Thermodynamic properties of the ionic vapor species over EMImNTf$_2$ ionic liquid studied by Knudsen effusion mass spectrometry

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ABSTRACT

In the temperature range of 437–519 K cations EMIm$^+$ (C$^+$), anions NTf$_2^-$ (A$^-$) and associative C$_2$A$^+$ and CA$_2^-$ ions were registered in saturated vapor over EMImNTf$_2$ ionic liquid. Their partial pressures and thermodynamic properties (desorption enthalpy, reaction enthalpy, formation enthalpy) were determined by Knudsen effusion mass spectrometry for the first time.

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1. Introduction

Ascertainment of nature of vapor over room temperature ionic liquids (RTILs) and determination of thermodynamic properties of the vapor species are at present actual tasks being solved by several scientific groups (see, *e.g.*, [1–7]). It has been established by mass spectrometric techniques (LOS-MS [2], FTICR-MS [8], FI-MS [9]) that under conditions of low pressure and temperature below decomposition the vapor of aprotic RTILs consists of neutral cation-anion ion pairs (NIP) exclusively. The existence with non-negligible concentrations of larger neutral species as well as of free ions and charged clusters in equilibrium with the liquid phase of RTILs at temperatures above 1000 K was predicted by Monte Carlo [10] and molecular dynamics [11] simulation. However, no experimental verification of the data [10,11] is possible due to decomposition of RTILs at the temperatures lower than 700 K.

One can suggest that in the temperature range of congruent vaporization of RTILs the fraction of ionic vapor species is quite low and they can be detected by applying special approaches only. The ion-molecular equilibria method [12,13] developed in the framework of Knudsen effusion mass spectrometry (KEMS) turned out to be such technique. It permits to work in the thermal ion emission mode and analyze the composition of charged species (positive and negative) in the saturated vapor.

It was demonstrated by this method that many inorganic compounds with ionic bond, in particular metal halides [14–17], contain the ionic species along with the neutral ones in their saturated vapors at high temperature. Typical examples of such compounds are molten salts, which have a similarity with organic ionic liquids [18] and can be considered as high temperature ionic liquids (HTILs). The first successful attempt of experimental detection of ionic species in equilibrium vapor over RTIL is reported in our recent article [19] on the example of prototypical RTIL 1-ethyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)imide (EMImNTf$_2$). The C$^+$, C$_2$A$^+$, A$^-$, and CA$_2^-$ species (C$^+$ is cation, A$^-$ anion) have been registered by KEMS and their partial vapor pressures were determined with the assumption that the sensitivity constant κ of mass spectrometer is the same for both positive and negative ions ($\kappa = \kappa_+ = \kappa_-$). In this work we have measured each of κ_+ and κ_- values directly and applied them to refine the partial pressures of ions obtained in [19]. The latter were used for determination of thermodynamic properties of the ionic species, which are compared to those of typical HTILs.

2. Experimental

A single-focusing magnetic sector type mass spectrometer MI1201 modified for high-temperature studies was used. The measurements were carried out in the thermal ion emission mode, in which the ions formed inside an effusion cell as a result of thermal ionization are analyzed. The commercial EMImNTf$_2$ sample (certified purity of 99.8%,
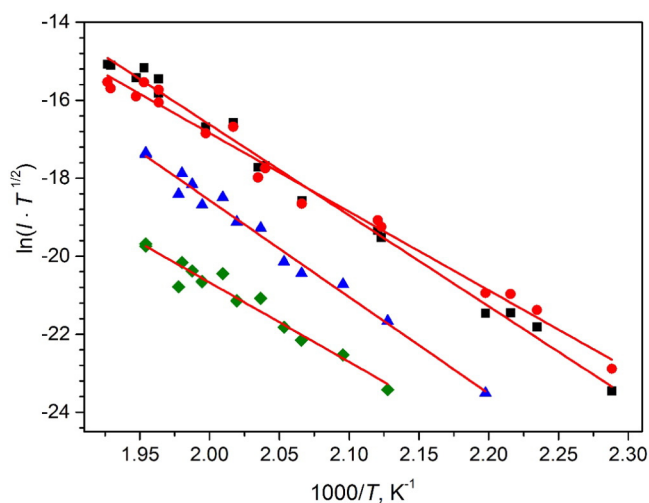
Fig. 1. Temperature dependences of C^+ (black squares), C_2A^+ (red circles), A^- (blue triangles), and CA_2^- (green diamonds) ion currents. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Sigma-Aldrich) was placed into a molybdenum effusion cell. A cup-shaped Mo liner was used to avoid any outflow of the ionic liquid from the horizontally oriented cell. The lid of the cell had a cylindrical effusion orifice (diameter of 0.8 mm, length of 1 mm). The vaporization-to-effusion area ratio was about 400. A resistance furnace performed the heating; the temperature of the cell was measured by the tungsten-rhenium thermocouple calibrated with ± 5 K accuracy. A special software "HTMSLab" was used to control the experimental parameters, collect the data, process them and export the results into the database. Detailed description of the apparatus and experimental procedure was given in [19,20,21].

3. Results and discussion

3.1. Mass spectra

In the temperature range of 437–519 K the cation $EMIm^+$ (C^+), anion NTf_2^- (A^-), and their associates with NIP (C_2A^+ and CA_2^-) were

Table 1
Partial vapor pressures of ions over EMImNTf$_2$.

	$p_j \cdot 10^{11}$, Pa			$p_j \cdot 10^{13}$, Pa	
T, K	C^+	C_2A^+	T, K	A^-	CA_2^-
484	13.0	31.6	506	67.4	9.26
491	30.5	61.8	501	51.0	10.5
501	85.7	192	487	11.9	3.27
514	302	496	512	188	26.2
518	421	607	512	194	27.7
519	428	716	503	86.9	13.9
509	205	425	495	33.1	6.46
490	31.8	78.4	484	8.81	2.35
471	5.06	17.4	470	2.59	0.66
455	0.723	3.19	477	6.69	1.61
437	0.098	0.458	491	28.3	6.86
451	0.727	3.10	498	62.0	12.9
448	0.509	2.06	505	115	17.2
472	6.08	20.7	455	0.41	
496	96.1	227			
509	294	584			
512	391	711			

The overall error in absolute vapor pressure is estimated by a factor of 2.

Table 2
Coefficients of Eq. (5).

Species	T, K	A	B
C^+	437–519	23.31 ± 0.54	25.82 ± 1.12
C_2A^+	437–519	20.15 ± 0.63	20.25 ± 1.30
A^-	455–512	24.73 ± 0.88	23.69 ± 1.79
CA_2^-	470–512	20.31 ± 1.34	13.15 ± 2.71

The standard deviation is given with a "$\pm$" sign.

observed [19]. The relative ion currents at $T = 493$ K are 100 (C^+), 76 (C_2A^+), 15 (A^-), and 1.4 (CA_2^-). The temperature dependencies of the ion currents are presented in Fig. 1.

3.2. Vapor pressure

The partial pressures of ions (p_j) were calculated according to the conventional procedure [22] using the equation:

$$p_j = \kappa \cdot \frac{I_j}{a_j \cdot \gamma_j} \cdot \sqrt{T \cdot M_j} \tag{1}$$

where κ is the sensitivity constant of mass spectrometer in thermal ion emission mode for positive (κ_+) or negative (κ_-) ions, I_j is the ion current of the measured isotope of the jth ion, a_j is its natural abundance, γ_j is the ion-electron conversion coefficient of secondary electron multiplier for the jth ion ($\gamma_j \sim M_j^{-1/2}$ [23], where M is the mass of ion), and T is the temperature of the cell.

In contrast to our previous paper [19], in which the assumption was used that the sensitivity constants for positive and negative ions are the same ($\kappa_+ = \kappa_- = \kappa$) in Eq. (1), in this work κ_+ ($4.21 \cdot 10^{-2}$ Pa A^{-1} mol$^{0.5}$ K$^{-0.5}$ kg$^{-0.5}$) and κ_- ($8.43 \cdot 10^{-4}$ Pa A^{-1} mol$^{0.5}$ K$^{-0.5}$ kg$^{-0.5}$) were determined directly in a separate experiment with CsI by solving the system of equations:

$$K_P = \frac{\kappa_+ \cdot \kappa_- \cdot T \cdot I_{Cs^+} \cdot I_{I^-} \cdot \sqrt{M_{Cs^+} \cdot M_{I^-}}}{p_{CsI}},$$
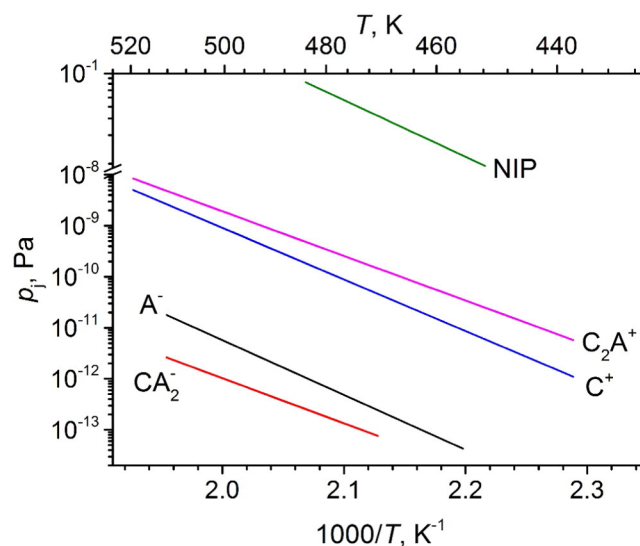$$\frac{\kappa_+}{\kappa_-} = \frac{g_+}{g_-}, \tag{2}$$

Fig. 2. Temperature dependences of partial pressures of vapor species over EMImNTf$_2$ (p(NIP) are taken from [7]).