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Low-temperature heat capacity of hydrophilic ionic liquids [BMIM][CF_3COO] and [BMIM][CH_3COO] and a correlation scheme for estimation of heat capacity of ionic liquids

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Abstract

Heat capacity for 1-butyl-3-methylimidazolium trifluoroacetate [bmim][CF_3COO] and acetate [bmim][CH_3COO] in the temperature range of (5 to 370) K has been measured by adiabatic calorimetry. Temperatures and enthalpies of phase transitions in [bmim][CF_3COO] have been determined. Thermodynamic functions for the compounds in the condensed state have been calculated. Physicochemical properties for the studied ionic liquids and alkali acetate salts have been compared. The correlation scheme for estimation of C_p of ionic liquids in a range of (190 to 370) K has been developed.

Keywords: Ionic liquid; Heat capacity; Adiabatic calorimetry; Correlations

1. Introduction

Room-temperature ionic liquids (ILs), which are combinations of a bulky organic cation and a counterion, possess unique physical and chemical properties making them attractive both for pure scientific and applied studies [1–5].

Studies of low-temperature heat capacities and parameters of phase transitions for ILs are of a particular interest. Especially, this concerns dependence of thermal properties on the nature of the anion. Earlier, the authors investigated a series of 1-butyl-3-methylimidazolium ([bmim]$^+$) ILs [6–10]. It was found that thermal behavior of ILs is strongly dependent on the nature of the anion. [bmim][PF_6], [bmim][Br] form a single crystal, [bmim][Tos] forms two polymorphs. Heat capacity of the [bmim][NTf_2] crystal at $T > 220$ K depend on the way the crystal was obtained. The latter phenomenon is probably related to a kind of disorder occurring in the crystal.

Among the studied ILs, all the compounds except [bmim][Tos] formed glass on cooling. Their spontaneous crystallization took place after de-vitrification. [bmim][Tos] crystallized immediately on cooling below T_{fus}.

It was also noted that specific heat capacity of IL crystals and glasses is higher than that for molecular crystals and glasses [7,9,10].

Due to a very large number of possible combinations of various cations and anions, it is very important to find correlations between the composition (cation + anion) of ILs and their physical properties. General trends of physicochemical properties of ILs (conductivity, viscosity, fusion temperature, and hygroscopicity) and the size of the ions were described in [11]. At the same time, there are some conflicting data in the present-day publications. For example, according to Bonhote *et al.* and Dupont [12,13], the de-vitrification of [bmim][CF_3COO] occurs in a range of (223 to 243) K that leads to $T_{fus} = 350$ K using an empirical rule

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$T_g/T_{fus} = 2/3$ [14]. However, this T_{fus} value is comparable to T_{fus} of [bmim][Br] [9] and seems to be too high.

In [15], it was found that the increment per CH_2-group to the heat capacity of liquid $[C_n mim][NTf_2]$ is close to that for liquid *n*-alkanes. However, no relationship for prediction of heat capacities of ILs with various anions has been proposed.

In this work, thermodynamic properties for 1-butyl-3-methylimidazolium trifluoroacetate [bmim][CF_3COO] and 1-butyl-3-methylimidazolium acetate [bmim][CH_3COO] are reported, based on the measurements by adiabatic calorimetry in the temperature range of (5 to 370) K. The correlation scheme for prediction of heat capacities of 1-butyl-3-methylimidazolium ILs in a range of temperatures of (190 to 370) K is developed.

2. Experimental section

2.1. Sample preparation

The samples of [bmim][CF_3COO] and [bmim][CH_3COO] were kindly provided by Prof. Ya.S. Vygodskii (INEOS RAS). The initial mass purity of the samples was >0.995: [bmim][CF_3COO] contained 0.4739 C, 0.612 H, 0.2252 N and [bmim][CH_3COO] contained 0.5964 C, 0.883 H, 0.1381 N as determined by elemental analysis. Water content was determined by Karl Fischer titration to be $1.2 \cdot 10^{-3}$ and $3.0 \cdot 10^{-3}$ mass fraction for [bmim][CF_3COO] and [bmim][CH_3COO], respectively. The samples of ILs were dried over P_2O_5.

Hygroscopicity of the compounds was studied in order to determine the procedure and conditions for [bmim][CF_3COO] and [bmim][CH_3COO] loading into the calorimeter. When exposed to air at $T = (292 \pm 1)$ K and relative humidity of air 50%, these compounds absorbed 5 mol% of water during the first 25 min. Therefore, the samples were loaded in a dry-box.

The mole fraction purity x of [bmim][CF_3COO] was determined by the fractional-melting technique. The experimental data (table 1 and figure 1) were fitted with the use of equation [16]:

$$\ln\left(\frac{v}{f}+1\right) = \frac{\Delta_{fus}H^\circ}{RT_{fus}^2}\cdot(T_{fus}-T) + \frac{\Delta_{fus}H^\circ}{RT_{fus}^2}\times \left(\frac{1}{T_{fus}} - \frac{\Delta C_p^\circ}{2\Delta_{fus}H^\circ}\right)\cdot(T_{fus}-T)^2, \quad (1)$$

where v is the amount of impurities in a sample, mole per mole of the main substance; f is the equilibrium melt fraction at temperature T; $\Delta_{fus}H^\circ$ is the enthalpy of fusion for a pure compound at the triple-point temperature T_{fus}; and ΔC_p° is the heat-capacity change at fusion of a pure compound. The mole fraction purity of the sample was found to be 0.977 (figure 1 and table 1). If one supposes water to be the main impurity, the mass-fraction purity w is 0.998.

TABLE 1
Results of fractional melting for [bmim][CF_3COO][a]

T/K	f
Series 5	
292.539	0.2119
293.475	0.2852
294.107	0.3691
294.539	0.4610
294.847	0.5579
295.082	0.6576
295.276	0.7590
$T_{fus} = (296.43 \pm 0.03)$ K, $x = (0.977 \pm 0.003)$	
Series 9	
292.955	0.2311
293.767	0.3081
294.313	0.3958
294.689	0.4902
294.963	0.5887
295.181	0.6897
$T_{fus} = (296.39 \pm 0.03)$ K, $x = (0.977 \pm 0.003)$	

[a] f is the melting fraction at temperature T.

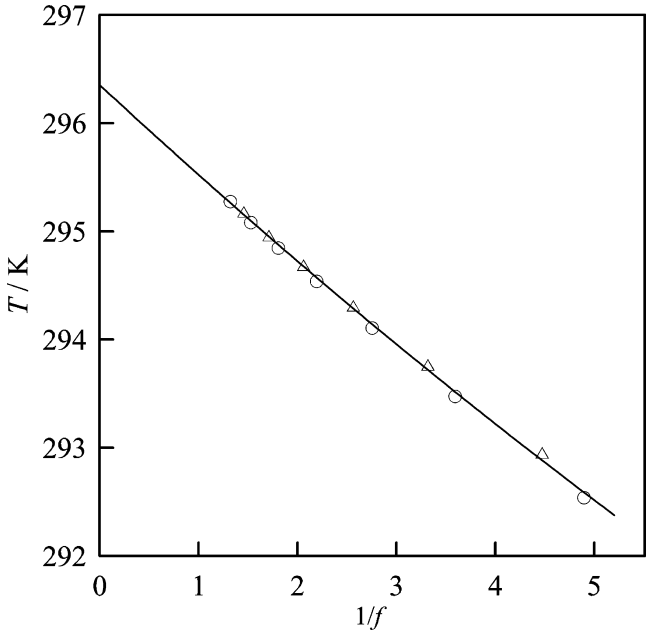

FIGURE 1. Results of the fractional-melting experiments for [bmim][CF_3COO]: (○) series 5 and (△) series 9.

2.2. Adiabatic calorimetry

Heat capacities of [bmim][CF_3COO] and [bmim][CH_3COO] in the condensed state in a range of temperatures of (5 to 370) K and phase-transition enthalpies were measured in a Termis TAU-10 adiabatic calorimeter. The calorimeter and the procedure of measurements were described in [17]. Sample masses in the measurements were 0.9697 g for [bmim][CF_3COO] and 0.4775 g for [bmim][CH_3COO].

The heat capacity c_s for a pure [bmim][CF_3COO] was determined using the following equation: