Short communication

Formation of metastable crystals of [C4mim][NTf2] and [C6mim][NTf2]

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Abstract

Heat capacities of crystalline 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C4mim][NTf2] and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C6mim][NTf2] in the range 80 K–T_{fus} were measured in an adiabatic calorimeter. Anomalies in the heat-capacity curves for the both compounds occurred near 240 K. Positions of the anomalies depended on thermal history of the samples. More stable crystals had higher heat capacities in the range 220–260 K. Below 200 K heat capacities of all the crystals of the same compound were indistinguishable.
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1. Introduction

A number of publications containing results of investigation of properties of room-temperature ionic liquids (IL) have been increased in the last few years. This is connected with unique properties of IL for application in chemistry and chemical technology [1]. Physicochemical properties of IL are also unique in many aspects. Earlier we demonstrated that 1-alkyl-3-methylimidazolium bromides differed in their ability to form crystals and glasses [2]. [C2mim]Br has a peak in the heat-capacity curve with a maximum at 13 K [2]. Specific heat capacity of [C4mim][PF6] below 30 K should be considered unusually high compared with most molecular organic crystals [3].

Thermal behavior of crystalline IL may be complicated. For example, Seeber et al. [4] reported existence of numerous stable and metastable solid-to-solid phase transitions in *N,N,N,N*-tetramethylammonium dicyanamide. During heat-capacity measurements for 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C4mim][NTf2] and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C6mim][NTf2] we found that these compounds formed different crystals in the temperature range 220–260 K. Since IL are promising compounds for industry, and [C6mim][NTf2] is expected to be a standard compound for physicochemical properties of IL [5] the fact of formation of different crystals depending on thermal and kinetic conditions of crystallization process is of great interest.

2. Experimental

A sample of [C4mim][NTf2] was kindly provided by Prof. A. Heintz from University of Rostock (Germany). The initial purity of the sample was >98 mass%. [C4mim][NTf2] contained 28.14% C, 3.59% H, 9.28% N as determined by elemental analysis. Chloride ion was not discovered on addition of AgNO3. The sample was evacuated at $p < 1$ Pa and $T = 290$ K for 10 h. From the fractional-melting study of the sample in an adiabatic calorimeter the purity was determined to be 98.5 mol% and $T_{tr} = 270.22$ K.

A sample of [C6mim][NTf2] was kindly provided by Dr. Mark Muldoon from University of Notre Dame. Purity of the sample was >99.5% as determined by ^{1}H and ^{19}F NMR. Water content was measured by Karl–Fisher titration to be 5 ppm. From the fractional-melting study purity was determined to be 99.4 mol% and $T_{tr} = 272.03$ K.

Heat-capacity measurements were conducted in a Termis BKT-10 adiabatic calorimeter. The sample under study was loaded in a titanium container with a volume of ∼1 cm³. The container was sealed with an indium ring. The container was inserted in a tube equipped with a heater. The tube with the container was situated inside an adiabatic shield. Temperature of

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Table 1
Description of the studied [C_4mim][NTf$_2$] crystals

Series	Preparation procedure			Measurements	
	1. Formation	2. Annealing	3. Cooling	Crystal	T-range (K)
1	Crystallization of supercooled liquid in the temperature range 200–252 K	10 h at 252–253 K	Down to 77 K	α	78–T_{fus}
2	Crystallization of supercooled liquid in the temperature range 200–230 K	18 h at 230 K	Down to 140 K	β	140–255
3	The sample after Series 2	–	Down to 200 K	α	200–248

Table 2
Description of the studied [C_6mim][NTf$_2$] crystals

Series	Preparation procedure			Measurements	
	1. Formation	2. Annealing	3. Cooling	Crystal	T range (K)
1	Crystallization of supercooled liquid in the temperature range 210–235 K	20 h at 235–236 K	From 260 to 77 K	γ	78–254
2	Crystallization of supercooled liquid in the temperature range 210–255 K	45 h at 255–257 K	Down to 77 K	β	78–T_{fus}
3	Crystallization of supercooled liquid in the temperature range 210–235 K	18 h at 235–236 K, then 10 h at 255 K	Down to 77 K	γ	200–T_{fus}
4	From γ-crystal	5 h at 265 K	Down to 213 K	α	213–264

the shield was measured with a Fe–Rh resistance thermometer. Temperature differences between the tube and the shield were controlled with the use of a Cu–Fe/Chromel thermocouple. Maximum deviation of the results of heat-capacity measurements for copper (80–300 K) and benzoic acid (80–350 K) from the recommended values [6] did not exceeded 0.3%, and RMS error was 0.1%. Reproducibility of the results was 0.1%.

The container filled with a substance was kept in vaccum ∼3 Pa not less than 0.5 h, and then it was filled with helium to pressure of 10 kPa at 290 K. Masses of the [C_4mim][NTf$_2$] and [C_6mim][NTf$_2$] samples were 1.2250 and 0.6579 g, respectively. After assembly, the measuring system was cooled in a liquid nitrogen bath. Initial cooling rate of the container with the sample was ∼20 mK s^{-1}. Subsequent evolution of the samples is described in Tables 1 and 2.

3. Results and discussion

Both the samples under study were supercooled and formed glasses at cooling in the calorimeter with a rate of 20–5 mK s^{-1}. The glass transition temperatures were $T_g = 181.5$ K for [C_4mim][NTf$_2$], and $T_g = 184.3$ K for [C_6mim][NTf$_2$]. The crystals were formed from the liquid obtained on heating the glasses above their de-vitrification temperature. Dependences $C_s(T)$ for the formed crystals in the temperature range from 80 K to T_{fus} are presented in Figs. 1 and 2 (Series 1). Inflection points occurred in the dependences at temperatures close to 240 K. A detailed study of heat capacities of crystals for [C_4mim][NTf$_2$] and [C_6mim][NTf$_2$] in the range of 80 K to T_{fus} was performed with the use of experimental procedures listed in Tables 1 and 2.

Differences in heat capacities of the crystals of the studied compounds with different thermal history reached 1.6% in the range 220–260 K (Figs. 3 and 4). It considerably exceeds reproducibility of the results. One may see in Figs. 3 and 4 and Table 1 that formation of the crystals with different heat capacities is reproducible if the sample is annealed at the same temperature. In this work the crystal with the highest heat capacity in the

specified range are designated as α, with lower heat capacity as β, and the lowest heat capacity as γ. Heat capacities of the crystals became indistinguishable below 200 K in the experimental conditions.

When heated above 230 K, the β-crystal of [C_4mim][NTf$_2$] were converted to the α-crystal with release of heat. This effect was determined by temperature trends in calorimetric experiments. Similar annealing for the γ-crystal of [C_6mim][NTf$_2$] at 255 K for 10 h did not result in transition into the crystal with higher heat capacity (Table 2, Series 3). However, annealing of the γ-crystal for 5 h at 265 K lead to formation of the α-crystal. The values of $(H_{liq}(T_{fus}) - H_{cr}(200\,\text{K}))$ 60.02 and 60.04 kJ mol^{-1} were determined from Series 2 (the β-crystal) and 3 (the γ-crystal) and subsequent fusion of [C_6mim][NTf$_2$], respectively. Difference between these results did not exceed reproducibility of the results. One may state that different crys-
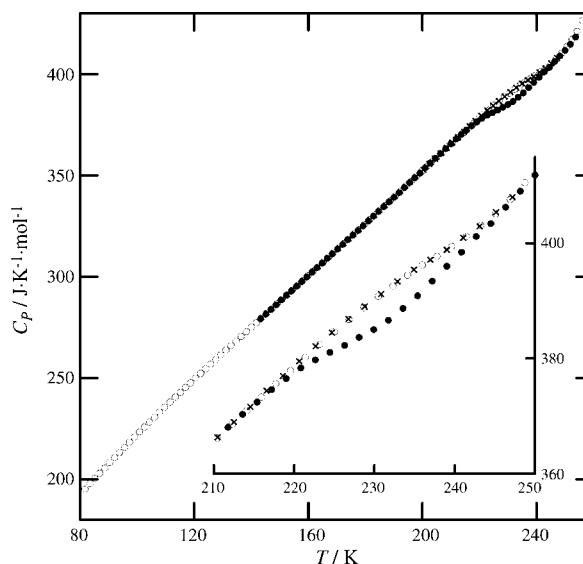

Fig. 1. Temperature dependence of heat capacity for [C_4mim][NTf$_2$], open circles for Series 1, closed circles for Series 2, multiplication sign for Series 3.
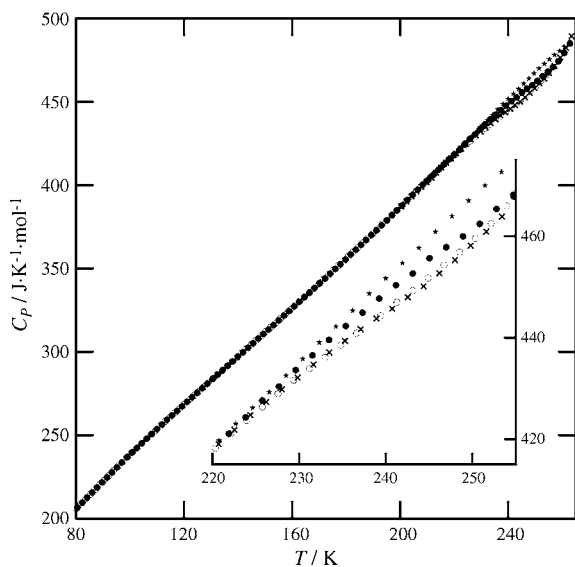
Fig. 2. Temperature dependence of heat capacity for [C$_6$mim][NTf$_2$], open circles for Series 1, closed circles for Series 2, multiplication sign for Series 3, stars for Series 4.
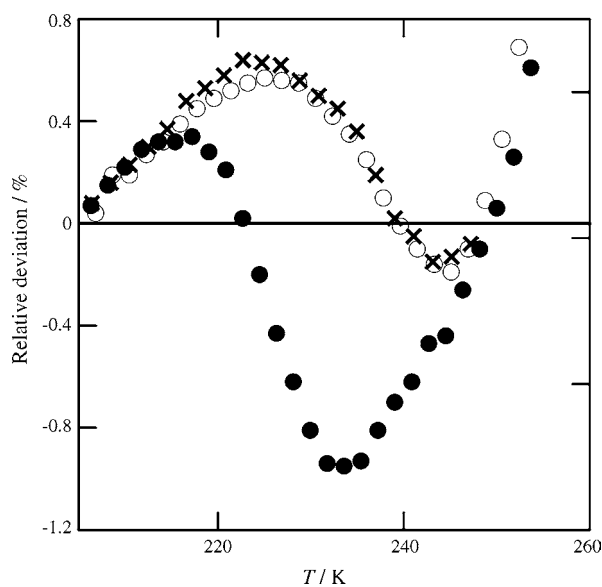

Fig. 4. Deviation of experimental values of C_P for [C$_6$mim][NTf$_2$] from line $C_P = 89.4 + 1.489T$. Designations are given in a legend of Fig. 2.

Fig. 3. Deviation of experimental values of C_P for [C$_4$mim][NTf$_2$] from line $C_P = 119.8 + 1.167T$. Designations are given in a legend of Fig. 1.

seems reasonable to connect the heat-capacity differences with conformational (internal rotation), but not orientational (overall rotation of the ions) changes.

More detailed information can be obtained in studying of the crystals obtained as described in Tables 1 and 2 by IR- and Raman spectroscopies, and X-ray crystallography.

Acknowledgements

tals are not distinguishable phases, but one phase with different conformational composition. These may be conformations of the anion caused by internal rotation with around a N–S bond, or conformations of the cations caused by internal rotation in the alkyl chain. The values of $(S(260\,\text{K}) - S(210\,\text{K}))$ for the crystals of the same compound differ by much less than $R\ln 2$. It
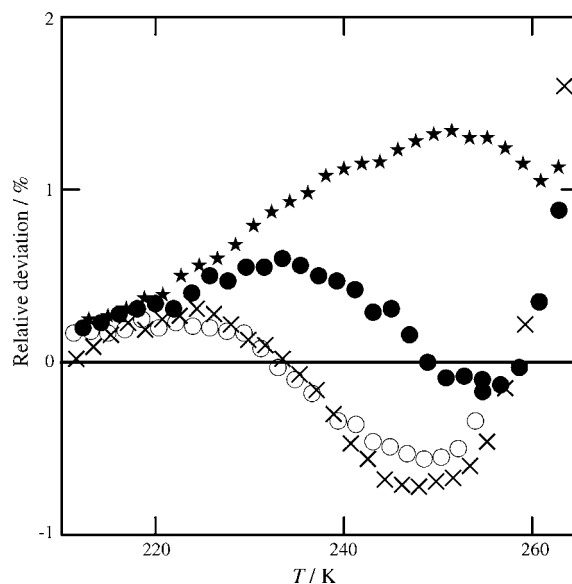
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