Properties of the Ionic Liquid BMIGaCl$_4$. *Chin. J. Chem.* **2006**, *24*, 331–335.

(13) Pan, C. Z.; Xu, X. H.; Liu, Q. Q. The Study of Preparation and Performance of BP$^+$Br$^-$ and BP$^+$BF$_4$$^-$ Room Temperature Molten Salts. *Fine Chem. Intermed.* **2002**, *32*, 22–23.

(14) Salvati, L.; Jones, G. L., Jr.; Hercules, D. M. An X-ray Photoelectron (ESCA) and Laser Raman Spectroscopic Investigation of Aluminum Perrhenate. *Appl. Spectrosc.* **1980**, *34*, 624–626.

(15) Lide, D. R., Ed. *Handbook of Chemistry and Physics*, 82nd ed.; CRC Press: Boca Raton, FL, 2001—2002.

(16) Glasser, L. Lattice and phase transition thermodynamics of ionic liquids. *Thermochim. Acta* **2004**, *421*, 87–93.

(17) Adamson, A. W. *Physical chemistry of surfaces*, 3rd ed.; translated by Gu, T. R.; John-Wiley: New York, 1976.

(18) Zaitsau, D. H.; Kabo, G. J.; Strechan, A. A.; Paulechka, Y. U.; Tschersich, A.; Verevkin, S. P.; Heintz, A. Experimental Vapor Pressures of 1-Alkyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imides and a Correlation Scheme for Estimation of Vaporization Enthalpies of Ionic Liquids. *J. Phys. Chem. A* **2006**, *110*, 7303.

(19) Rebelo, L. P. N.; Lopes, J. N. C.; Esperança, J. M. S. S.; Filipe, E. On the Critical Temperature, Normal Boiling Point, and Vapor Pressure of Ionic Liquids. *J. Phys. Chem. B* **2005**, *109*, 6040.