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Measurement and estimation of the vaporization enthalpy for amino acid ionic liquids [C$_n$mim][Thr]($n = 2, 4$)

Jing Tong *, Lu Liu, Hui Li, Wei Guan, Xia Chen *

College of Chemistry, Liaoning University, Shenyang 110036, People's Republic of China

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ABSTRACT

The molar enthalpy of vaporization, $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(T_{\mathrm{av}})$, at the average temperature, $T_{\mathrm{av}} = 438.15$ K, for the ionic liquids (ILs), 1-alkyl-3-methylimidazolium threonine salt [C$_n$mim][Thr]($n = 2, 4$) were determined by using the isothermogravimetrical analysis. With the use of Verevkin's method, the difference of heat capacities between the gaseous phase and the liquid phase, $\Delta_{\mathrm{l}}^{\mathrm{g}}C_{\mathrm{p}}^{\mathrm{o}}$, for [C$_n$mim][Thr]($n = 2, 4$) were calculated based on the statistical thermodynamics. Therefore, with the use of $\Delta_{\mathrm{l}}^{\mathrm{g}}C_{\mathrm{p}}^{\mathrm{o}}$, the values of $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(T_{\mathrm{av}})$ were transformed into $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(298)$. According to the new scale of polarity for ILs, the order of the polarity of [C$_n$mim][Thr]($n = 2, 4$) was predicted, that is, the polarity reduces with the increasing of methylene. In addition, a new model about the enthalpy of vaporization for aprotic ILs was proposed and used to predict the vaporization enthalpy for [C$_n$mim][Thr]($n = 3, 5, 6$), but these predicted values also need to be verified in our future experiments.

1. Introduction

Since Wilkes and Zaworotko [1] prepared a series of novel air and water stable ionic liquids (ILs), many unique features of the new generation of IL have been developed into a rich [2–5], amino acid ionic liquid (AAIL) is one of them [6–10]. AAIL has become one of the most rapidly growing new research areas since they are derived from natural ions and are heralded a new "natural ILs" or "bio-ILs" and can be expected to find application in all of the biological, medical, and pharmaceutical sciences.

One of the most attractive features of ILs is their negligible vapor pressure at room temperature. However, when ILs are applied at elevated temperatures, their vapor pressure is to approximate a few Pa and no longer negligible, even high vacuum treatment can be implemented [11,12]. These results suggest enticing possibilities for gas-phase purification, high-temperature crystallization, and novel synthetic routes. This intriguing potential has stimulated a strong interest in understanding the nature of the volatilization process for ILs and for theoretical research and practical application of ILs, knowledge of the molar vaporization enthalpies, $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$, is indispensable. However, experimental determination of the vaporization enthalpy of ILs is a challenging task because with the exception of the Knudsen method [13,14], traditional experimental techniques for vapor pressure measurement have not been applicable for ILs. This has stimulated the development of new direct experimental methods, and thermogravimetry (TGA) [15–17] is one of them. Among all new methods, the TGA method has some crucial advantages [15]: small amounts of sample, short experimental times, and the commercial availability of the experimental setup, as well as the simplicity of measuring technique. Using a commercially available TGA, Verevkin et al. [17] carefully made experimental study and recommended the optimal experimental conditions according to which the molar vaporization enthalpy of the IL can be measured with a reasonable accuracy ± 3 kJ·mol^{-1}.

To the best of our knowledge, there is no study on the molar enthalpy of vaporization of AAILs. As a continuation of our previous investigation [18,19], this paper reports the followings: (1) Ionic liquids 1-alkyl-3-methylimidazolium threonine salt [C$_n$mim][Thr] ($n = 2, 4$) were prepared by the neutralization method; (2) The molar vaporization enthalpies for the ILs were determined using the thermogravimetric approach; (3) A new scale of polarity, δ_{μ} (δ_{μ}^{2} is the contribution of dipole moment to the cohesive energy), for the ILs was proposed, and the value of δ_{μ} can be estimated; (4) A new theory model on the relationship between the surface tension and the molar enthalpy of vaporization for aprotic ILs is put forward and used to predict the molar vaporization enthalpy for the ILs.

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* Corresponding authors.
E-mail addresses: tongjinglnu@sina.com (J. Tong), chenxia@lnu.edu.cn (X. Chen).

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2. Experimental section

2.1. Chemicals

DL-threonine was recrystallized twice and dried in the pressure of (1 with standard uncertainty ± 0.1) kPa. *N*-methylimidazole, 1-bromoethane and 1-bromobutane were distilled in vacuum prior to use. Ethyl acetate and acetonitrile were distilled and then stored over molecular sieves in tightly sealed glass bottles. Anion-exchange resin (type 717) was activated by the regular method before use. The source and purity of the materials are listed in Table S1.

2.2. Preparation of the ILs

The ILs, [$C_n$mim][Thr](n = 2, 4), were prepared by a neutralization method according to Fukumoto et al. [8]. The structures of the resulting materials and their condensate and residue (T = 463.15 K) were confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy (see Section A and B in the Supporting Information). Element analysis (Flash EA1112 type produced by THERMO) showed that the purities of the synthesized ILs are more than 0.99 (see Section C in the Supporting Information). Thermogravimetry analysis (METTLER TOLEDO Instruments TGA/SDTA851e) showed that the initial decomposition temperature of the synthesized ILs is about 225 °C that is 498 K (see Section D in the Supporting Information). The mass fractions of water in the ILs determined by Karl Fischer moisture titrator ZSD-2 were (0.00620, 0.00640 with standard uncertainty ± 0.0001), respectively.

2.3. Isothermal gravimetric analysis for the ILs

In this work a METTLER TOLEDO Instruments TGA/SDTA851e was used and was calibrated for temperature according to Stewart's method [20] 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 was checked with standard milligram masses. Firstly, in order to determine the range of temperature, a conventional TGA curve with about 60 mg sample weight for [$C_n$mim][Thr](n = 2, 4) were measured in argon at a flow rate of 100 mL·min^{-1}. The heating rate is 10 K·min^{-1} by using METTLER TOLEDO Instruments TGA/SDTA851e (Fig. D.1 and D.2 in the Supporting Information). It can be seen that the initial decomposition temperature of the synthesized ILs is about 225 °C, that is, 498 K. In addition, the structures of the condensate and residue of the studied ionic liquids were confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy in order to ensure the ILs have not decomposed but only evaporated at the highest measured temperature (T = 463.15 K). Then, the isothermal gravimetric analysis curve for the ILs was measured according to optimal conditions recommended by Verevkin et al. [17] and our preliminary work [19], some suitable experimental parameters are selected: (1) The mass of samples, m, used for isothermal gravimetric analysis were about 50 mg; (2) 10 K·min^{-1} heating ramp was used and it stayed for 1 h at 393 K in order to remove the volatile impurities, such as traces of water, and the mass fractions of water in the ILs after 1 h at 393 K determined by SFY-2000 type micro moisture meter were both 0.000010 with standard uncertainty ±0.00001; (3) According to the stability of the ILs, the temperature and the length of the experimental time, t, at each isotherm was taken: 35 min at 423 K, 30 min at 433 K, 25 min at 443 K, 20 min at 453 K, 10 min at 463 K; (4) The purge gas is argon which is 100 ml·min^{-1}; (5) The same platinum crucible was used for each sample, in order to maintain an uniform cross-sectional area; (6) The instrument is METTLER TOLEDO Instruments TGA/SDTA851e.

According to the isothermal gravimetric experiments, plotting (m_0–m)/kg *vs* (t–t_0)/s (m is the sample mass, t is the time, subscript 0 means the initial state) for the ILs at each isotherm in the temperature range from 413.15 K to 463.15 K, a series of good straight lines were obtained (see Fig. 1). These 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 1. As can be seen from Fig. 1, the isothermal TGA mass loss curves are all rigorously linear with correlation coefficient square exceeding 0.996. The high

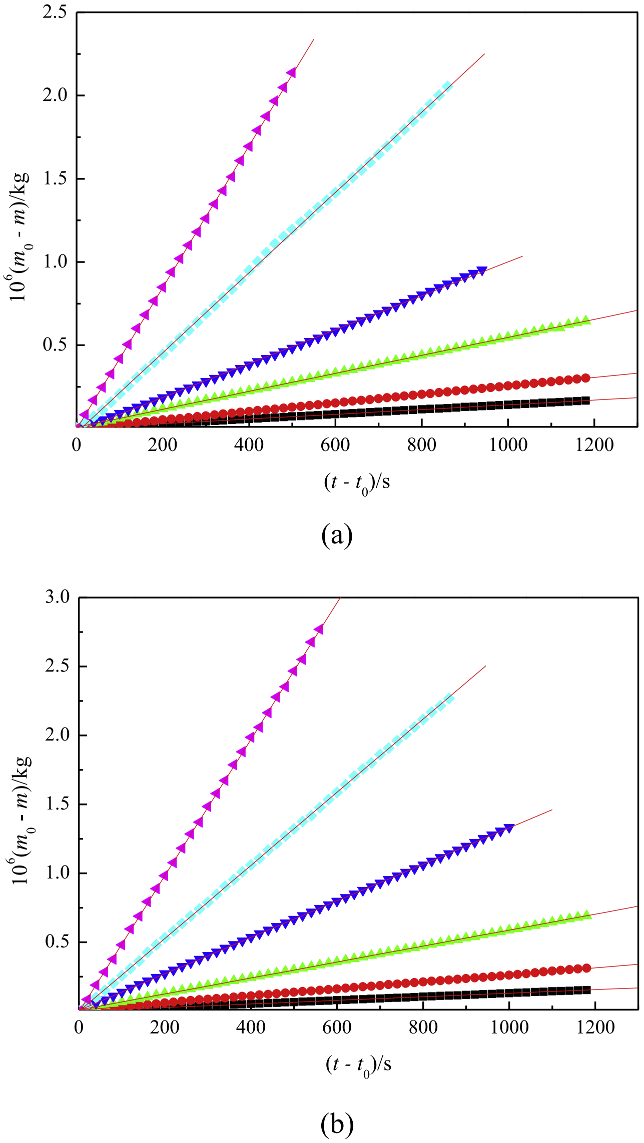

Fig. 1. Plot of (m_0–m)/kg vs (t–t_0)/s. (a) [C_2mim][Thr] x: (t–t_0)/s; y: 10^6(m_0–m)/kg. ■ 413.15 K: $y = 3.56 \times 10^{-11} + 1.42 \times 10^{-10}x$, $r = 0.99993$, $s = 5.87 \times 10^{-10}$. ● 423.15 K: $y = -5.93 \times 10^{-10} + 2.56 \times 10^{-10}x$, $r = 0.99999$, $s = 4.35 \times 10^{-10}$. ▲ 433.15 K: $y = 7.52 \times 10^{-9} + 5.40 \times 10^{-10}x$, $r = 0.99993$, $s = 2.17 \times 10^{-9}$. ▼ 443.15 K: $y = -1.69 \times 10^{-8} + 1.02 \times 10^{-9}x$, $r = 0.9996$, $s = 8.11 \times 10^{-9}$. ◆ 453.15 K: $y = -2.53 \times 10^{-8} + 2.41 \times 10^{-9}x$, $r = 0.99982$, $s = 1.18 \times 10^{-8}$. ◄ 463.15 K: $y = -5.35 \times 10^{-9} + 4.26 \times 10^{-9}x$, $r = 0.99992$, $s = 8.17 \times 10^{-9}$. (b) [C_4mim][Thr] x: (t–t_0)/s; y: 10^6(m_0–m)/kg. ■ 413.15 K: $y = -5.82 \times 10^{-10} + 1.30 \times 10^{-10}x$, $r = 0.99998$, $s = 2.58 \times 10^{-10}$. ● 423.15 K: $y = 6.05 \times 10^{-9} + 2.57 \times 10^{-10}x$, $r = 0.99974$, $s = 2.06 \times 10^{-9}$. ▲ 433.15 K: $y = 8.35 \times 10^{-9} + 5.79 \times 10^{-10}x$, $r = 0.99994$, $s = 2.22 \times 10^{-9}$. ▼ 443.15 K: $y = 5.16 \times 10^{-9} + 1.32 \times 10^{-9}x$, $r = 0.99998$, $s = 2.51 \times 10^{-9}$. ◆ 453.15 K: $y = -3.52 \times 10^{-9} + 2.65 \times 10^{-9}x$, $r = 0.99997$, $s = 5.28 \times 10^{-9}$. ◄ 463.15 K: $y = -8.34 \times 10^{-9} + 4.95 \times 10^{-9}x$, $r = 0.99995$, $s = 8.62 \times 10^{-9}$.