JOURNAL OF
CHEMICAL &
ENGINEERING
DATA

ARTICLE

pubs.acs.org/jced

Estimation of Physicochemical Properties of Ionic Liquids $[H_2N\text{-}C_2mim][BF_4]$ and $[H_2N\text{-}C_3mim][BF_4]$

Kiki A. Kurnia,*[†] M. I. Abdul Mutalib,[†] and Bambang Ariwahjoedi[‡]

[†]Department of Chemical Engineering and [‡]Department of Fundamental and Applied Science, Universiti Teknologi PETRONAS, Tronoh 31750, Malaysia

ABSTRACT: The density and surface tension of the ionic liquids 1-(2-aminoethyl)-3-methylimidazolium tetrafluoroborate, $[H_2N\text{-}C_2mim][BF_4]$, and 1-(3-aminopropyl)-3-methylimidazolium tetrafluoroborate, $[H_2N\text{-}C_3mim][BF_4]$, were measured from (293.15 to 343.15) K. The coefficient of thermal expansion, molecular volume, standard molar entropy, and lattice energy were calculated using experimental density data. Meanwhile, the surface entropy and enthalpy were calculated from surface tension data. The critical temperature of the ionic liquids was estimated using the Guggenheim and Eötvos equations. The values were then used to estimate the boiling temperature of the ionic liquids according to methods of Rebelo et al. The molar enthalpy vaporization, $\Delta_l^g H_m^0$, of the ionic liquid at 298.15 K was estimated using the methods of Kabo et al. According to the interstice model, the thermal expansion coefficient of the ionic liquids, α, was calculated, and the result was in very good agreement with the experimental value.

■ INTRODUCTION

Ionic liquids are liquids at ambient or even far below ambient temperature. These are comprised entirely of ions and are receiving an upsurge of interest in multidisciplinary areas for their unique physicochemical properties such as high thermal stability, negligible vapor pressure, relatively high ionic conductivity, and good electrochemical stability.[1] Recently, work has focused on the preparation and application of functionalized ionic liquids with special tasks.[2−9] The application of the ionic liquids with an amino functional group as a medium to absorb CO_2 from natural gas was reported in the literature.[4] However, the properties of these functionalized ionic liquids were not investigated in detail, which may restrict their application. To expand our knowledge of the ionic liquid chemistry,[10−21] we have synthesized ionic liquids with an amino functional group, namely, 1-(2-aminoethyl)-3-methylimidazolium tetrafluoroborate, $[H_2N\text{-}C_2mim][BF_4]$, and 1-(3-aminopropyl)-3-methylimidazolium tetrafluoroborate, $[H_2N\text{-}C_3mim][BF_4]$, and measured their density and surface tension in the temperature range of (293.15 to 343.15) K. The coefficient of thermal expansion, molecular volume, standard entropy,[22] and lattice energy[22] were calculated using experimental density data. Meanwhile, the surface entropy and enthalpy were calculated from surface tension data. The critical temperature of the ionic liquids was estimated using the Guggenheim[23] and Eötvos[24] equations. The values were then used to estimate the boiling temperature of the ionic liquids according to methods of Rebelo et al.[25] The molar enthalpy vaporization, $\Delta_l^g H_m^0$, of the ionic liquid at 298.15 K was estimated using the methods of Kabo et al.[26] The coefficient of thermal expansion, α, was calculated according to the interstice model, and the result was compared with the experimental value.

■ EXPERIMENTAL SECTION

Chemicals. The purity of the chemicals is reported in mass fraction as follows. The 1-methylimidazole ($\geq$ 0.99) was purchased from Merck. The 2-bromoethylamine hydrobromide (0.99), 3-bromopropylamine hydrobromide (0.98), and potassium tetrafluoroborate (0.96) were purchased from Aldrich. All chemicals were used without further purification.

Preparation of the Ionic Liquids. The ionic liquids were synthesized according to the standard methods developed and reported in the literature.[4,9] The $[H_2N\text{-}C_nmim][BF_4]$ was prepared through an anion exchange reaction between $[H_2N\text{-}C_nmim][Br]$ and KBF_4. For the preparation of $[H_2N\text{-}C_2mim][Br]$, 1-imidazole was refluxed with slightly excess 2-bromoethylamine hydrobromide in acetonitrile at 323.15 K for 72 h under nitrogen atmosphere. The product was then recrystallized using ethyl acetate as solvent and dried under reduced pressure at 343.15 K and finally in a vacuum oven for 24 h to ensure complete removal of the solvent. Similar procedures were adopted for the preparation of $[H_2N\text{-}C_3mim][Br]$. To prepare $[H_2N\text{-}C_nmim][BF^4]$, $[H_2N\text{-}C_nmim][Br]$ was mixed with KBF_4 in methanol and stirred at room temperature for 24 h. The product was then separated from the methanol phase and washed several times with cold deionized water until the washed water is free from bromide. The product was then dried in vacuum oven at 323.15 K for 3 days to ensure possible complete removal of water. The synthesized ionic liquids were kept in sealed bottle with PTFE septum.

The purity of the synthesized ionic liquids was determined using nuclear magnetic resonance (NMR) spectroscopy and elemental analysis. In NMR, (5 to 10) mg of sample was dissolved ~0.7 cm^3 of deuterated methanol solvent (MeOD). The ^{1}H NMR spectra was recorded at room temperature on JEOL JNM-ECA400. The 1H chemical shifts (δ) are reported in parts per million (ppm) references with tetramethyl silane (TMS) as an internal standard. Multiplicities are abbreviated as s, singlet; d, doublet; t, triplet; and m, multiplet. Elemental analysis to

Received: January 20, 2011
Accepted: March 28, 2011
Published: April 04, 2011

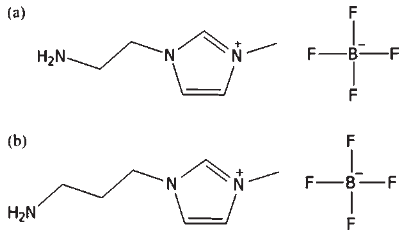

Figure 1. Structure of the studied ionic liquids: (a) 1-(2-aminoethyl)-3-methylimidazolium tetrafluoroborate, [H_2N-C_2mim][BF_4]; and (b) 1-(3-aminopropyl)-3-methylimidazolium tetrafluoroborate, [H_2N-C_3mim][BF_4].

determine the individual percentage of elements in the products was measured using CHNS-932 (LECO Instruments) elemental analyzer. The instrument was calibrated using standard calibration sample with known chemical composition provided by supplier before each measurement. A sample size of ± 2 mg was used for each measurement and the analysis for each sample was done at least three times and the average values were reported.

The bromide content was determined by ion chromatography (Metrohm model 761 Compact IC) Metrosep A Supp 5−150 (6.1006.520) analytical column (150 mm × 4.0 mm and a Metrosep A Supp 4/5 guard column (4.0 mm × 5 mm). The injection volume was 0.020 cm^3. A mixture of (3.2 mM Na_2CO_3 + 1.0 mM $NaHCO_3$) was used as eluent, and the regenerating solution was 1.0 M H_2SO_4. Each sample was prepared by dissolving 0.5 cm^3 of the ionic liquids in 10 cm^3 of acetonitrile before being diluted to 50 cm^3 with deionized water. The results were analyzed using Metrodata IC Net 2.3 software. The water content of the ionic liquids was determined using coulometric Karl Fischer autotitrator, Mettler Toledo DL39 with Combi-Coulomat fritless Karl Fischer reagent (Merck).

The NMR, elemental analysis, water, and bromide content of the ionic liquids are as follows: [H_2N-C_2mim][BF_4]: ^{1}H NMR (400 MHz MeOD): δ 9.12 [(s, 1H ring, (im)], 7.45 [d, 1H, ring H], 7.19 [d, 1H, ring H], 3.72 (s, 3H, H_3C-N_{ring}), 3.41 (t, 2H, H_2C-N_{ring}), 2.77 (m, 2H, H_2C-N_{amine}), 2.07 (t, 2H, H−N_{amine}). Analysis % found (% calculated): C, 33.86 (33.84); H, 5.66 (5.68); N, 19.72 (19.73); water $218 \cdot 10^{-6}$, bromide $74 \cdot 10^{-6}$. [H_2N-C_3mim][BF_4]: ^{1}H NMR (400 MHz MeOD): δ 9.12 [(s, 1H ring, (im)], 7.44 [d, 1H, ring H], 7.19 [d, 1H, ring H], 3.71 (s, 3H, H_3C-N_{ring}), 3.62 (t, 2H, H_2C-N_{ring}), 2.96 (m, 2H, CH_2), 2.42 (m, 2H, H_2C-N_{amine}), 2.02 (t, 2H, H-N_{amine}). Analysis % found (% calculated): C, 37.05 (37.04); H, 6.20 (6.22); N, 18.50 (18.51); water 164 ppm, bromide 61 ppm. The structure of the synthesized ionic liquids is shown in Figure 1.

Measurement of Density. A digital vibrating glass U-tube densimeter (DMA 5000, Anton-Paar) was used to measure the density of the protic ionic liquids. The densimeter was calibrated frequently using Millipore quality water and dried air. The calibrated densimeter was validated by measuring the density of several ionic liquids for which the data have been established by our research group.[27−30] A built-in platinum resistance thermometer was used to determine temperature with an accuracy of ± 0.01 K. The density was measured by achieving thermal equilibrium at a slow mode with successive increments of 5 K within the temperature range (293.15 to 353.15) K. The accuracy of all density measurements was found to be better than ± 0.5 $kg \cdot m^{-3}$. All measurements for each sample were performed in triplicate, and the values are reported as the average. The uncertainty was found to be ± 0.3 $kg \cdot m^{-3}$, which is within the accuracy of the measurement.

Table 1. Experimental Values of Density, ρ, of the Ionic Liquids [H_2N-C_2mim][BF_4] and [H_2N-C_3mim][BF_4] from (293.15 to 353.15) K

T/K	$\rho/kg \cdot m^{-3}$	
	[H_2N-C_2mim][BF_4]	[H_2N-C_3mim][BF_4]
293.15	1427.12	1358.01
298.15	1422.31	1354.60
303.15	1418.96	1349.29
308.15	1413.23	1345.68
313.15	1409.18	1343.18
318.15	1404.69	1336.97
323.15	1401.78	1333.57
328.15	1395.42	1328.96
333.15	1391.77	1325.35
338.15	1388.54	1321.05
343.15	1384.79	1317.25
348.15	1380.94	1313.04
353.15	1375.11	1309.44

Table 2. Experimental Values of Surface Tension, γ, of the Ionic Liquids [H_2N-C_2mim][BF_4] and [H_2N-C_3mim][BF_4] from (293.15 to 353.15) K

T/K	$10^2\ \gamma/J \cdot m^{-2}$	
	[H_2N-C_2mim][BF_4]	[H_2N-C_3mim][BF_4]
293.15	5.38	4.72
298.15	5.35	4.71
303.15	5.32	4.64
308.15	5.24	4.62
313.15	5.20	4.61
318.15	5.15	4.54
323.15	5.13	4.52
328.15	5.08	4.48
333.15	5.03	4.46
338.15	5.02	4.41
343.15	4.98	4.38
348.15	4.94	4.34
353.15	4.88	4.31

Measurement of Surface Tension. The surface tensions of the studied ionic liquids were measured using the pendant drop method. From a syringe, a drop was generated, pending on the outlet of the cannula. The drop was photographed by a charge coupled device (CCD) camera (OCA 20, Dataphysics).The evaluation of the drop shape was carried out using commercially available software, SCA 22 from Data Physics. It adapts a theoretical drop profile according to the Young−Laplace equation which describes the curvature of a liquid drop surface. The readings were taken within the temperature range (293.15 to 323.15) K with the accuracy of ± 0.1 K. All of the measurements for each sample were performed five times, and the values are reported as an average. The uncertainty of the measurement was found to be ± 0.0002 $J \cdot m^{-2}$.

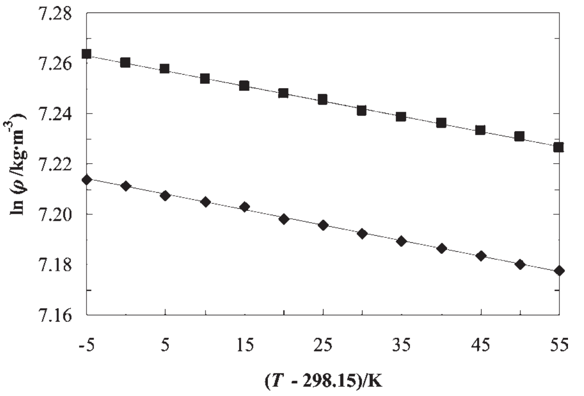

Figure 2. Plot of ln ρ vs temperature T of the ionic liquids: ■, $[H_2N\text{-}C_2mim][BF_4]$; ◆, $[H_2N\text{-}C_3mim][BF_4]$.

RESULTS AND DISCUSSION

The experimental values of density and surface tension of the studied ionic liquids $[H_2N\text{-}C_2mim][BF_4]$ and $[H_2N\text{-}C_3mim][BF_4]$ are listed in Tables 1 and 2, respectively. Both the density and surface tension of the ionic liquids decreased with increasing temperature. The density and surface tension of the ionic liquids $[H_2N\text{-}C_2mim][BF_4]$ at 298.15 K were reported in the literature, which were found to be 1420 $\mathrm{kg\cdot m^{-3}}$ and 53.42 $\mathrm{N\cdot m^{-1}}$, respectively. Our value for the density and surface tension of the ionic liquids $[H_2N\text{-}C_2mim][BF_4]$ at 298.15 K are 1423.3 $\mathrm{kg\cdot m^{-3}}$ and 53.48 $\mathrm{N\cdot m^{-1}}$, respectively, which is in good agreement with the literature.[9] As can be seen from Table 2, the surface tensions of these ionic liquid are higher than those corresponding ionic liquids with alkyl groups instead of amine group termination at the end. It seems that the presence of the amine functional group increases the surface tension due to hydrogen bonding.

Estimation of Volumetric Properties. The experimental values of ln ρ against $(T - 298.15\ \mathrm{K})$ were fitted by the method of least squares as the following equation:

$$\ln[\rho/(\mathrm{g\cdot cm^{-3}})] = c - \alpha(T/\mathrm{K} - 298.15) \qquad (1)$$

where c is an empirical constant and $\alpha = -(\partial \ln \rho/\partial(T - 298.15))_p$ is the coefficient of thermal expansion. Then $\alpha = [(6.07\cdot 10^{-4}) \pm (8.18\cdot 10^{-6})]$ and $[(6.14\cdot 10^{-4}) \pm (6.41\cdot 10^{-6})]$ $\mathrm{K^{-1}}$ obtained by the fitting of ln p versus $(T - 298.15)$ (see Figure 2) for $[H_2N\text{-}C_2mim][BF_4]$ and $[H_2N\text{-}C_3mim][BF_4]$, respectively. Although both $[H_2N\text{-}C_2mim][BF_4]$ and $[H_2N\text{-}C_3mim][BF_4]$ exhibit different values of density, they show very similar behavior with temperature. For this reason, the differences in the coefficient of thermal expansion are slight. The values are comparable to the coefficient of thermal expansion of the other ionic liquids.[10−21] It might be concluded that the thermal coefficient of imidazolium-based ionic liquids was slightly influenced by the functional group attached to the imidazolium ring.

From the experimental density, the molecular volumes, V_m, were calculated using the following equation:

$$V_m = \frac{M}{(N_A\rho)} \qquad (2)$$

where M is molecular weight of the ionic liquids and N_A is Avogadro's constant. The molecular volumes, V_m, of $[H_2N\text{-}C_2mim][BF_4]$ and $[H_2N\text{-}C_3mim][BF_4]$ at 298.15 K are listed in Table 3. Compared with $[H_2N\text{-}C_2mim][BF_4]$, $[H_2N\text{-}C_3mim][BF_4]$ shows a decrement of molecular volume of $\Delta V = 0.0296\ \mathrm{nm^3}$. This indicates that a mean contribution per methylene $(-CH_2-)$ to the molecular volume is 0.0296 $\mathrm{nm^3}$. The value is in good agreement with that of methylene contributions of 0.0280 $\mathrm{nm^3}$ from n-alcohols, 0.0272 $\mathrm{nm^3}$ from n-amines, 0.0267 $\mathrm{nm^3}$ from n-paraffins, and reported ionic liquids in the literature.[10−21]

Table 3. Estimated Values of Volume Properties of the Ionic Liquids $[H_2N\text{-}C_2mim][BF_4]$ and $[H_2N\text{-}C_3mim][BF_4]$ at 298.15 K

	ρ	V_m	S^0	U_{POT}
	$\mathrm{kg\cdot m^{-3}}$	$\mathrm{nm^3}$	$\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$	$\mathrm{kJ\cdot mol^{-1}}$
$[H_2N\text{-}C_2mim][BF_4]$	1422.31	0.2487	339.6	477
$[H_2N\text{-}C_3mim][BF_4]$	1354.60	0.2783	376.5	463

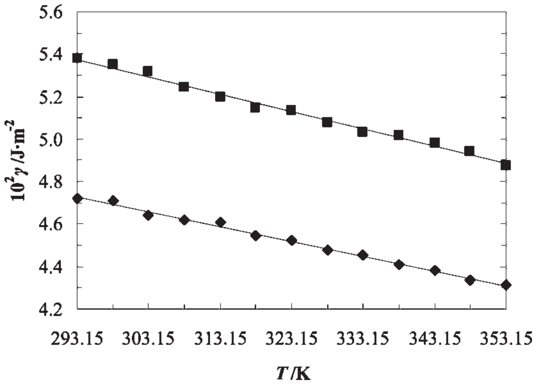

Figure 3. Plot of γ vs temperature (T) of the ionic liquids: ■, $[H_2N\text{-}C_2mim][BF_4]$; ◆, $[H_2N\text{-}C_3mim][BF_4]$.

According to Glasser's theory,[22] the standard molar entropy for ionic liquids, S^0, is given by

$$S^0(298.15)/\mathrm{J\cdot K\cdot mol^{-1}} = 1246.5(V_m/\mathrm{nm^3}) + 29.5 \qquad (3)$$

The value of standard molar entropy of $[H_2N\text{-}C_2mim][BF_4]$ and $[H_2N\text{-}C_3mim][BF_4]$ at 298.15 K are listed in Table 3. As can be seen in Table 3, the mean entropy contribution per methylene $(-CH_2-)$ group to the standard for $[H_2N\text{-}C_2mim][BF_4]$ and $[H_2N\text{-}C_3mim][BF_4]$ is 36.9 $\mathrm{J\cdot K\cdot mol^{-1}}$.

The lattice energy, U_{POT}, of the ionic liquids may be estimated in terms of Glasser's empirical equation:

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

The values of lattice energy of $[H_2N\text{-}C_2mim][BF_4]$ and $[H_2N\text{-}C_3mim][BF_4]$ at 298.15 K are listed in Table 3. The lattice energy for the studied ionic liquids is close to those of ionic liquid series reported in the literature.[10−21] It is also shown that the lattice energy of the studied ionic liquids is much less than those of fused salts, for example, U_{POT} is 613 $\mathrm{kJ\cdot mol^{-1}}$ for fused CsI, which has the lowest lattice energy among all of the alkali halides.[31] This fact shows that the interaction energy among ions in $[H_2N\text{-}C_2mim][BF_4]$ and $[H_2N\text{-}C_3mim][BF_4]$ is less than that in fused salts. The low lattice energy may explain why ionic liquids are liquids at room temperature.

Estimation of Surface Properties. The variation of the surface tension of the studied ionic liquids with temperature was linear as shown in Figure 3. The temperature dependence of the surface

Table 4. Surface Entropy, S_s, and Surface Enthalpy, E_s, of the Ionic Liquids $[H_2N\text{-}C_2mim][BF_4]$ and $[H_2N\text{-}C_3mim][BF_4]$

	$10^3 \cdot S_s$	E_s
	$mJ \cdot K^{-1} \cdot m^{-2}$	$mJ \cdot m^{-2}$
$[H_2N\text{-}C_2mim][BF_4]$	82.1 ± 2.3	77.8 ± 0.7
$[H_2N\text{-}C_3mim][BF_4]$	70.1 ± 1.6	67.8 ± 0.5

tension is presented as:

$$\gamma = a - bT \tag{5}$$

where γ is the surface tension, a and b are fitting coefficients, and T is the absolute temperature. From the experimental surface tension data, the entropy and enthalpy of surface formation per unit surface area can be calculated. The surface entropy values are obtained from the slopes $S_a = b = -(\partial\gamma/\partial T)_P$ of the temperature plots of the surface tension. The enthalpies of surface formation per unit area, E_a, likewise were obtained from the equation: $E_a = a = \gamma - (\partial\gamma/\partial T)_P$. The surface entropy and the surface enthalpy values for the studied ionic liquids in this work are shown in Table 4.

The studied ionic liquids present remarkably low surface entropies as compared to other organic compounds. These low surface entropies are in agreement with the reported result for the other ionic liquids in the literature.[32−36] The lower values of entropy of surface formation could indicate an enhancement of the degree of surface orientation. The surface enthalpy of fused $NaNO_3$ is 146 $mJ \cdot m^{-2}$, and the value for the ionic liquids studied is much lower and is close to an organic liquid, such as benzene at 67 $mJ \cdot m^{-2}$ and octane at 51.1 $mJ \cdot m^{-2}$.[37] This fact shows that interaction energy among ions in the ionic liquids is less than that in fused salts.

Estimation of the Critical Temperatures and Molar Enthalpies of Vaporization. The critical temperature, T_c, of ionic liquids is the most relevant thermophysical property since it can be used in many corresponding state correlations for equilibrium and transport properties of fluids.[20] However, reliable data are relatively hard to acquire due to the intrinsic nature of ionic liquids. Some estimation methods are usually used to predict the critical temperature value of ionic liquids. In this work, the prediction of the critical temperature was carried out using the Guggenheim[23] and Eötvos[24] empirical equations, which are described in the following equation:

$$\gamma = K\left(1 - \frac{T}{T_c}\right)^{11/9} \tag{6}$$

$$\gamma\left(\frac{M}{\rho}\right)^{2/3} = K(T_c - T) \tag{7}$$

respectively, where γ is the surface tension, T_c is critical temperature, K is an empirical constant, M is the molecular weight, and ρ is the density of the ionic liquid. The estimated critical temperature values of ionic liquids in the current work are shown in Table 5. The difference in the estimated critical temperatures equated between the Guggenheim and the Eötvos empirical equations is less than 8 %.

The prediction of T_c can also lead to an estimated value of the normal boiling temperature of an ionic liquid T_b. Rebelo et al.[25] put forward a method of estimating the normal boiling point temperature, T_b, in terms of critical temperature, T_c, obtained from the Guggenheim and Eötvos empirical equations. They thought that the relationship between T_b and T_c is $T_b \approx 0.6T_c$ for an ionic liquid. The estimation of boiling temperature for the studied ionic liquids is also presented in Table 5.

Table 5. Estimated Critical Temperatures, T_c, Normal Boiling Temperature, T_b, and Enthalpy of Vaporization, $\Delta_l^g H_m^0$, of the Ionic Liquids $[H_2N\text{-}C_2mim][BF_4]$ and $[H_2N\text{-}C_3mim][BF_4]$

ionic liquid	Guggenheim		Eötvos		$\Delta_l^g H_m^0$(298.15 K)
	T_c/K	T_b/K	T_c/K	T_b/K	$kJ \cdot mol^{-1}$
$[H_2N\text{-}C_2mim][BF_4]$	1087	652	1160	696	145.1
$[H_2N\text{-}C_3mim][BF_4]$	1111	667	1199	720	137.8

Ionic liquids have extremely low vapor pressures. The measurable vapor pressure in a temperature interval is large enough for a proper evaluation of thermodynamic parameters such as the enthalpy of vaporization. An expression for the estimation of the enthalpy of vaporization of ionic liquids has been proposed by Kabo et al.:[26]

$$\Delta_l^g H_m^0 = 0.01121(\gamma V^{2/3} N_A{}^{1/3}) + 2.4 \tag{8}$$

The molar enthalpy of vaporization for the ionic liquids $[H_2N\text{-}C_2mim][BF_4]$ and $[H_2N\text{-}C_3mim][BF_4]$ estimated using eq 8 was found to be (145.1 and 137.8) $kJ \cdot mol^{-1}$ (see Table 5), respectively.

Interstice Model for the Ionic Liquids. For a pure ionic liquid, a new theoretical model is put forward on the basis of the following assumptions: (1) Because of the large size and the asymmetric shape, the ions may not be closely packed, and lots of interstices between ions come into existence. (2) To calculate the volume easily, the interstice is considered as a bubble. (3) There are $2N_A$ interstices for a 1 mole 1−1 ionic liquid, where N_A is Avogadro's constant. (4) The interstice in ionic liquids can move about 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 based on classical statistical mechanics:[10−21]

$$v = 0.6791(k_b T/\gamma)^{3/2} \tag{9}$$

where k_b is Boltzmann's constant, T is the thermodynamic temperature, and γ is the surface tension of the ionic liquid. According to eq 9, the values of average volume of the interstices of the ionic liquid at 298.15 K may be obtained, $v = 14.49 \cdot 10^{-24}$ cm^3 for $[H_2N\text{-}C_2mim][BF_4]$ and $v = 17.54 \cdot 10^{-24}$ cm^3 for $[H_2N\text{-}C_3mim][BF_4]$, respectively. Then the molar volume of the interstice is $\Sigma v = 2N_A v = 17.45$ cm^3 for $[H_2N\text{-}C_2mim][BF_4]$ and 21.12 cm^3 for $[H_2N\text{-}C_3mim][BF_4]$. The volume fractions of interstice, $\Sigma v/V$, are about 11.7 % and 12.6 % for the ionic liquids $[H_2N\text{-}C_2mim][BF_4]$ and $[H_2N\text{-}C_3mim][BF_4]$, respectively. The values are close to those for a majority of materials, which exhibit ~(10 to 15) % volume expansion in the transformation from the solid to the liquid state. This result means that the interstice model is reasonable.

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

$$V = V_i + 2N_A v \tag{10}$$

Table 6. Parameters of Interstice Model for the Ionic Liquids $[H_2N\text{-}C_2mim][BF_4]$ and $[H_2N\text{-}C_3mim][BF_4]$ at 298.15 K

ionic liquid	$10^{-24}\cdot v/\mathrm{cm}^3$	$\Sigma v/\mathrm{cm}^3$	$\Sigma v/V$	$10^4\cdot\alpha(\mathrm{calc})/\mathrm{K}^{-1}$	$10^4\cdot\alpha(\mathrm{exp})/\mathrm{K}^{-1}$
$[H_2N\text{-}C_2mim][BF_4]$	14.49	17.45	11.7	5.86	6.07
$[H_2N\text{-}C_3mim][BF_4]$	17.54	21.12	12.6	6.34	6.14

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

$$\alpha = (1/V)(\partial V/\partial T)_p = 3N_A v/VT \qquad (11)$$

The values of α(calc) using eq 11 and of corresponding experimental values, α(exp), for the ionic liquids $[H_2N\text{-}C_2mim][BF_4]$ and $[H_2N\text{-}C_3mim][BF_4]$ are listed in Table 6. The magnitude order of the coefficient of thermal expansion α(calc) are in good agreement with α(exp). It means that the interstice model is reasonable and may be used to estimate the coefficient of thermal expansion of the ionic liquids.

CONCLUSIONS

In this work, the density and surface tension of the ionic liquids $[H_2N\text{-}C_2mim][BF_4]$ and $[H_2N\text{-}C_3mim][BF_4]$ at temperatures from (293.15 to 323.15) K were reported. Both density and surface tension decrease with increasing temperature. The coefficient of thermal expansion, molecular volume, standard entropy, and lattice energy were calculated using experimental density data. The surface entropy and enthalpy were calculated from surface tension data. The results showed the calculated data in comparison with the other ionic liquids reported in the literature. The critical temperature of the ionic liquids was estimated using the Guggenheim and Eötvos equations. The values were then used to estimate the boiling temperature of the ionic liquids according to methods of Rebelo et al. The molar enthalpy vaporization, $\Delta_l^g H_m^0$, of the ionic liquid at 298.15 K was estimated using the methods of Kabo et al. The coefficient of thermal expansion, α, was calculated according to the interstice model. It showed that the calculated values were in good agreement with the experimental ones. It suggested that the interstice model can be applied for the ionic liquid system.

AUTHOR INFORMATION

Corresponding Author

*Phone: +60146431260. Fax: +6053654090. E-mail: kiki_g00754@utp.edu.my, idiothiquetotal@yahoo.com.

REFERENCES

(1) Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*, 2nd ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Darmstadt, Federal Republic of Germany, 2009; Vol. 1.

(2) Nockemann, P.; Thijs, B.; Pittois, S.; Thoen, J.; Glorieux, C.; Van Hecke, K.; Van Meervelt, L.; Kirchner, B.; Binnemans, K. Task-Specific Ionic Liquid for Solubilizing Metal Oxides. *J. Phys. Chem. B* **2006**, *110*, 20978–20992.

(3) Egorov, V. M.; Djigailo, D. I.; Momotenko, D. S.; Chernyshov, D. V.; Torocheshnikova, I. I.; Smirnova, S. V.; Pletnev, I. V. Task-specific ionic liquid trioctylmethylammonium salicylate as extraction solvent for transition metal ions. *Talanta* **2010**, *80*, 1177–1182.

(4) Bates, E. D.; Mayton, R. D.; Ntai, I.; Davis, J. H. CO_2 Capture by a Task-Specific Ionic Liquid. *J. Am. Chem. Soc.* **2002**, *124*, 926–927.

(5) Gui, J.; Deng, Y.; Hu, Z.; Sun, Z. A novel task-specific ionic liquid for Beckmann rearrangement: a simple and effective way for product separation. *Tetrahedron Lett.* **2004**, *45*, 2681–2683.

(6) Xing, H.; Wang, T.; Zhou, Z.; Dai, Y. Novel Bronsted-Acidic Ionic Liquids for Esterifications. *Ind. Eng. Chem. Res.* **2005**, *44*, 4147–4150.

(7) Luo, H.; Dai, S.; Bonnesen, P. V.; Buchanan, A. C., III. Separation of fission products based on ionic liquids: Task-specific ionic liquids containing an aza-crown ether fragment. *J. Alloys Compd.* **2006**, *418*, 195–199.

(8) Sun, X.; Ji, Y.; Chen, J.; Ma, J. Solvent impregnated resin prepared using task-specific ionic liquids for rare earth separation. *J. Rare Earths* **2009**, *27*, 932–936.

(9) Cai, Y. Q.; Lu, F.; Peng, Y. Q.; Song, G. H. Preparation and characterization of amino or carboxyl-functionalized ionic liquids. *Chin. Chem. Lett.* **2007**, *18*, 21–23.

(10) Zang, S.-l.; Fang, D.-W.; LI, J.-x.; Zhang, Y.-Y.; Yue, S. Estimation of Physicochemical Properties of Ionic Liquid HPReO4 Using Surface Tension and Density. *J. Chem. Eng. Data* **2009**, *54*, 2498–2500.

(11) Tong, J.; Hong, M.; Guan, W.; Li, J.-B.; 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.

(12) Yang, J.-Z.; Zhang, Q.-G.; Xue, F. Studies on the properties of $EMIGaCl_4$. *J. Mol. Liq.* **2006**, *128*, 81–84.

(13) Tong, J.; Liu, Q.-S.; Guan, W.; Yang, J.-Z. Estimation of Physicochemical Properties of Ionic Liquid $C_6MIGaCl_4$ Using Surface Tension and Density. *J. Phys. Chem. B* **2007**, *111*, 3197–3200.

(14) Tong, J.; Liu, Q.-S.; Xu, W.-G.; Fang, D.-W.; Yang, J.-Z. Estimation of Physicochemical Properties of Ionic Liquids 1-Alkyl-3-methylimidazolium Chloroaluminate. *J. Phys. Chem. B* **2008**, *112*, 4381–4386.

(15) Sun, S.-G.; Wei, Y.; Fang, D.-W.; Zhang, Q.-G. Estimation of properties of the ionic liquid $BMIZn_3Cl_7$. *Fluid Phase Equilib.* **2008**, *273*, 27–30.

(16) Zang, S.-l.; Fang, D.-W.; Li, J.-x.; Zhang, Y.-Y.; Yue, S. The estimation of physico-chemical properties of ionic liquid *N*-propylpyridine rheniumate. *Fluid Phase Equilib.* **2009**, *283*, 93–96.

(17) Zang, S.-L.; Zhang, Q.-G.; Huang, M.; Wang, B.; Yang, J.-Z. Studies on the properties of ionic liquid $EMIInCl_4$. *Fluid Phase Equilib.* **2005**, *230*, 192–196.

(18) Zhang, Q.-G.; Yang, J.-Z.; Lu, X.-M.; Gui, J.-S.; Huang, M. Studies on an ionic liquid based on FeCl3 and its properties. *Fluid Phase Equilib.* **2004**, *226*, 207–211.

(19) Liu, Q.-S.; Tong, J.; Tan, Z.-C.; Welz-Biermann, U.; Yang, J.-Z. Density and Surface Tension of Ionic Liquid $[C_2mim][PF_3(CF_2CF_3)_3]$ and Prediction of Properties $[C_nmim][PF^3(CF_2CF_3)_3]$ ($n = 1, 3, 4, 5, 6$). *J. Chem. Eng. Data* **2010**, *55*, 2586–2589.

(20) Wang, J.-y.; Zhao, F.-Y.; Liu, R.-j.; Hu, Y.-q. Thermophysical properties of 1-methyl-3-methylimidazolium dimethylphosphate and 1-ethyl-3-methylimidazolium diethylphosphate. *J. Chem. Thermodyn.* **2010**, *43*, 47–50.

(21) 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.

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

(23) Guggenheim, E. A. The Principle of Corresponding States. *J. Phys. Chem.* **1945**, *13*, 253–261.

(24) Shereshefsky, J. L. Surface Tension of Saturated Vapors and the Equation of Eotvos. *J. Phys. Chem.* **1931**, *35*, 1712–1720.

(25) Rebelo, L. P. N.; Canongia Lopes, J. N.; 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*, 6040–6043.

(26) 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*, 7303–7306.

(27) Muhammad, A.; Abdul Mutalib, M. I.; Wilfred, C. D.; Murugesan, T.; Shafeeq, A. Thermophysical properties of 1-hexyl-3-methyl imidazolium based ionic liquids with tetrafluoroborate, hexafluorophosphate and bis(trifluoromethylsulfonyl)imide anions. *J. Chem. Thermodyn.* **2008**, *40*, 1433–1438.

(28) Yunus, N. M.; Abdul Mutalib, M. I.; Man, Z.; Bustam, M. A.; Murugesan, T. Thermophysical properties of 1-alkylpyridinum bis(trifluoromethylsulfonyl)imide ionic liquids. *J. Chem. Thermodyn.* **2010**, *42*, 491–495.

(29) Ziyada, A. K.; Wilfred, C. D.; Bustam, M. A.; Man, Z.; Murugesan, T. Thermophysical Properties of 1-Propyronitrile-3-alkylimidazolium Bromide Ionic Liquids at Temperatures from (293.15 to 353.15) K. *J. Chem. Eng. Data* **2010**, *55*, 3886–3890.

(30) Kurnia, K. A.; Wilfred, C. D.; Murugesan, T. Thermophysical properties of hydroxyl ammonium ionic liquids. *J. Chem. Thermodyn.* **2009**, *41*, 517–521.

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

(32) Tong, J.; Liu, Q.-S.; Zhang, P.; Yang, J.-Z. Surface Tension and Density of 1-Methyl-3-hexylimidazolium Chloroindium. *J. Chem. Eng. Data* **2007**, *52*, 1497–1500.

(33) Wandschneider, A.; Lehmann, J. K.; Heintz, A. Surface Tension and Density of Pure Ionic Liquids and Some Binary Mixtures with 1-Propanol and 1-Butanol. *J. Chem. Eng. Data* **2008**, *53*, 596–599.

(34) Klomfar, J.; Soukov, M.; Ptek, J. Surface Tension Measurements for Four 1-Alkyl-3-methylimidazolium-Based Ionic Liquids with Hexafluorophosphate Anion. *J. Chem. Eng. Data* **2009**, *54*, 1389–1394.

(35) Klomfar, J.; Soucková, M.; Pátek, J. Surface tension measurements with validated accuracy for four 1-alkyl-3-methylimidazolium based ionic liquids. *J. Chem. Thermodyn.* **2010**, *42*, 323–329.

(36) Carvalho, P. J.; Freire, M. G.; Marrucho, I. M.; Queimada, A. J.; Coutinho, J. A. P. Surface Tensions for the 1-Alkyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide Ionic Liquids. *J. Chem. Eng. Data* **2008**, *53*, 1346–1350.

(37) Adamson, A. W. *Physical chemistry of surfaces*, 3rd ed.; John-Wiley: New York, 1986.