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Thermodynamics of long-chain 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ionic liquids

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ABSTRACT

The heat capacities in the temperature range (5 to 370) K and the parameters of solid-phase transitions and fusion were determined for three $[C_n\text{mim}][\text{NTf}_2]$ ($n = 10, 14, 16$) ILs. The temperature-dependent vapour pressures of $[C_{14}\text{mim}][\text{NTf}_2]$ and $[C_{16}\text{mim}][\text{NTf}_2]$ were measured with a Knudsen effusion apparatus combined with a quartz crystal microbalance. Thermodynamic properties of these compounds in the crystal, liquid, and gas states were derived from the obtained data. The results obtained in this work were combined to those available in the literature for the short-chain homologues to discuss regularities in thermodynamic properties of the series. While some properties demonstrate simple linear dependence on the alkyl chain length, a more complicated behaviour with strong non-linearity or a break at $n = 6$ is observed for others.

1. Introduction

1-Alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imides $[C_n\text{mim}][\text{NTf}_2]$ are among the most studied room-temperature ionic liquids (ILs). Most studies and particularly the thermodynamic studies were conducted on the short-chain homologues. Heat capacities for the temperature range (5 to 370) K and parameters of phase transitions from adiabatic calorimetry have been reported for $[C_n\text{mim}][\text{NTf}_2]$ ($n = 2, 4, 6, 8, 18$) [1–6]. Most of the heat-capacity values on $[C_{18}\text{mim}][\text{NTf}_2]$ [5] were presented graphically and, therefore, they are of limited use. Rocha *et al.* [7] used a drop calorimeter [8] to determine heat capacities at $T = 298.15$ K for $[C_n\text{mim}][\text{NTf}_2]$ ($n = 2$ to 12). Dzyuba and Bartsch [9] determined parameters of a solid-phase transition and fusion for $[C_{10}\text{mim}]\text{NTf}_2$ with DSC. The parameters of fusion were determined by DSC for the liquids with $n = 12, 14, 16, 18$ [10] and $n = 18, 22$ [11]. Therefore, entropy and other thermodynamic functions for the long-chain NTf_2 containing ILs in the condensed state have not been reported.

The vapour pressures have been reported for the compounds with $n \leqslant 12$ [12,13]. For series members with longer chains, only enthalpies of vapourization are available [14,15].

In this work, we report the results of studies on the long-chain $[C_n\text{mim}][\text{NTf}_2]$ ionic liquids by adiabatic calorimetry and the quartz-microbalance Knudsen effusion method. The results are used to calculate thermodynamic properties of these compounds in various phases over wide temperature ranges and to analyse regularities in thermodynamic properties of these ILs.

2. Experimental

2.1. Sample purification and characterisation

Characteristics of the samples studied are given in table 1. The samples of $[C_{10}\text{mim}][\text{NTf}_2]$, $[C_{14}\text{mim}][\text{NTf}_2]$, and $[C_{16}\text{mim}][\text{NTf}_2]$ used for the vapour-pressure measurements were purchased from IoLiTec with a stated mole fraction purity of better than 0.98. The purity of each ionic liquid was further evaluated with ^{1}H NMR spectra (see Supplementary Material), and all ILs were found to be >0.99 mass fraction. The halide content was assumed to be that given by the supplier, <100 ppm. $[C_{14}\text{mim}][\text{NTf}_2]$ and $[C_{16}\text{mim}][\text{NTf}_2]$ were solid at room temperature and were dried under reduced pressure (<10 Pa) at $T = 323$ K to reduce the presence of water or other volatile contents. Water mass fraction content was found to be below 100×10^{-6} measured in a Metrohm 831

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TABLE 1
Provenance and purity of the samples studied.

Abbreviation	Source	Initial mole fraction purity	Purification method	Final fraction purity	Analysis method
[C_{10}mim][NTf_2]	IOLITEC	>0.98	Vacuum treatment	0.975 mol	Fractional melting
				>0.99 mass	NMR
[C_{14}mim][NTf_2]	IOLITEC	>0.98	Vacuum treatment	>0.99 mass	NMR
	INEOS RAS	N/A	Vacuum treatment	0.982 mol	Fractional melting
[C_{16}mim][NTf_2]	IOLITEC	>0.98	Vacuum treatment	0.997 mol	Fractional melting
				>0.99 mass	NMR

Karl Fischer coulometer using a Hydranal-Coulomat AG from Riedel-de Haën. The ILs were additionally purified by evacuation at $T = 533$ K under high vacuum ($<10^{-4}$ Pa) inside the Knudsen effusion cell before the vapour-pressure measurements.

The sample of [C_{14}mim][NTf_2] used for calorimetric measurements was provided by Prof. Ya.S. Vygodskii of the A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences (INEOS RAS). The sample was exposed to a vacuum ($p \approx 1$ Pa) at $T = 293$ K prior to the measurements. Purities of all samples studied in the adiabatic calorimeter were also determined by fractional melting (figure 1).

The purity of [C_{10}mim][NTf_2] determined by fractional melting is significantly lower than that found with NMR. The fractional melting procedure gives the total amount of impurity species in a sample. If the sample contains an ionic impurity containing single-charged ions (for example, isomeric IL), the purity will be 0.9875 mol fraction that is comparable with the NMR value.

2.2. Adiabatic calorimetry

Heat capacity over the temperature range from (5 to 370) K was measured in a TAU-10 adiabatic calorimeter (Termis, Moscow, Russia) [16]. The experimental procedures were published elsewhere [2]. The heat capacity of the sample contributed about 0.8 of the total heat capacity of the system near $T = 5$ K, and 0.3 to 0.5 outside the phase transition ranges at $T = (80$ to $370)$ K. The equilibration times were close to 100 s at the lowest temperatures. At higher temperatures, the equilibration times were typically (300 to 400) s. In the pre-melting range, the equilibration times to 3900 s were allowed. The relative expanded uncertainty (0.95 confidence interval) in the heat-capacity measurements was 0.4% above $T = 20$ K and 2% near $T = 5$ K [2].

The triple-point temperatures T_{fus} and the sample purities were determined with the van't Hoff equation in the form:

$$\ln\left(1 + \frac{n_2}{f}\right) = \frac{\Delta_{\text{fus}}H_{\text{m}}}{R}\left(\frac{1}{T_{\text{fus}}} - \frac{1}{T}\right), \tag{1}$$

where n_2 is the amount of impurity, mole per mole of the main component; f is the fraction melted at temperature T, $R = 8.314460$ J·K^{-1}·mol^{-1} [17], and $\Delta_{\text{fus}}H_{\text{m}}$ is the molar enthalpy of fusion at T_{fus}.

The baselines for the solid-phase transitions and fusion were selected using the following criteria: (i) smooth heat capacity over the ranges of the solid phase transition and the pre-melting range; (ii) concave baseline shape ($dC_p/dT > 0$); (iii) the baseline should involve the minimum heat capacity between the phase transitions.

Sample masses used for the calorimetric measurements were corrected for buoyancy. The reported uncertainties correspond to the 95% confidence interval for the normal distribution (coverage factor $k = 2$) unless specified otherwise.

2.3. Quartz crystal microbalance Knudsen effusion apparatus

Vapour pressures of the ILs were measured with a Knudsen effusion apparatus combined with a quartz crystal microbalance (KEQCM) described in the literature [18]. This approach allows gravimetric determination of the overall mass loss, as well as monitoring of the effusion rate with the quartz crystal microbalance. In

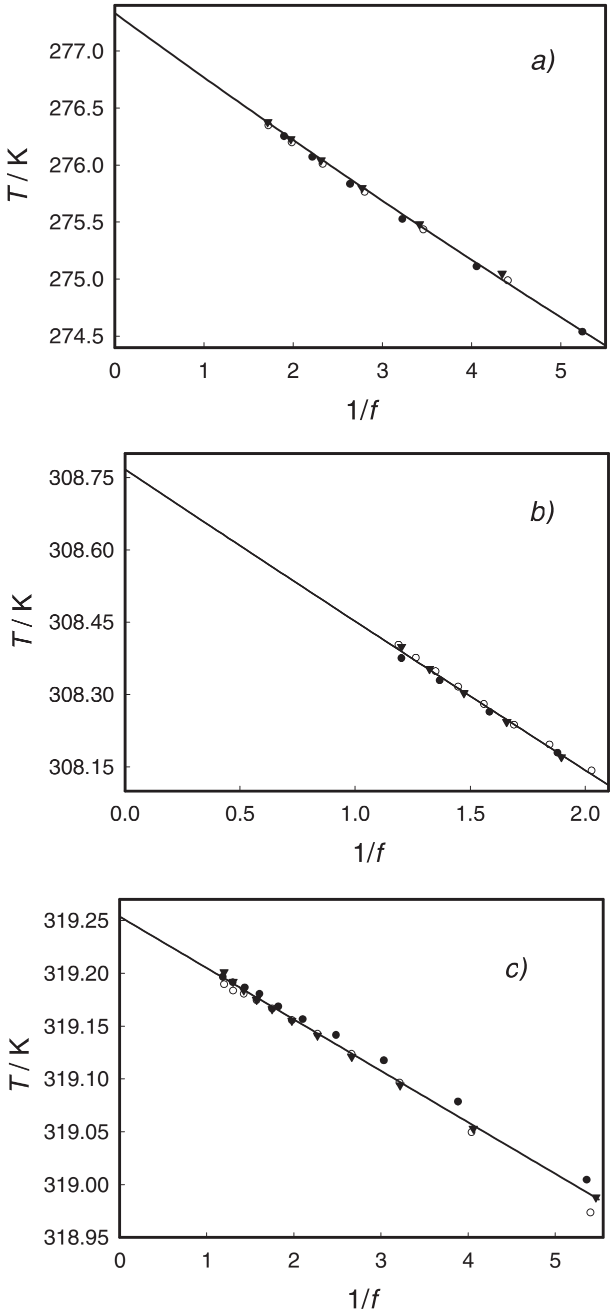

FIGURE 1. Results of fractional melting experiments for (a) [C_{10}mim][NTf_2], (b) [C_{14}mim][NTf_2], and (c) [C_{16}mim][NTf_2], where f is the fraction of the sample in the liquid state and T is the corresponding equilibrium temperature. Various symbols are used for different series of measurements.