

## Effects of Thermal History on Thermal Anomaly in Solid of Ionic Liquid Compound, [C<sub>4</sub>mim][Tf<sub>2</sub>N]

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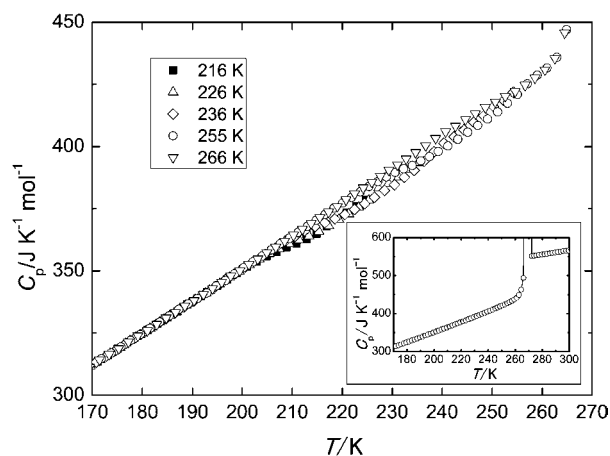
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Heat capacity of [C<sub>4</sub>mim][Tf<sub>2</sub>N] (1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) was measured by adiabatic calorimetry. Broad heat capacity anomaly and change in spontaneous endothermic effect were observed for crystal phase. The relation between these anomalies and thermal history after crystallization is described.

Room-temperature ionic liquids attract increasing attention because of their unique characteristics useful for application such as low melting point, low vapor pressure, nonflammability, etc.<sup>1,2</sup> [C<sub>*n*</sub>mim][Tf<sub>2</sub>N] (1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) with a short alkyl chain are known as room-temperature ionic liquids. Heat capacities (*C<sub>p</sub>*'s) of [C<sub>*n*</sub>mim][Tf<sub>2</sub>N] (*n* = 2, 4, 6, and 8) were measured by Kabo et al., and broad *C<sub>p</sub>* anomalies were reported for their crystal phase.<sup>3–5</sup> These *C<sub>p</sub>* anomalies were observed from ca. 210 K and the temperature ranges are variable. The *C<sub>p</sub>* anomaly can disappear upon appropriate thermal treatment, for example, in our previous paper on [C<sub>6</sub>mim][Tf<sub>2</sub>N].<sup>6</sup> At present, the origin of *C<sub>p</sub>* anomaly is not known. Considering suggestions that rather concrete local structure is expected in liquid state,<sup>7</sup> however, it is important to clarify thoroughly the structure even in the solid state with the definite energy state. In this respect, it is meaningful for crystal structure analysis to know how we can control energy state of the crystal. Although for crystalline [C<sub>8</sub>mim][Tf<sub>2</sub>N], Kabo et al. reported the relation between temperature ranges of *C<sub>p</sub>* anomalies and annealing temperatures,<sup>5</sup> they did not discuss in detail on other members.<sup>3–5</sup> We have measured *C<sub>p</sub>* of [C<sub>4</sub>mim][Tf<sub>2</sub>N] by adiabatic calorimetry. In this letter, we report the trend of the variation of *C<sub>p</sub>* anomalies and that of spontaneous endothermic effects for crystalline [C<sub>4</sub>mim][Tf<sub>2</sub>N] in relation to their thermal history after crystallization.

Commercial specimen (Solvent Innovation, Lot. No. 99/748) of [C<sub>4</sub>mim][Tf<sub>2</sub>N] (Mw; 419.37) was washed with *n*-hexane and pure water. It was then dried in a vacuum oven around at 50 °C for more than 12 h. Purity in mole fraction of the calorimetric sample was estimated as 99.7% by the fractional melting method<sup>8</sup> assuming formation of solid solution.<sup>9</sup> Water content of the sample was determined to be 110 μg/g by coulometric Karl-Fischer titration after the *C<sub>p</sub>* measurement. The dried sample (6.7166 g) was loaded into a chromium-plated copper calorimeter vessel with a platinum resistance thermometer calibrated according to the ITS-90.<sup>10</sup> *C<sub>p</sub>* was measured with an adiabatic calorimeter (JTA-2000C, Jecc Torisha Co., Ltd.) The *C<sub>p</sub>* values reported in this letter were calculated in a normal way without special procedure even for anomalous endothermic effects observed above 215 K because the correction term is smaller than



**Figure 1.** Main panel: Heat capacities of crystalline [C<sub>4</sub>mim][Tf<sub>2</sub>N] with thermal history. Temperatures following to the symbols in an explanatory note are the highest temperatures experienced after crystallization. Inset: Heat capacities of [C<sub>4</sub>mim][Tf<sub>2</sub>N] around fusion in crystal and liquid phases.

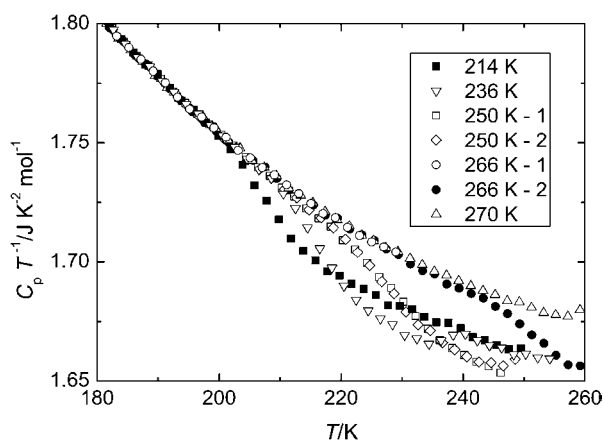
the *C<sub>p</sub>* anomaly discussed. The sample contributed to the total *C<sub>p</sub>* more than 30% in the whole temperature range. The crystalline state was realized as follows: The supercooled liquid was kept in adiabatic condition until the exothermic effect owing to crystallization ceased. The initial and the final temperatures of the crystallization were ca. 200 and 215 K, respectively.

The *C<sub>p</sub>* of [C<sub>4</sub>mim][Tf<sub>2</sub>N] in crystal and liquid phase from 170 to 300 K are shown in the inset of Figure 1. Fusion was observed around 270 K. Melting point, molar enthalpy, and entropy of fusion are 270.35 K, 23.8 kJ mol<sup>-1</sup>, and 88.0 J K<sup>-1</sup> mol<sup>-1</sup>, respectively. Temperature (*T*) dependence of *C<sub>p</sub>* in liquid phase (*C<sub>p,liq</sub>*) from 250 to 300 K is approximated with a quadratic polynomial expressed by eq 1 within 0.1%.

$$(C_{p,liq}/\text{J K}^{-1} \text{ mol}^{-1}) = 458.9 + 0.145(T/\text{K}) + 0.000714(T/\text{K})^2 \quad (1)$$

*C<sub>p,liq</sub>* at 298.15 K obtained from eq 1 is 565.6 J K<sup>-1</sup> mol<sup>-1</sup>.

*C<sub>p</sub>* of crystalline [C<sub>4</sub>mim][Tf<sub>2</sub>N] from 170 K to various temperatures, repeated without fusion, are shown in Figure 1. The measurements were repeated up to the temperatures at least 10 K higher than the final temperature of the *C<sub>p</sub>* measurement before. Although *C<sub>p</sub>* measured in all series below 200 K coincided within the experimental scatter, the differences in *C<sub>p</sub>* above 200 K among the series were apparent. These differences are caused by a *C<sub>p</sub>* anomaly, negative deviations from the extrapolation of *C<sub>p</sub>* below 200 K. A similar anomaly was reported previously by Kabo et al.<sup>3,5</sup> with a higher onset temperature. The

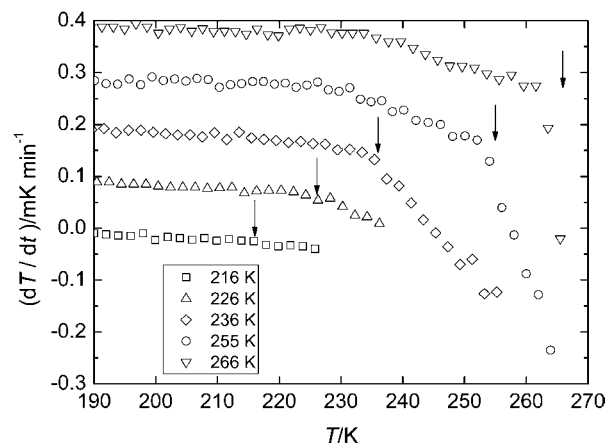


**Figure 2.**  $C_p T^{-1}$  of crystalline  $[C_4mim][Tf_2N]$  with thermal history. Temperatures following to the symbols in an explanatory note are the highest temperatures experienced after crystallization.

onset temperature of the negative deviation seems to shift to higher side in the order of the measurement series.

Figure 2 shows  $C_p T^{-1}$  of the crystalline  $[C_4mim][Tf_2N]$  heated up to various temperatures after crystallization. These results indicate that as the highest temperatures experienced after crystallization increase, the onset temperatures of the anomaly shift to higher temperatures. At last,  $C_p$  anomaly almost vanishes upon reaching 270 K, where a part of the sample melted. To confirm the thermal behavior is solely determined by the highest temperature experienced after crystallization, the series “266 K-2” was measured just after “266 K-1,” which was measured from 170 to 230 K after heating to 266 K. The  $C_p$ 's in these two series agree with each other in spite of the difference of the temperature ranges in the measurement just before. This indicates that the highest temperature experienced after crystallization governs the  $C_p$  anomaly. Annealing at 226 K (40 and 100 min) and 230 K (70 min) affected values of  $C_p$  up to 0.14% at the onset temperature of the negative  $C_p$  anomalies. This result indicates that the annealing effect is smaller in comparison with the negative deviation under discussion. To check the reproducibility of  $C_p$  through fusion and crystallization, two series of measurements were repeated as indicated “250 K-1” and “250 K-2.” After “250 K-1,” the sample was melted then crystallized again for the series “250 K-2.” Difference between “250 K-1” and “250 K-2” is negligible in spite of the experience of the fusion. The fusion resets the memory of the thermal history stored in the sample.

Temperature drifts recorded under the same adiabatic condition are shown in Figure 3. The temperature drifts were evaluated by linear regressions for temperature readings during the latter half of equilibration period (30 min). The temperature drifts below 215 K are due to imperfection of the adiabatic control and essentially the same regardless of their thermal history. Those above 215 K are, however, different from measurement series to series. As the highest temperature experienced after crystallization goes higher, the onset temperature also increases and the deviations of temperature drifts from those below 215 K. This negative deviation can be regarded as a symptom of the spontaneous endothermic effect. The onset temperature of the spontaneous endothermic effect is higher than that of the nega-



**Figure 3.** Temperature drifts of crystalline  $[C_4mim][Tf_2N]$  with thermal history. The temperatures following to the symbols in an explanatory note are the highest temperatures experienced after crystallization. Ordinate is for the series “216 K” and other data are successively shifted by  $0.1 \text{ mK min}^{-1}$  upward.

tive  $C_p$  deviation in every series. Besides, sudden drops in temperature drifts appear at almost the same temperatures as the highest temperatures experienced after crystallization as indicated by arrows in Figure 3. Clear differences in time required for equilibration at higher temperatures than the highest temperatures experienced after crystallization were not observed in comparison with lower temperatures. However, the time required for equilibration became longer as the endothermic effects became stronger (typically  $-0.3 \text{ mK min}^{-1}$ ). The crystal memorizes the highest temperature experienced.

In summary, we have shown the relation between thermal anomaly in crystal phase of  $[C_4mim][Tf_2N]$  and the highest temperatures experienced after crystallization. As the highest temperature experienced goes higher, thermal anomaly appears at a higher temperature, i.e., negative deviation from extrapolation of heat capacity below 200 K goes higher, and sudden enhancement of spontaneous endothermic effect appears at almost the same temperature as the highest temperature experienced after crystallization. The thermal anomaly is reproducibly affected by its thermal history. These findings will be helpful for elucidation of the subtle but characteristic structural features of ionic liquids.

## References

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