

Short communication

Vapor pressure and thermal stability of ionic liquid 1-butyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)amide

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Abstract

Vapor pressure of an ionic liquid, 1-butyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)amide, was first experimentally determined. Temperature dependence of vapor pressure $\ln P_{\text{sat}} \text{ (Pa)} = (27.11 - 14.42) \times 10^3/T \text{ (K)}$ and enthalpy of vaporization $\Delta_{\text{vap}}H_{487} = 120 \pm 5 \text{ kJ mol}^{-1}$ were obtained from measurements by the Knudsen method in the range of 458–517 K.

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1. Introduction

Very low vapor pressure of ionic liquids (IL), a widely studied class of compounds, is considered as one of their advantages (e.g. [1]). IL $[\text{C}_4\text{mim}][\text{PF}_6]$ was found to decompose in vacuum at $T > 470 \text{ K}$ [2]. Measurements of vapor pressure of this compound by the integral effusion Knudsen method failed. However, up to now, only one attempt to calculate this value has been made [2] by the authors of this work. Rebelo et al. [3] demonstrated in a qualitative experiment that Bis(trifluoromethylsulfonyl)amide IL could evaporate without decomposition.

The aim of this work is to determine thermal stability of 1-butyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)amide $[\text{C}_4\text{mim}][\text{NTf}_2]$ in vacuum, and possibility of measurement of vapor pressure and enthalpy of vaporization for this compound.

2. Experimental

A sample of $[\text{C}_4\text{mim}][\text{NTf}_2]$ was kindly provided by Prof. A. Heintz from University of Rostock (Germany). The initial purity of the sample was $>98 \text{ mass\%}$. $[\text{C}_4\text{mim}][\text{NTf}_2]$ contained 28.14% C, 3.59% H, 9.28% N as determined by elemental analysis. Chloride ion was not discovered on addition of AgNO_3 . The sample was evacuated at $P < 1 \text{ Pa}$ and $T = 290 \text{ K}$ for 10 h.

Afterwards, the purity of the sample was determined by the fractional-melting technique in an adiabatic calorimeter to be 98.6 mol.%. Before effusion measurements, the sample was kept in vacuum of $\sim 10^{-3} \text{ Pa}$ at $T = 448 \text{ K}$ until the rate of mass loss became constant.

Vapor pressures by the Knudsen method were measured with an apparatus described in Ref. [4]. The apparatus was equipped with a thermostating block for experiments at 320–530 K. The temperature was controlled within $\pm 0.01 \text{ K}$. This was measured with a platinum resistance thermometer placed in the block. A cylindrical cell with a height of 10.0 mm and an internal diameter of 10.0 mm was used. It was covered by a plate with an orifice of a diameter of $d = 3.1 \text{ mm}$ and a thickness of $l = 2.1 \text{ mm}$. All the details were made of stainless steel. A Teflon ring was used for sealing. The residual pressure in the system was $P_{\text{res}} < 10^{-3} \text{ Pa}$.

Vapor pressures in the Knudsen method were calculated by equation:

$$P = \left(1 + \frac{kS}{S'\alpha} \right) \frac{\Delta m}{kS\tau} \sqrt{\frac{2\pi RT}{M}} \quad (1)$$

where Δm is the mass loss during an elapsed time τ , S the area of an orifice, k the transmission coefficient, M the molar mass of a vapor, S' the surface area of a liquid assumed equal to the cross-section area of a cell and α the vaporization coefficient. Normally, $\alpha = 1$ holds for liquids. The vapor was assumed to consist of ionic pairs $[\text{C}_4\text{mim}][\text{NTf}_2]$. The values of k were cal-

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Table 1
Vapor pressures of [C₄mim][NTf₂] from the Knudsen method

No.	<i>T</i> (K)	Δ <i>m</i> (mg)	τ (s)	<i>k</i>	<i>P</i> × 10 ² (Pa)
1	457.66	4.17	18780	0.607	1.22
2	467.52	7.46	18120	0.609	2.29
3	477.68	13.09	14400	0.613	5.07
4	487.54	5.63	3600	0.619	8.74
5	497.53	9.97	3660	0.628	15.2
6	507.54	9.70	1950	0.643	27.4
7	517.45	15.96	1850	0.663	46.6

culated as described in Ref. [4] with the use of the estimated diameter of the [C₄mim][NTf₂] ionic pair of 0.78 nm. The sum in the parentheses takes into account undersaturation in the cell connected with the finite diameter of the orifice [5].

The estimated uncertainty in *P*_{sat} in this study is ~10% at *T* near 460 K and ~5% near 500 K. This estimate does not take into account possible effect of impurities on the vapor pressure.

3. Results

3.1. Stability

Decomposition of the samples was visually controlled during the experiments. The initial [C₄mim][NTf₂] was colorless. Thermal decomposition of IL in the cell did not occur in the temperature range studied. The liquid condensed on the internal walls of the cell in the Knudsen method also had no color. The condensation products in a nitrogen trap were normally yellow, but sometimes they remained colorless. In the latter case, partial decomposition was probably caused by the contact of the IL vapor with copper parts of the apparatus outside the cell. So, one may presume that vaporization of the liquid is not directly related with its decomposition. Rebelo et al. [3] came to a similar conclusion based on mass-spectral measurements.

3.2. Vapor pressure

The results from the Knudsen method are presented in Table 1 and Fig. 1. They can be approximated by equation:

$$\ln P \text{ (Pa)} = (27.11 \pm 1.15) - (14.42 \pm 0.56) \times 10^3 / T \quad (2)$$

Deviations of the experimental values from those calculated from Eq. (2) are shown in Fig. 2.

3.3. Enthalpy of vaporization

Enthalpy of vaporization can be evaluated from Eq. (2): Δ_{vap}*H*₄₈₇ = 120 ± 5 kJ mol⁻¹. To adjust the obtained value to 298 K, one should estimate Δ₁^g*C_p* at 393 K, the average temperature of the interval. If one assumes that rotational and translational motion of particles in liquid makes a contribution to *C_v* of ≈*R* per degree of freedom (totally ≈6*R*), similar contribution in ideal gas is ≈*R*/2 per degree of freedom (totally 3*R*), and contributions of intramolecular vibrations and internal rotation are close in liquid and gas, then the following equation can be

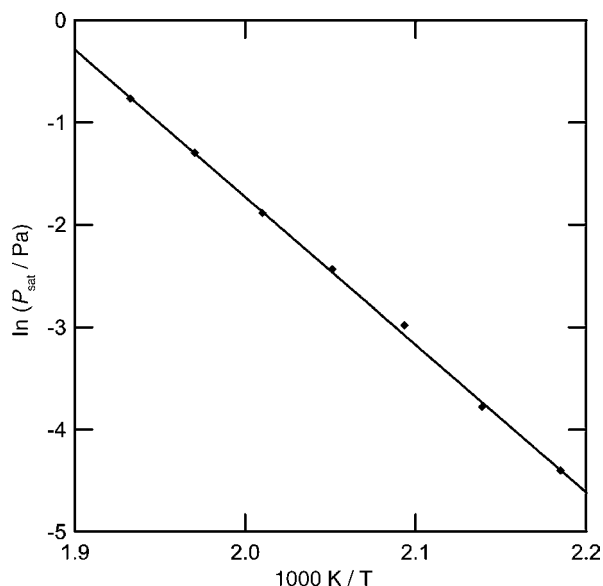


Fig. 1. Temperature dependence of vapor pressures for [C₄mim][NTf₂], (♦) experimental data, solid line is obtained from Eq. (2).

derived:

$$\begin{aligned} \Delta_1^g C_P &= C_{P,g} - C_{P,l} \approx (3R + R) - \left(6R + \frac{\alpha_P^2}{\kappa_T} V_m T \right) \\ &= -2R - \frac{\alpha_P^2}{\kappa_T} V_m T \end{aligned} \quad (3)$$

where α_{*P*} is the thermal expansion coefficient, κ_{*T*} the coefficient of isothermal compressibility and *V_m* is the molar volume of a liquid. These values for [C₄mim][NTf₂] are available only at *T* = 323.15 K [6]. That is why in calculations, we used the value Δ₁^g*C_p* = -94 J K⁻¹ mol⁻¹ corresponding to the mentioned temperature. Then, Δ_{vap}*H*₂₉₈ = 138 kJ mol⁻¹. This value is in good agreement with Δ_{vap}*H*₂₉₈ = 134 kJ mol⁻¹ evaluated

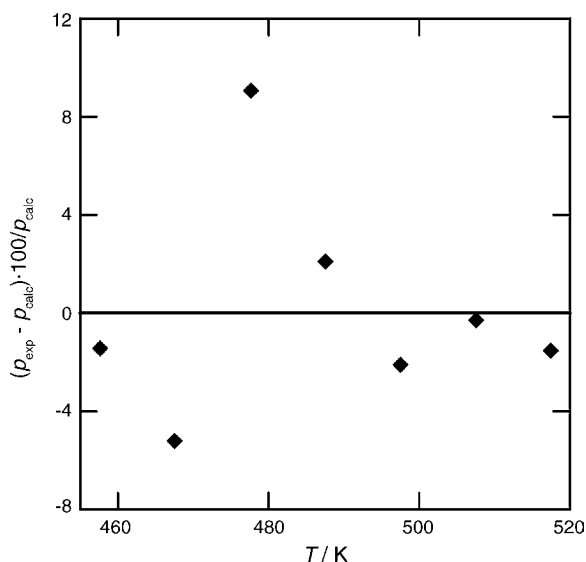


Fig. 2. Percentage deviation of the measured vapor pressures for [C₄mim][NTf₂] from those calculated from Eq. (2).

from the additive scheme for $\Delta_{\text{vap}}H$ calculation based on classification of effective atoms by kind [7]:

$$\begin{aligned} \Delta_{\text{vap}}H_{298} \text{ (kJ mol}^{-1}\text{)} \\ = 6.2n_C + 5.7n_O + 10.4n_N - 0.5n_F + 10.6n_S \end{aligned} \quad (4)$$

where n_i is the number of atoms of the i th kind in a molecule or an ionic pair.

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