J. Chem. Eng. Data **2010,** *55,* 3693–3696

Physicochemical Properties of an Ionic Liquid $[C_2mim][B(CN)_4]$

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The density and surface tension of the ionic liquid (IL) $[C_2mim][B(CN)_4]$ (1-ethyl-3-methylimidazolium tetracyanoborate) were measured in a temperature range from (283.15 to 338.15) K. In terms of Glasser's semiempirical relation of ILs, the standard molar entropy and the lattice energy of the homologous series of ILs $[C_nmim][B(CN)_4]$ were estimated, respectively. Using Kabo's method and Rebelo's method, the molar enthalpy of vaporization of $[C_2mim][B(CN)_4]$, $\Delta_l^gH_m^0$ (298 K), at 298 K, and $\Delta_l^gH_m^0$ (T_b), at hypothetical normal boiling point, $T_b = 680$ K, was estimated, respectively. According to the interstice model, the thermal expansion coefficient of $[C_2mim][B(CN)_4]$, $\alpha = 4.77 \cdot 10^{-4}\ K^{-1}$, was estimated and was in good agreement with experimental value.

Introduction

The rapid increase in both academic and industrial interest in ionic liquids (ILs) as a "green solvent" has led to a remarkable growth in the number of applications for these materials in the last 20 years.[1−6] However, much of the research on ILs has involved the synthesis of new ILs and their application in an ever-increasing number of areas. In contrast, there have been relatively few studies on fundamental physicochemical properties of ILs, which are extremely important for their applications.[7,8] Recently, there is a developing trend in the literature towards 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.[8−11] As a continuation of our previous investigation,[12,13] in this paper we report the following: (1) The density and surface tension of the IL $[C_2mim][B(CN)_4]$ were measured in the temperature range from (283.15 to 338.15) K. (2) In terms of Glasser's semiempirical relation of IL[14] and a semiempirical method proposed in this work, physicochemical properties of homologous compounds of ILs, $[C_nmim][B(CN)_4]$ ($n = 2$, 3, 4, 5, 6), were estimated. (3) Using Kabo's method and Rebelo's method, the molar enthalpy of vaporization of $[C_2mim][B(CN)_4]$ was estimated. (4) According to the interstice model, the thermal expansion coefficients of $[C_2mim][B(CN)_4]$ were predicted.

Experimental Section

$[C_2mim][B(CN)_4]$ (> 0.999 mass fraction, water (K. F.) $\leq 1 \cdot 10^{-4}$ mass fraction) was purchased from Merck Corp. in Germany. The density of the sample was measured with an Anton Paar DMA 4500 oscillating U-tube densitometer, provided with automatic viscosity correction under dry argon from (283.15 to 338.15) 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. Using the tensiometer of the forced bubble method (DP-AW type produced by Sang Li Electronic Co.), the surface tension of water was measured from (283.15 to 338.15) ± 0.05 K and was in good agreement with literature[15] within the experimental error, $\pm 0.1\ mJ \cdot m^{-2}$. After being dried in an oven, the surface tension of the IL $[C_2mim][B(CN)_4]$ 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 the IL $[C_2mim][B(CN)_4]$ are listed in Table 1, respectively.

Estimating the Volumetric Properties of the Homologous Series of ILs $[C_nmim][B(CN)_4]$. 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, $\ln(\rho/\rho_0) = 0.03579 - 7.59 \cdot 10^{-4}(T/K - 298.15)$, was obtained (see Figure 1), where $\rho_0 = 1\ g \cdot cm^{-3}$. The correlation coefficient of the fitting is 0.99999, with a standard deviation $s = 5.0 \cdot 10^{-5}$. According to the definition of the coefficient of thermal expansion, α is calculated as the following:

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

The slope of the empirical equation is the experimental value of α for the IL $[C_2mim][B(CN)_4]$, that is, $\alpha(\text{exp.}) = 7.59 \cdot 10^{-4}\ K^{-1}$. In eq 1 V is molar volume.

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

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

where M is molar mass ($226.05\ g \cdot mol^{-1}$) and N is Avogadro's constant. Using eq 2, $V_m = 0.3623\ nm^3$ for $[C_2mim][B(CN)_4]$ was obtained from the density value at 298.15 K.

According to our previous investigation, the contribution to the molecular volume per methylene ($-CH_2-$) group is 0.0270

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10.1021/je100228t

Table 1. Values of Density, ρ, and Surface Tension, γ, of $[C_2mim][B(CN)_4]$ at $T = (283.15 \text{ to } 338.15) \pm 0.05$ K

T/K	T/K = 283.15	T/K = 288.15	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15
ρ/g·cm^{-3}	1.04837 ± 0.00001	1.04437 ± 0.00001	1.04038 ± 0.00001	1.03641 ± 0.00001	1.03246 ± 0.00001	1.02855 ± 0.00001
$10^3\gamma$/mJ·m^{-2}	49.4 ± 0.2	48.9 ± 0.2	48.2 ± 0.2	47.8 ± 0.2	47.6 ± 0.2	47.1 ± 0.2
T/K	T/K = 313.15	T/K = 318.15	T/K = 323.15	T/K = 328.15	T/K = 333.15	T/K = 338.15
ρ/g·cm^{-3}	1.02466 ± 0.00001	1.02078 ± 0.00001	1.01695 ± 0.00001	1.01311 ± 0.00001	1.00932 ± 0.00001	1.00554 ± 0.00001
$10^3\gamma$/mJ·m^{-2}	46.8 ± 0.1	46.4 ± 0.2	46.2 ± 0.2	45.5 ± 0.1	45.0 ± 0.2	44.8 ± 0.2

nm^3 in ILs $[C_n\text{mim}][AlCl_4]$ ($n = 1, 2, 3, 4, 5, 6$)[12] and 0.0278 nm^3 in ILs $[C_n\text{mim}]$[Ala] (1-alkyl-3-methylimidazolium α-aminopropionic acid salt) ($n = 2, 3, 4, 5, 6$),[13] which is in excellent agreement with a mean contribution of 0.0275 nm^3 obtained by Glasser[14] from ILs $[C_n\text{mim}][BF_4]$ and $[C_n\text{mim}][NTf_2]$. This confirms that we may apply the mean value, 0.0275 nm^3, to predict the volumetric properties of the homologues of $[C_n\text{mim}][B(CN)_4]$ ($n = 3, 4, 5, 6$) at 298.15 K. The predicted values are given in Table 2.

According to Glasser's semiempirical relation,[14] the standard entropy for ILs, S^0, can be calculated applying the following equation:

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

Using eq 3, the calculated values of S^0 for the homologous series $[C_n\text{mim}][B(CN)_4]$ ($n = 2, 3, 4, 5, 6$) were obtained and listed in Table 2.

The values of lattice energy for the homologous series $[C_n\text{mim}][B(CN)_4]$, U_{POT}, may be estimated using eq 4:[14]

$$U_{\text{POT}}/\text{kJ}\cdot\text{mol}^{-1} = 1981.2[(\rho/\rho_0)/(M/M_0)]^{1/3} + 103.8 \qquad (4)$$

where $M_0 = 1$ g·mol^{-1}. The calculated results are listed in Table 2. From Table 2, it follows that the highest value, $U_{\text{POT}} = 433$ kJ·mol^{-1}, of $[C_2\text{mim}][B(CN)_4]$ is much smaller than the value of fused salts, for example, $U_{\text{POT}} = 613$ kJ·mol^{-1} for the fused CsI,[15] which possesses the lowest lattice energy among alkali halides. The low lattice energy is the underlying reason for forming an IL at room temperature.

Predicting Vaporization Enthalpies for $[C_2mim][B(CN)_4]$. Kabo and colleagues[16] put forward an empirical equation for the estimation of the enthalpy of vaporization, $\Delta_l^g H_m^0$ (298 K), of ILs:

$$\Delta_l^g H_m^0\,(298\text{ K}) = A(\gamma V^{2/3} N^{1/3}) + B \qquad (5)$$

where V is molar volume, N is Avogadro's constant, A and B are empirical parameters,[16] and their values are $A = 0.01121$ and $B = 2.4$ kJ·mol^{-1}, respectively. The molar enthalpy value of vaporization for $[C_2\text{mim}][B(CN)_4]$ was 166.3 kJ·mol^{-1} calculated from eq 5.

In addition, Rebelo et al.[17] put forward a method of estimating the hypothetical temperature of normal boiling point (TNBP) of IL, T_b, in terms of critical temperature, T_c. They thought that the relationship between T_b and T_c is $T_b \approx 0.6T_c$ for ILs. The molar enthalpy of vaporization for the ILs at TNBP, $\Delta_l^g H_m^0$ (T_b), can be estimated by the Trouton constant (≈ 90 J·mol^{-1}·K^{-1}). The critical temperature, T_c, of the ILs was estimated using the Eötvös equation:[18]

$$\gamma V^{2/3} = k(T_c - T) \qquad (6)$$

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 $[C_2\text{mim}][B(CN)_4]$ against absolute temperature T was made. A good straight line was obtained (see Figure 2), and the correlation coefficient is 0.993. From the slope of the straight line, the values of $k = 2.081\cdot10^{-7}$ J·K^{-1} and from the intercept $T_c = 1134$ K were obtained, respectively.

According to Rebelo, T_b of $[C_2\text{mim}][B(CN)_4]$ is approximately 680 K. The molar enthalpy of vaporization at TNBP, $\Delta_l^g H_m^0$ (T_b), can be estimated by a Trouton constant (≈ 90 J·mol^{-1}·K^{-1}). In this case, $\Delta_l^g H_m^0$ (680 K) = 61.2 kJ·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 a linear change of $\Delta_l^g H_m^0$ with the temperature in the range between 298 K and T_b was supposed, the hypothetical vapor pressures, p, of $[C_2\text{mim}][B(CN)_4]$ at different temperatures may be estimated by eq 7 (that is, the Clapeyron−Clausius equation). The calculated values of $\Delta_l^g H_m^0$ and p at various temperatures are listed in Table 3. Figure 3 is the plot of vapor pressure, p, and $\Delta_l^g H_m^0$ of $[C_2\text{mim}][B(CN)_4]$ against temperature, T.

$$\ln(p_2/p_1) = (\Delta_l^g H_m^0/R)(1/T_1 - 1/T_2) \qquad (7)$$

From Figure 3 the vapor pressure at 300 K is very small, 10^{-10} kPa, and could be neglected. The result is in agreement with our experience: very low vapor pressure before the decomposition of the ILs and negligible vapor pressure at ambient temperature. The fact shows that the method of estimating vapor pressure of ILs is somewhat reasonable.

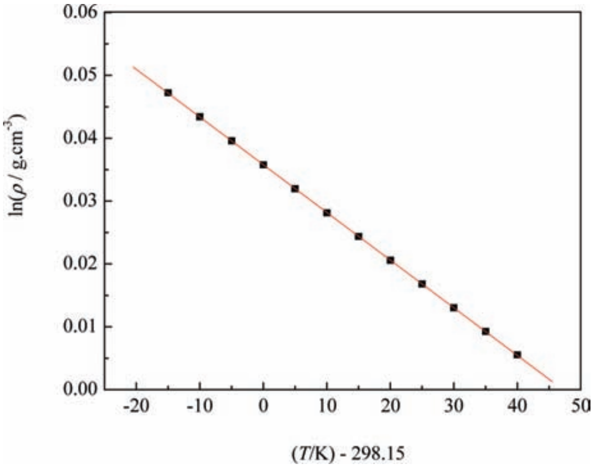

Figure 1. Fitting of ln ρ vs ($T - 298.15$) for the IL $[C_2\text{mim}][B(CN)_4]$ (ln $\rho = 0.03579 - 7.59\cdot10^{-4}(T - 298.15)$, $r = 0.9999$, $s = 5.0\cdot10^{-5}$).

Table 2. Predicted Volumetric Properties of the Homologous Series $[C_n mim][B(CN)_4]$ (n = 2, 3, 4, 5, 6) at 298.15 K

IL	ρ / $g\cdot cm^{-3}$	V_m / nm^3	S^0 / $J\cdot K^{-1}\cdot mol^{-1}$	V / $cm^3\cdot mol^{-1}$	U_{POT} / $kJ\cdot mol^{-1}$
$[C_2mim][B(CN)_4]$	1.03641 ± 0.00001^a	0.3623^a	481.1^a	218.1^a	433^a
$[C_3mim][B(CN)_4]$	1.02295	0.3898	515.4	234.7	425
$[C_4mim][B(CN)_4]$	1.01127	0.4173	549.7	251.2	418
$[C_5mim][B(CN)_4]$	1.00103	0.4448	584.0	267.8	411
$[C_6mim][B(CN)_4]$	0.99199	0.4723	618.2	284.3	405

[a] Experimental value.

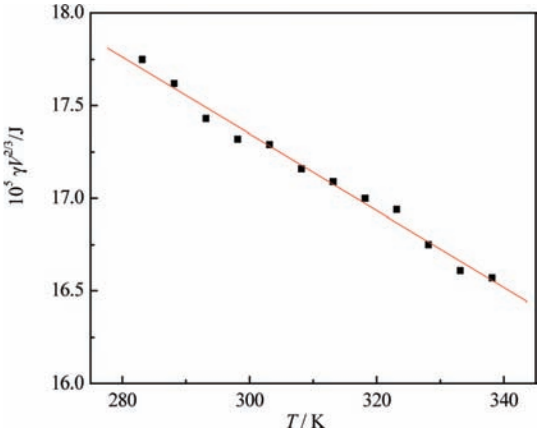

Figure 2. Fitting of $\gamma V^{2/3}$ vs T for $[C_2mim][B(CN)_4]$ ($\gamma V^{2/3} = 2.3593\cdot10^{-4} - 2.0813\cdot10^{-7}\ T$, $r = 0.993$, $s = 4.67\cdot10^{-7}$).

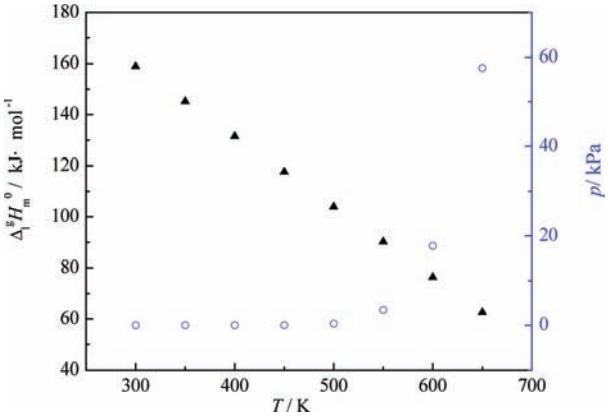

Figure 3. Plot of vapor pressure, p, and $\Delta_l^g H_m^0$ of $[C_2mim][B(CN)_4]$ vs temperature T (○, for vapor pressure; ▲, for molar enthalpy of vaporization).

Predicting the Thermal Expansion Coefficient of $[C_2mim][B(CN)_4]$. According to the interstice model,[19] the expression of the calculation of interstice volume, v, was obtained on the classical statistical mechanics:

$$\nu = 0.6791[k_b(T/K)/(\gamma/mN\cdot m^{-1})]^{3/2} \qquad (8)$$

where k_b is the Boltzmann constant, T the thermodynamic temperature, and γ the surface tension of IL. According to eq 8, the values of average volume of the interstices of the IL at different temperatures are obtained. At 298.15 K, the average volume of interstice is $v = 17.16\cdot10^{-24}$ cm^3, and then total volume of the interstice is $\sum v = 2Nv = 20.66$ cm^3 (formula unit)$^{-1}$. The volume fraction of interstice, $\sum v/V$, is about 9.5 % for the IL $[C_2mim][B(CN)_4]$ according to eq 8. It is the closest approach to that of the majority of materials which exhibit (10 to 15) % volume expansion in the process from the solid to liquid state.

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

$$V = V_i + 2N\nu \qquad (9)$$

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

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

Using the surface tension and molar volume, the value of expansion coefficients of $[C_2mim][B(CN)_4]$ is obtained. The magnitude order of α(cal.) = 4.77 K^{-1} is in good agreement with α(exp.) = (7.59 ± 0.03) K^{-1} for $[C_2mim][B(CN)_4]$, so this result implies that the surface tension predicted in our work is somewhat reasonable.

Conclusions

The density and surface tension of the IL, $[C_2mim][B(CN)_4]$, were measured in the temperature range (283.15 to 338.15) ± 0.05 K, respectively. Since the per methylene ($-CH_2-$) group in the alkyl chains of the imidazolium-based ILs has almost the same chemical environment, we may predict physicochemical properties of 1-alkyl-3-methylimidazolium tetracyanoborate $[C_n mim][B(CN)_4]$ (n = 2, 3, 4, 5, 6): the molecular volume, V_m, and the standard molar entropy, S^0. Using Kabo's method and Rebelo's method, the molar enthalpy of vaporization of $[C_2mim][B(CN)_4]$ is $\Delta_l^g H_m^0$ (298 K) and $\Delta_l^g H_m^0$ (680 K), respectively. In terms of the interstice model the predicted value

Table 3. Predicted Values of $\Delta_l^g H_m^0$ and p of $[C_2mim][B(CN)_4]$ at Various Temperatures

	$\Delta_l^g H_m^0/J\cdot mol^{-1}$							
T/K	650	600	550	500	450	400	350	300
$[C_2mim][B(CN)_4]$	65.3	76.3	90.1	103.9	117.6	131.4	145.2	158.9

	p/kPa							
T/K	650	600	550	500	450	400	350	300
$[C_2mim][B(CN)_4]$	58.7	30.8	19.4	2.00	$8.61\cdot10^{-2}$	$1.07\cdot10^{-3}$	$2.09\cdot10^{-6}$	$2.33\cdot10^{-10}$

of thermal expansion coefficients for $[C_2mim][B(CN)_4]$ is in good agreement with the experimental one within magnitude order.

Supporting Information Available:

Values of density, surface tension, and parachor of $[C_n mim][B(CN)_4]$ ($n = 1, 2, 3, 4, 5, 6$) in Tables A, B, and C, respectively. Plots of $\gamma V^{2/3}$ vs T in Figures A1−A3 and plots of vapor pressure and $\Delta_l^g H_m^0$ in Figures B1−B3. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review March 11, 2010. Accepted July 2, 2010. This project was supported by NSFC (20903053), the Education Bureau of Liaoning Province (LS2010069), P. R. China.

JE100228T