Evaluation of thermodynamic properties for non-crystallizable ionic liquids

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ABSTRACT

Heat capacity of three glass-forming imidazolium ionic liquids (ILs) was studied by adiabatic calorimetry in the temperature range (5–370) K. Using the experimental data obtained in this work and those available in literature it was demonstrated that for all the studied glass-forming imidazolium ILs except [C$_8$mim]BF$_4$ the T_g/T_{fus} quotient is close to 2/3. The anion symmetry and the alkyl chain length were found to be the most important factors affecting heat capacity changes at the glass transition. The values of the residual entropy for the [C$_4$mim]An ILs can be explained by conformational disorder of the ions. However, since no statistically significant dependence of this quantity of the alkyl chain length was observed it is possible that the conformational disorder of the alkyl chains in ILs is lower than in molecular liquids or gases.

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1. Introduction

Many ionic liquids (ILs) do not crystallize on cooling and form glasses at low temperatures. For example, crystallization of 1-alkyl-3-methylimidazolium tetrafluoroborates [C$_n$mim]BF$_4$ ($n = 4$–9) ILs was not observed in DSC [1] and the corresponding crystal phases have not been obtained. Some ILs crystallize only after vitrification and heating of the obtained glass above the glass-transition temperature.

The glass transition is not a thermodynamic phase transition, and properties of glass depend on the cooling rate. However, thermodynamic properties like the glass transition temperature T_g, the heat capacity change at the glass transition $\Delta_{gl}^{l} C_{p,m}^{o}$, the residual entropy $\Delta_{cr}^{gl} S_m^{o}(T \rightarrow 0)$, and the residual enthalpy $\Delta_{cr}^{gl} H_m^{o}(T \rightarrow 0)$ for the glass obtained by cooling of liquid moderately change when the cooling rate varies by an order of magnitude or even more. For example, Chang et al. [2] obtained glassy diethyl phthalate by cooling of liquid at rates ≥ 2.5 K min^{-1} and 1 K h^{-1} near T_g. The residual entropies of quenched and annealed glasses were 23 and 20 J K^{-1} mol^{-1}, respectively. This difference was less than 0.01 $S_m^{o}(l, 298$ K$)$. The residual enthalpies of the glasses differed by 0.6 kJ mol^{-1}, which is again less than 0.01 $(H_m^{o}(l, 298$ K$) - H_m^{o}(cr, 0$ K$))$. The glass transition temperatures were 176.5 K and 180.8 K, respectively.

The calorimetric study of vapor-deposited and liquid-quenched glasses was performed for butyronitrile [3] and 1-pentene [4]. The configurational entropies and enthalpies frozen in the vapor-deposited glasses were significantly higher than those in the liquid-quenched glasses. However, the vapor deposited glasses relaxed during the heat capacity measurements, and the residual entropies and the residual enthalpies of the resulting glasses were close to those of the liquid-quenched glasses.

$\Delta_{gl}^{l} C_{p,m}^{o}$ and $\Delta_{cr}^{gl} S_m^{o}(T \rightarrow 0)$ give insight into the behavior of liquids close to T_g. Heat capacity of liquid is related to the structural changes occurring when the liquid is heated by 1 K. $\Delta_{gl}^{l} C_{p,m}^{o}$ characterizes the changes due to the degrees of freedom unfrozen when going from glass to liquid that is conformational, rotational, and translational ones. Glass possesses non-zero entropy even at $T = 0$ K because it keeps the structure of the corresponding liquid close to T_g and, therefore, has the frozen disorder.

The residual entropy and the residual enthalpy can be found experimentally only if the compound forms both glass and crystal. If the heat capacity of crystal is not available from very low temperatures and the compound is non-volatile, the entropy of liquid cannot be found. In this case, serious restrictions appear on the possibility of using the thermodynamic data for calculation of phase and chemical equilibria involving this compound. This problem can be solved if the general trends in the residual entropies in series of similar compounds are known thus allowing prediction of this property.

Previously, we reported the liquid heat capacities for a number of ILs [5] including non-crystallizable 1-ethyl-3-methylimidazolium ethylsulfate [C$_2$mim]EtSO$_4$ and 1-butyl-3-methylimidazolium tetrafluoroborate [C$_4$mim]BF$_4$, and 1-methyl-3-octylimidazolium

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tetrafluoroborate [C$_8$mim]BF$_4$ studied in this work. The detailed comparison of all the available data for these compounds was carried out in [6]. Some additional data on liquid heat capacities of [C$_4$mim] BF$_4$ have been published [7,8]. These results differ from the recommended values [6] by (0.06–0.07)C_p and >0.15C_p, respectively. The measurements of heat capacity for glassy [C$_2$mim]EtSO$_4$ [9] and [C$_4$mim]BF$_4$ [10] above T = 80 K were performed by adiabatic calorimetry. However, to evaluate thermodynamic properties, especially the entropy, for these compounds, the low-temperature data are required.

In this work we report the results of calorimetric study for [C$_2$mim]EtSO$_4$, [C$_4$mim]BF$_4$, and [C$_8$mim]BF$_4$ ILs in the temperature range (5–370) K and propose the procedures for prediction of thermodynamic properties for non-crystallizable 1-alkyl-3-methylimidazolium ILs.

2. Experimental

The characteristics of the IL samples used in this study are presented in Table 1. The purity and the triple-point temperature T_{fus} of [C$_8$mim]BF$_4$ were determined by the fractional-melting technique in an adiabatic calorimeter (Fig. 1).

Heat capacity of ILs in the temperature range from 5 to 370 K and parameters of fusion for [C$_8$mim]BF$_4$ were measured in a TAU-10 adiabatic calorimeter described earlier [11]. The uncertainty of the heat capacity measurements was less than $4 \times 10^{-3}C_p$ above 20 K, it gradually increased with temperature decrease and became $2 \times 10^{-2}C_p$ at T = 5 K. All operations with the samples were performed in a glove box. The masses of the samples obtained during weighting with the uncertainty of 2×10^{-5} g were corrected for buoyancy. All the masses were about 1 g.

The triple-point temperature T_{fus} for [C$_8$mim]BF$_4$ was determined by the fractional melting method. The results were fitted by the van't Hoff equation:

$$\ln\left(\frac{n}{f} + 1\right) = \frac{\Delta_{cr}^l H_m^o}{RT_{fus}^2}(T_{fus} - T) \tag{1}$$

where f is a fraction melted at temperature T, n is an amount of the impurity in a sample, per mole of the main component, $\Delta_{cr}^l H_m^o$ is a standard molar enthalpy of fusion for a pure compound. To determine $\Delta_{cr}^l H_m^o$, the following equation was applied:

$$
\Delta_{cr}^l H_m^o = Q_m - \Delta_{T_i}^{T_{fus}} H_m(cr) - \Delta_{T_{fus}}^{T_f} H_m(l)
$$
$$
= Q - \int_{T_i}^{T_{fus}} C_{p,m}(cr)dT - \int_{T_{fus}}^{T_f} C_{p,m}(l)dT \tag{2}
$$

where Q_m is the energy needed to heat 1 mol of a compound from T_i to T_f. The initial T_i and final T_f temperatures lay outside the premelting region. The heat capacities of the crystalline $C_{p,m}(cr)$ and liquid $C_{p,m}(l)$ compound were extrapolated to T_{fus} based on the experimental values obtained outside the pre-melting region.

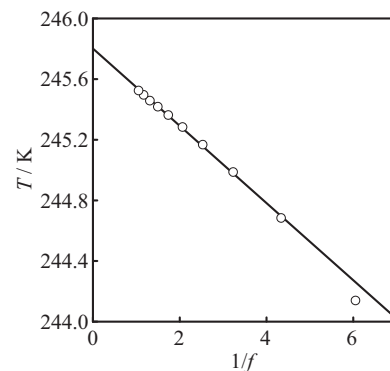The glass transition temperature T_g was determined as the temperature corresponding to the average heat capacity of a

Fig. 1. Fractional melting curve for [C$_8$mim]BF$_4$: f is a fraction melted at temperature T.

substance in the glass-transition range. The heat-capacity change at the transition "glass → supercooled liquid" $\Delta_{gl}^l C_{p,m}^o$ was determined as the heat-capacity difference between the supercooled liquid and the glass at T_g. The residual entropy and the residual enthalpy were found with the use of the equations:

$$\Delta_{cr}^{gl} S_m^o(T \to 0) = \frac{\Delta_{cr}^l H_m^o(T_{fus})}{T_{fus}} - \int_0^{T_{fus}} \frac{C_{p,m}(gl,l) - C_{p,m}(cr)}{T'}dT' \tag{3}$$

$$\Delta_{cr}^{gl} H_m^o(T \to 0) = \Delta_{cr}^l H_m^o(T_{fus}) - \int_0^{T_{fus}} (C_{p,m}(gl,l) - C_{p,m}(cr))dT' \tag{4}$$

All the reported uncertainties correspond to the 0.95 confidence interval for normal distribution ($k \approx 2$).

Extrapolation of heat capacity for crystal and glasses from 5 K to 0 K required for calculation of thermodynamic properties of the compounds was performed using the emipirical function:

$$C_{p,m} = D_3(\theta_D/T) + 3E(\theta_E/T) \tag{5}$$

where $D_3(\theta_D/T)$ is the Debye heat-capacity function for three degrees of freedom, $E(\theta_E/T)$ is the Einstein heat capacity function for one degree of freedom.

3. Results

The experimental heat capacities of the studied ILs are presented in Fig. 2 and in Supplementary data. On cooling in the calorimeter from T = 300 K at an initial rate of 30 mK s^{-1} the considered liquids tend to supercooling followed by vitrification. The characteristics of the glassy ILs are presented in Table 2.

Among the studied compounds, only [C$_8$mim]BF$_4$ was obtained in the crystalline state. The liquid formed after devitrification was heated during the heat capacity measurements that corresponded to a heating rate of about 10 K h^{-1}. Crystallization began at T = 230 K and proceeded much slower than in the case of other ILs studied in

Table 1
Characteristics of the used IL samples.

Chemical name	Source	Initial mass fraction purity[a]	Purification method	Final mole fraction purity	Analysis method
[C$_2$mim]EtSO$_4$	Solvent Innovation	>0.99	Exposed to vacuum	n/a	n/a
[C$_4$mim]BF$_4$	Solvent Innovation	>0.99	Exposed to vacuum	n/a	n/a
[C$_8$mim]BF$_4$	Iolitec	>0.99	Exposed to vacuum	0.9921	Fractional melting

[a] stated by supplier