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Vaporization enthalpy and the molar surface Gibbs free energy for ionic liquids [C$_n$Dmim][NTF$_2$] ($n = 2, 4$)

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A B S T R A C T

Using thermogravimetrical analysis, the enthalpies of vaporization at an average temperature, $\Delta^{g}_{l}H^{o}_{m}(T_{av})$, for ionic liquids (ILs) {1-alkyl-2,3-dimethyimidazolium-N,N-bis(trifluoromethyl sulfonyl)imide} [C$_n$Dmim][NTF$_2$] ($n = 2, 4$) were firstly determined and transformed into $\Delta^{g}_{l}H^{o}_{m}(298\ \text{K})$ based on the $\Delta^{g}_{l}C^{o}_{p\,m}$. Then, on the basis of Tong's vaporization enthalpy model, a new thermodynamic quantity-molar surface Gibbs free energy, g was put forward and the values of g were calculated for [C$_n$Dmim][NTF$_2$] ($n = 2, 4$). In terms of the molar surface Gibbs free energy, a new Eötvös empirical equation was derived so that the new Eötvös parameters have clear physical meanings: its slope is molar surface entropy, s, and the intercept is the molar surface enthalpy, h, the value of which is not change with temperature. Moreover, the values of molar surface Gibbs free energy can be estimated using the b and T_c easily, according to the new Eötvös equation and $g = N^{1/3}\gamma V^{2/3}$, the surface tensions for [C$_n$Dmim][NTF$_2$] ($n = 2, 4$) and other ILs could be predicted, and the predicted values were in good agreement with the experimental values.

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1. Introduction

Ionic liquids (ILs) are versatile materials with unique properties, and their practical applications have expanded rapidly, such as electrolytes [1], engineering fluids [2], pre-treatment agents for wood grinding/biomass extraction [3] and as solvents and catalysts for synthetic chemical reactions [4].

As one of the most attractive features is the negligible vapor pressure at room temperature. However, many applications of ILs are carried out at elevated temperature so that the vapor pressure of some ILs can't be ignored, even though it remains small (approximately a few Pa). Hence, the knowledge of vapor pressure and enthalpy of vaporization is indispensable for theoretical research and practical application of ILs [5,6]. But experimental determining the vaporization enthalpy are challenging task, because with the exception of the Knudsen method [7,8], traditional experimental techniques for vaporization enthalpy measurement have not been applicable for ILs. With the deepening of the research, some new direct experimental methods have stimulated to be quickly developed, such as transpiration [9,10], temperature-programmed desorption and line-of-sight mass spectrometry (LOSMS) [11,12], thermogravimetry [13–15], high-temperature UV spectroscopic techniques [16].

The end of the last century and the beginning of this century, Alexander et al. [17] and Price et al. [18,19] had applied isothermogravimetrical analysis to the research for sublimation enthalpy of some solids, Dai et al. [13] was the first to extend this method to ILs systems. Notably, the method has some crucial advantages: small amounts of sample, short experimental time, the commercial availability of the experimental setup, and the simplicity of measuring technique. As a result, isothermogravimetrical analysis has attracted more and more attention from scientific communities [14,15,20]. Lately, Verevkin et al. [15] made great efforts to improve experimental conditions and recommended the optimal ones according to which the vaporization enthalpy of the ILs can be measured with a reasonable accuracy ±3 kJ·mol^{-1}. Tong et al. [15,20] measured the vaporization enthalpy of ILs [C$_n$mim][Pro] ($n = 2, 3, 4, 5, 6$) and put forward a new model on vaporization enthalpy for ILs.

In recent years, 1-alkyl-2,3-dimethylimidazolium ionic liquids due to unique structures have been employed as model RTILs in some structural analysis [21], and most studies have focused on investigating these kinds of RTILs [22–24]. Hence, in order to study these ILs on the thermodynamics and also continue our previous investigation [25–27], this paper reports the following: (1) The preparation of ionic liquids {1-alkyl-2,3-dimethyimidazolium-N,N

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-bis(trifluoromethyl sulfonyl)imide} [C_nDmim][NTF_2] ($n = 2, 4$) using the neutralization method and confirmation by ^{1}H NMR spectroscopy, ^{13}C NMR and differential scanning calorimetry (DSC); (2) Determination the enthalpy of vaporization for ionic liquids [C_nDmim][NTF_2] ($n = 2, 4$) at the average temperature by using isothermogravimetrical analysis; (3) On the basis of Tong's vaporization enthalpy model, a new concept-molar surface Gibbs free energy was put forward; (4) The traditional Eötvös empirical equation was improved and the new Eötvös parameters have clear physical meanings: its slope is molar surface entropy, *s*, and the intercept is the molar surface enthalpy, *h*, the value of which is not change with temperature; (5) According to the new Eötvös equation, and $g = N^{1/3}\gamma V^{2/3}$, the surface tensions for [C_nDmim][NTF_2] ($n = 2, 4$) and other ILs could be predicted, and the predicted values were in good agreement with the experimental values.

2. Experimental section

2.1. Chemicals

Deionized water with a conductance of $(0.8–1.2) \times 10^{-4}$ S·m^{-1} was used in experiments. 1,2-Dimethyimidazolium (AR-grade reagent) was purchased from ACROS and vacuum-distilled prior to use. Lithium bis(trifluoromethanesulfonyl)imide [$LiN(SO_2CF_3)_2$], 1-bromoethane and 1-bromobutane (AR-grade reagent) were purchased from Shanghai Chemical Reagent Co. Ltd. The source and purities of the chemicals were listed in Table S1.

2.2. Preparation of the ILs [C_nDmim][NTF_2] ($n = 2, 4$)

The ILs [C_nDmim][NTF_2] ($n = 2, 4$) were prepared and purified in our laboratory using established method, and the specific procedure has been reported elsewhere [28]. Using ion selective electrode, halogen content (Br^-) in each of two ionic liquids [C_nDmim][NTF_2] ($n = 2, 4$) was less than 210 ppm and the water contents in two samples determined by a Karl Fischer moisture titrator (ZSD-2 type) were 210 ppm and 230 ppm, hence, the purities could be estimated better than 0.990 in mass and were listed in Table S1. Structures of two ILs were confirmed by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy (see Figs. S1–S4 in Supporting Information).

2.3. The thermogravimetric analysis of the ILs [C_nDmim][NTF_2] ($n = 2, 4$)

Thermogravimetric analysis (TGA) was carried out on a Netzsch Instrument TG209F1 apparatus which is calibrated for temperature according to the method of Stewart [29] using indium, tin, bismuth and lead. The accuracy of the temperature measurements was adjusted to be better than ±0.2 K, the magnitude and linearity of the balance response were checked with standard milligram masses.

Firstly, in order to determine the range of constant temperature, temperature-ramp TGA experiments were performed on *ca* 10 mg of [C_nDmim][NTF_2] ($n = 2, 4$), using a heating rate of 10 K·min^{-1} in nitrogen flow of 120 mL·min^{-1}, and the decomposition temperatures (T_d) were determined through the TG curves derivative, i.e., DTG curves (see Figs. S5 and S6): $T_d = 670.25$ K for [C_2Dmim][NTF_2], and $T_d = 671.95$ K for [C_4Dmim][NTF_2], respectively, in addition, combined with Kiefer's [21]: $T_d = 639.15$ K for [C_2Dmim][NTF_2], and $T_d = 632.15$ K for [C_4Dmim][NTF_2], the isotherm temperature range from 573.15 K to 618.15 K was obtained. Then, the isothermal TGA curve for the ILs was measured according to optimal conditions recommended by Verevkin et al. [15] and our preliminary work [30]: (1) The sample weights used for isothermal gravimetric analysis were in *ca* 55 mg range; (2) Nitrogen flow of 120 mL·min^{-1} was used as the inert purge gas rate; (3) A heating ramp of 10 K·min^{-1} was used followed by a 3 h static hold period at 563.15 K, allowing for the slow removal of volatile impurities such as traces of water prior to a stepwise temperature programmed run; (4) In the experiments, the same platinum crucible was used for each sample, in order to maintain a uniform cross-sectional area.

According to the isothermal gravimetric experiments, plotting $(m_0 - m)$ *vs.* $(t - t_0)$ (*m* is sample mass, *t* is time, subscript 0 means initial state) for the ILs at each isotherm in the temperature range from 573.15 K to 618.15 K, two good straight lines were obtained (see Figs. 1 and 2). Both straight lines are typical time-course isothermal TGA mass loss curves and the values of their slopes of the ILs, $-dm/dt$, are listed in Table S2. From Figs. 1 and 2, the isothermal TGA mass loss curves are all rigorously linear with correlation coefficient square exceeding 0.999. The high linearity associated with the isothermal TGA curves reveals zero-order mass loss kinetics, providing strong evidence that the observed decrease in mass over time at constant temperature results from vaporization of the IL and does not originate from evolution of thermal degradation product or from impurity [31]. And in order to confirm the absence of decomposition of ILs in the experimental conditions, the residual ILs in the crucible were analyzed by ^{1}H NMR spectroscopy (see Figs. S7 and S8 in Supporting Information) and ^{13}C NMR spectroscopy (see Figs. S9 and S10 in Supporting Information), and it turns out that no decomposition of ILs in the experimental conditions was detected.

3. Discussion and results

3.1. The vaporization enthalpies of the ILs [C_nDmim][NTF_2] ($n = 2, 4$)

Alexander et al. [17] and Price et al. [18,19] had conducted extensive research to establish the measurement method of vaporization enthalpy based on TGA methodology. They pointed that

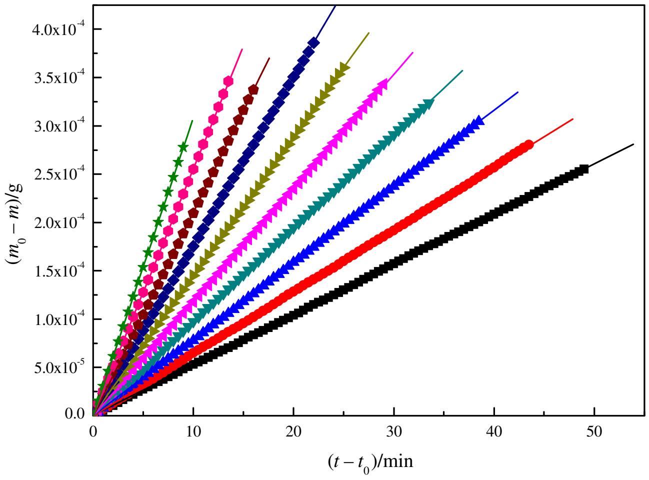

Fig. 1. Plot of $(m_0 - m)$ *vs.* $(t - t_0)$ for [C_2Dmim][NTF_2] at the temperature rang from 573.15 K to 618.15 K. ■ 573.15 K: $m_0 - m = 5.697 \times 10^{-7} + 4.9701 \times 10^{-6}(t - t_0)$, $r^2 = 0.9999$, $s = 4.90 \times 10^{-7}$; ● 578.15 K: $m_0 - m = -1.899 \times 10^{-7} + 6.1341 \times 10^{-6}(t - t_0)$, $r^2 = 0.9999$, $s = 5.35 \times 10^{-7}$; ▲ 583.15 K: $m_0 - m = 1.499 \times 10^{-7} + 7.5519 \times 10^{-6}(t - t_0)$, $r^2 = 0.9999$, $s = 5.46 \times 10^{-7}$; ▼ 588.15 K: $m_0 - m = 2.857 \times 10^{-7} + 9.2509 \times 10^{-6}(t - t_0)$, $r^2 = 0.9999$, $s = 4.23 \times 10^{-7}$; ◀ 593.15 K: $m_0 - m = -7.239 \times 10^{-8} + 1.1520 \times 10^{-5}(t - t_0)$, $r^2 = 0.9999$, $s = 5.27 \times 10^{-7}$; ▶ 598.15 K: $m_0 - m = 7.596 \times 10^{-7} + 1.5071 \times 10^{-5}(t - t_0)$, $r^2 = 0.9999$, $s = 4.67 \times 10^{-7}$; ◆ 603.15 K: $m_0 - m = 3.634 \times 10^{-7} + 1.8324 \times 10^{-5}(t - t_0)$, $r^2 = 1$, $s = 3.19 \times 10^{-7}$; ⬟ 608.15 K: $m_0 - m = -4.303 \times 10^{-7} + 2.2028 \times 10^{-5}(t - t_0)$, $r^2 = 0.9999$, $s = 6.90 \times 10^{-7}$; ⬢ 613.15 K: $m_0 - m = 7.965 \times 10^{-8} + 2.6717 \times 10^{-5}(t - t_0)$, $r^2 = 0.9999$, $s = 4.69 \times 10^{-7}$; ★ 618.15 K: $m_0 - m = -3.092 \times 10^{-7} + 3.2283 \times 10^{-5}(t - t_0)$, $r^2 = 1$, $s = 2.48 \times 10^{-7}$.

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