Calorimetric study of polymorphism in 1-butyl-3-methylimidazolium hexafluorophosphate

Eugene Paulechka^{1,2*}, Tatsiana Liavitskaya^{2,3}, and Andrey V. Blokhin²

¹ *Applied Chemicals and Materials Division, National Institute of Standards and Technology, Boulder, CO 80305-3337, United States*

² *Chemistry Faculty, Belarusian State University, Leningradskaya 14, 220030 Minsk, Belarus*

³ *Department of Chemistry, University of Alabama at Birmingham, Birmingham, AL 35294-1240, United States*

* To whom correspondence should be addressed. E-mail: yauheni.paulechka@nist.gov

Abstract

Stable and metastable crystal phases of 1-butyl-3-methylimidazolium hexafluorophosphate were obtained in an adiabatic calorimeter providing precise temperature control during crystallization. Heat capacities, as well as temperatures and enthalpies of phase transitions, including fusion, were determined for three polymorphic sequences (I, II, and III). Structures of the crystal phases were assigned using crystallographic studies from the literature. The standard entropy of the liquid phase at $T = 298.15$ K determined using the calorimetric data for each sequence was the same within the uncertainty of the measurements. This, in combination with the crystallographic results, implies that the lowest-temperature crystal form is ordered for all sequences. The complete pattern of phase transformations in this ionic liquid at ambient pressure is described, and results show that the relative stability of Sequences II and III invert at $T \approx 281$ K.

1. Introduction

Room-temperature ionic liquids (ILs) are salts that typically incorporate bulky cations and, sometimes, bulky anions. As a result, the energy of interaction between the ions is lower than that of typical salts, favoring a low temperature of fusion. This effect is further enhanced due to the asymmetry of the cations typically used in ILs. Those two factors result in the possibility of multiple crystal packing with little difference in lattice energy and polymorphism. Multiple crystal phases have been reported for various ILs (*cf.*, $[\text{C}_n\text{mim}]\text{NTf}_2$, $[\text{C}_4\text{mim}]\text{An}$ ($\text{An} = \text{Cl}$, NO_3), $[\text{Et}_4\text{N}]\text{NTf}_2$. [1–5]). The polymorphs are often formed by different conformers of the ions [1, 2, 3]. In some cases, conformational disordering of a crystal phase occurs [4, 5, 6].

1-butyl-3-methylimidazolium hexafluorophosphate $[\text{C}_4\text{mim}][\text{PF}_6]$ is probably the most studied polymorphic IL [6–26], though its behavior in the crystal state is not completely understood. Due to precise temperature control and the ability to observe subtle heat effects associated with crystal transformations, adiabatic calorimetry can be a powerful tool in determining relative

phase stabilities, as well as temperatures and enthalpies of phase transitions. An assignment of the structures of crystal phases for [C₄mim][PF₆] to the observed phase transformations has been proposed by Saouane *et al.* [6] as a part of an X-ray study. The X-ray works [6], [7], [15], [16] were mainly focused on structural identification of the polymorphs, and we will show that assignments made require further refinement. Similarly, interpretations based on spectroscopy or differential scanning calorimetry can also be misleading due to the inability to carefully monitor the solid-state transformations. As demonstrated below, different phases were sometimes obtained from the same sample placed in a calorimeter, an X-ray diffractometer, or a spectrometer.

In this work, we combine experimental data obtained by adiabatic calorimetry with structural and calorimetric data available in the literature to identify crystal phases of [C₄mim][PF₆] and determine relative stability and thermodynamic properties for various polymorphs of this compound from 0 K to the corresponding triple-point temperatures T_{fus} .

2. Experimental

A commercial sample of [C₄mim][PF₆] (Merck) with the stated purity of 99 mass percent was exposed to a vacuum of approximately 1 kPa at room temperature with constant stirring. The mole fraction purity of the sample was determined to be 99.68 % by fractional melting analysis of two distinct polymorphs in the adiabatic calorimeter (figure 1).

Heat capacities of the sample in the temperature range (5 to 370) K were measured in a small-volume TAU-10 adiabatic calorimeter (Termis, Moscow, Russia) [27]. The experimental procedures have been previously described [28]. Each heat-capacity determination involved initial measurement of temperature and its drift rate, as well as the electrical heating of the sample cell, which was followed by an equilibration period and measurement of the final

temperature, adjusted for the background drift rate. This procedure is typical for adiabatic calorimetry [29]. Temperatures were measured with a Fe/Rh resistance thermometer ($R_0 = 50 \, \Omega$) calibrated on ITS-90 by VNIIFTRI (Moscow).

A

B

FIGURE 1. Fractional melting curves for (a) crystal III, (b) crystal II₄. Various symbols are used for different measurement series, and f is the fraction melted at temperature T . Crystal phase designations are described in the first paragraph of the *Results* section of the text.

In series 1 and 3, in which liquid helium was used as a coolant, the buoyancy-corrected sample mass was 0.9787 g. In other series, a sample of 1.0591 g was used. For the measurements, the samples were loaded in a calorimetric container of a 1.1 cm³ volume in a dry box. The heat capacity of a sample contributed about 80% of the total heat capacity of the system near 5 K, about 40% near 100 K, and 54% near 370 K. The equilibration times were close to 100 s at the lowest temperatures. At higher temperatures the typical equilibration times were 300 s. The expanded uncertainty (0.95 confidence interval) in the heat capacity measurements was determined to be 0.4 % above $T = 20$ K and 2 % near $T = 5$ K [28].

Most experiments were performed in the step heating mode described above. Sequence II became unstable on heating at $T > 226$ K, and the regular measurements could not be performed. A cooling curve for this sequence revealed a phase transition in this temperature range. To obtain quantitative parameters of the phase transition, the following procedure was applied.

The Fe/Rh thermometer is placed on an adiabatic shield and the temperature difference between the shield and the container is measured with a differential thermocouple [28]. Normally, the thermocouple works at small ΔT . To make the temperature calibration at the large temperature differences (up to 30 K) occurring on cooling, the temperatures of peaks $T = (176.4 \text{ and } 216.8)$ K were used. The expanded uncertainty after this calibration was estimated to be $u(T) = 1$ K.

The heat capacity was derived from the cooling curve with the following differential equation:

$$(C_P(s) + C_P(\text{cont})) \frac{dT}{d\tau} + k_1(T - T_0) + k_2(T_s - T_0) = 0 \quad (1)$$

where $C_P(s)$ and $C_P(\text{cont})$ are the heat capacities of the sample and the container, respectively; T , T_s , and T_0 are the temperatures of the container, the adiabatic shield, and the liquid nitrogen bath. The empirical parameters k_1 and k_2 were found using the experimental heat capacity of Sequence II obtained during regular measurements in the temperature range of $T = (150 \text{ to } 225)$

K. The relative expanded uncertainty in the enthalpy of phase transition derived from the heat capacity was estimated to be $U_r(\Delta H) = 20\%$.

The reported uncertainties correspond to the 95 % confidence interval for the normal distribution (coverage factor $k = 2$) unless specified otherwise.

3. Results

3.1 Calorimetry

The experimental heat capacities for the studied IL are presented in figures 2–4 and in table S1. On cooling, the liquid super cooled and formed a glass. Crystallization occurred when the glass de-vitrified and then was heated to $T = 213$ K. Three sequences of crystalline phases were obtained. These sequences are designated as Sequence I, Sequence II, and Sequence III in order of their appearance on continuous heating. Solid phases within a given sequence are distinguished by numeric indices starting with the lowest temperature phase. For example, crII₁ is the lowest temperature phase observed in Sequence II, crII₂ is the next higher temperature phase, etc. Sequence III has only one crystal phase crIII. One crystal phase crI was also observed in Sequence I. However, during the measurements, the sequence became unstable significantly below T_{fus} and other polymorphs may be missing.

Formation of the polymorphs was controlled by various temperature programs applied to the sample prior to different series of measurements. The programs providing the maximum content of each polymorph were worked out during preliminary experiments.

FIGURE 2. Experimental heat capacities and temperature drifts during calorimetric measurements (—) for Sequence I: Blue circles, heat capacities in the region of kinetic stability; $-\cdot-\cdot-$, baseline used for extrapolation of heat capacity; $---$, temperature of phase transition. Heat capacities near $T = 250$ K (red circles) have large uncertainties, as discussed in the text. Above $T = 252$ K (red line), the experiments were continued to track changes in temperature drifts; heat capacities in that range could not be determined. The temperature drifts were measured at 300 s after the end of heating.

FIGURE 3. Experimental heat capacities and temperature drifts during calorimetric measurements (—) for Sequence II: Blue circles, heat capacity in the region of kinetic stability; - · - · -, baseline used for extrapolation of heat capacity to T_{fus} ; - - -, peak temperatures of phase transitions; —, heat capacity derived from the cooling curve. Above $T = 252$ K (red line), the experiments were continued to track changes in temperature drifts; heat capacities in that range could not be determined. The temperature drifts were measured at 300 s after the end of heating.

Liquid. Heat capacities for the liquid phase obtained in this work (Figure 4, Series 5 in Table S1) were combined with the literature data considered in the review by Paulechka [30] and a general equation was obtained for the temperature range (191 to 370) K:

$$C_{P,m} / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 326.94 - 26.201(T / 100 \text{ K}) + 26.149(T / 100 \text{ K})^2 - 2.7848(T / 100 \text{ K})^3 \quad (2)$$

Deviations of the experimental heat capacity values from those calculated with eq. (2) are presented in Figure 5. With exception of two early DSC works [31, 32], the deviations do not exceed 1.1 %.

FIGURE 4. Experimental heat capacities of Sequence [21] (blue circles) and liquid (red circles)

FIGURE 5. Deviation of heat capacities for $[C_4mim][PF_6]$ available in the literature from those calculated with Eq. (2). Adiabatic calorimetry: yellow circles, this work; cyan circles, Kabo *et al.* [21]; DSC: cyan squares, Kabo *et al.* [21]; triangles, Yu *et al.* [32]; diamonds, Troncoso *et al.* [9]; stars, Nieto de Castro *et al.* [33]; +, Fredlake *et al.* [14]. The results by Holbrey *et al.* [34] deviating by (11 to 20) % are not shown

Sequence I (crI). Phase crI was first formed (Figure 2, Series 1 and 2 in Table S1) when crystallization began near $T = 213$ K. If adiabatic conditions were hold during the crystallization process, the sample warmed spontaneously to about $T = 234$ K. Annealing at this temperature would finally result in formation of crII₃, so measurements for the quenched crystals are reported here for crI. This crystal contained (0.6 ± 0.1) % of the phases belonging to Sequence II, as estimated from the area of the very small peak with $T_{\max} = 176$ K, which is characteristic of Sequence II. The heat capacity curve had a hump with a maximum at $T \approx 190$ K. As demonstrated in the Results section, this hump is related to disordering in the crystal phase.

An endothermic peak with a maximum at $T = (250 \pm 1)$ K and with a standard molar enthalpy $\Delta_{\text{crI}_1}^{\text{crII}_4} H_m^\circ = 1.48 \pm 0.15 \text{ kJ}\cdot\text{mol}^{-1}$ was observed. These parameters were obtained in three experiments with the freshly obtained quenched crystals (Table S2). The observed decrease of heat capacity just before the peak is an artifact caused by incomplete equilibration. This artifact has no effect on the enthalpy of transition reported above. The equilibration time was not increased since it would favor transformation into crIII before this solid-solid phase transition. This phenomenon is similar to the transformations reported earlier [18], [6] and should be assigned to the irreversible transition to crII₄, the stable phase of Sequence II above $T = 250$ K.

Upon continued heating ($\sim 7 \text{ K}\cdot\text{h}^{-1}$), the transition near $T = 250$ K was followed by an exothermic transformation of crII₄ into crIII (figure 2). With freshly obtained quenched crystals, the initial rate of this exothermic process was significantly less than that for the annealed crystal or the crystal cooled to $T = 80$ K before the measurements. The maximum heat evolution rate was observed at $T \approx 265$ K, as determined from the temperature drifts observed in the calorimetric experiments.

The measurements were continued until the sample liquefied completely to determine the enthalpy change $H_m^\circ(\text{l}; 286 \text{ K}) - H_m^\circ(\text{crI}, 230 \text{ K}) = (31.00 \pm 0.12) \text{ kJ}\cdot\text{mol}^{-1}$ (table S3). This value in combination with $H_m^\circ(\text{crI}; 230 \text{ K}) - H_m^\circ(\text{crI}, 0 \text{ K}) = (39.46 \pm 0.16) \text{ kJ}\cdot\text{mol}^{-1}$ obtained

by integration of heat capacities in this work yields the enthalpy difference between the liquid at $T = 286$ K and crI at $T = 0$ K. With the analogous enthalpy change for Sequence III ($H_m^\circ(\text{l}; 286 \text{ K}) - H_m^\circ(\text{crIII}, 0 \text{ K}) = (75.39 \pm 0.30) \text{ kJ}\cdot\text{mol}^{-1}$) [21], we calculate the enthalpy of crI relative to crIII to be $H_m^\circ(\text{crI}; 0 \text{ K}) - H_m^\circ(\text{crIII}, 0 \text{ K}) = (4.93 \pm 0.36) \text{ kJ}\cdot\text{mol}^{-1}$.

Although not measured directly, it is possible to approximate the melting temperature and enthalpy of fusion for crI using the following reasoning. The heat capacity curve in Figure 2 shows no evidence of positive curvature that would indicate pre-melting. Pre-melting for crIII was detected ~ 20 K below T_{fus} . Based on this, the melting temperature for crI should be greater than 267 K. In addition, Sequence I has the lowest thermodynamic stability relative to the other sequences, so its melting point would also be the lowest. As demonstrated below, it means $T_{\text{fus}} < 283.6$ K. These two criteria allow one to make estimates: $T_{\text{fus}}(\text{crI}) = (275 \pm 8) \text{ K}$ and $\Delta_{\text{fus}}H_m^\circ = (12.85 \pm 0.60) \text{ kJ}\cdot\text{mol}^{-1}$.

Sequence II. If a mixture of crII₄ + crIII obtained as described above is heated a few tenths of a Kelvin above the melting temperature of crIII, the sample will contain only the phase belonging to Sequence II in equilibrium with liquid.

Fractional melting of this crystal (Figure 1) allowed us to determine its triple-point temperature to be $T_{\text{fus}} = (284.55 \pm 0.06) \text{ K}$. If the (crII₃ + liquid) mixture is cooled at an initial rate of $20 \text{ mK}\cdot\text{s}^{-1}$, a sample suitable for measurements can be obtained. The heat capacity curve for Sequence II (Figure 3, Series 3 and 4 in Table S1) is distinguished by two non-isothermal phase transitions with maxima at $T = (176.4 \pm 0.7) \text{ K}$ and $T = (216.8 \pm 0.4) \text{ K}$ determined in three experiments and averaged. The corresponding enthalpies of phase transitions were $\Delta_{\text{crII}_1}^{\text{crII}_2}H_m^\circ = (0.75 \pm 0.05) \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_{\text{crII}_2}^{\text{crII}_3}H_m^\circ = (0.89 \pm 0.06) \text{ kJ}\cdot\text{mol}^{-1}$ (Tables S6 and S7).

Polymorph crII₃ became unstable at $T = 226$ K and transformed into crIII during regular measurements. The large and positive temperature drifts for $T > 200$ K are evidence of this transformation (Figure 3).

To obtain more information about Sequence II, the heat capacity was derived from the cooling curve in the calorimeter (Figure 3). In addition to the transitions observed during regular measurements, the peak with a maximum at $T = (250 \pm 1)$ K was detected. The enthalpy of this phase transition was estimated to be $\Delta_{\text{crII}_3}^{\text{crII}_4} H_m^\circ = (0.5 \pm 0.1) \text{ kJ} \cdot \text{mol}^{-1}$ based on cooling-curve analysis.

To determine the enthalpy of fusion for crII₃, the enthalpy change $H_m^\circ(\text{l}; 286 \text{ K}) - H_m^\circ(\text{crII}_3, 220 \text{ K}) = (33.15 \pm 0.13) \text{ kJ} \cdot \text{mol}^{-1}$ was measured (Table S4) and the contributions from the heating of crII₃ and the liquid were subtracted. The following equation, based on the experimental data in the range (220.1 to 224.0) K, was used to estimate the crystal-phase heat capacity in the calculation of the enthalpy of fusion.

$$C_{P,m}^\circ / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 194.18 + 0.41657(T / \text{K}) \quad (3)$$

At $T = 0$ K, crII₁ is less stable than crIII by $H_m^\circ(\text{crII}_1; 0 \text{ K}) - H_m^\circ(\text{crIII}, 0 \text{ K}) = (4.02 \pm 0.42) \text{ kJ} \cdot \text{mol}^{-1}$.

Sequence III (crIII). Heat capacities (Figure 4) as well as temperature and enthalpy of fusion (Table 1) were reported in our previous publication [21]. This crystal had a smooth heat capacity curve with no solid-solid phase transitions.

In this work, spontaneous crystallization of crI resulted in formation of crII₄. If this crystal was cooled to $T = 80$ K and then heated to $T \approx 260$ K, crIII could be obtained with a negligible content of other phases. The enthalpy change $H_m^\circ(\text{l}; 286 \text{ K}) - H_m^\circ(\text{crIII}, 260 \text{ K}) = (28.53 \pm 0.11) \text{ kJ} \cdot \text{mol}^{-1}$ obtained in this work (Table S5) is in a very good agreement with the value $(28.63 \pm 0.11) \text{ kJ} \cdot \text{mol}^{-1}$ reported earlier [21].

The triple-point temperature for crIII determined in this work by fractional-melting (Figure 4) was 0.04 K higher than the value reported in our previous work [21]. Since the reliability of the earlier measurements is comparable to that of this work, we estimate the expanded uncertainty for this value to be $U(T_{\text{fus}}) = 0.03$ K (for 0.95 confidence interval).

At temperatures a few tenths of a kelvin below the temperature of fusion of crIII, heat evolution due to the formation of crII₄ was observed. Further heating of the sample resulted in formation of the (crII₄ + liquid) mixture. In all series of measurements, the heat capacity curve in the melting region had the melting peak of crIII followed by the melting peak of crII₄ (Figure 6). The relative peak heights differed in various series of measurements.

FIGURE 6. Typical melting curve for the studied sample, the first peak was assigned to melting of crIII, the second one was assigned to crII₄, – – – are corresponding triple points. The line is a guide for the eye. Uncertainties for the heat capacities are large due to long equilibration times that precluded high-precision measurements in this region.

The observed phase transformations are summarized in Figure 7.

FIGURE 7. Observed phase transformations of $[\text{C}_4\text{mim}][\text{PF}_6]$, black arrows are used for equilibrium transitions, red arrows designate non-equilibrium transformations

3.2 Thermodynamic functions and relative stability of polymorphs

Calculation of the absolute entropy of a polymorph requires heat capacities from the temperature of interest to 0 K. Extrapolation of heat capacities for the crystals from 5 K to 0 K were performed with the use of the empirical function:

$$C_{P,m} = D_3(\theta_D/T) + E(\theta_E/T) \quad (4)$$

where $D_3(\theta_D/T)$ is the Debye heat-capacity function for three degrees of freedom and $E(\theta_E/T)$ is the Einstein heat capacity function for one degree of freedom. The parameters θ_D and θ_E were 47.3 K and 52.1 K for crI and 58.2 K and 46.0 K for crII. They were determined from the experimental data in the temperature range (5.1 to 7.1) K and (5.4 to 7.9) K, respectively.

The experimental heat capacities were smoothed with polynomials. The whole temperature range, in which the measurements for a phase were performed, was split into a number of overlapping temperature intervals. In each interval, the heat capacity was fitted by a function $\sum_{i=0}^n a_i T^i$, where $n \leq 4$. The connection points between the polynomials were found in the

overlapping regions. The relative root-mean-square deviation was 0.067% and 0.085% for Sequences I and II, accordingly. The deviation plot is presented in Supplementary Material. The thermodynamic functions (Table S8), including those in the non-isothermal phase transition regions (except crII₃–crII₄), were calculated using the smoothed heat capacities. In narrow ranges where the heat capacities changed abruptly, numerical integration of the experimental heat capacities was applied. The baselines were used for calculations of the thermodynamic functions only in the pre-melting ranges.

The relative thermodynamic stability of the polymorphs is demonstrated in Figure 8. Sequence I remains metastable at all temperatures. At temperatures below $T = 281$ K, crIII is the stable phase, while above this temperature, crII₄ becomes the thermodynamically stable phase.

FIGURE 8. Relative Gibbs energy of [C₄mim][PF₆] phases: blue, Sequence I; green, Sequence II; black, Sequence III [21]; red, liquid [21].

The entropy differences $S_m^0(l, 298.15 \text{ K}) - S_m^0(X, 0 \text{ K})$, where $X = \text{crI}$, crII_1 , or crIII , determined with the experimental data for Sequences I, II, and III are $(490.6 \pm 2.3) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$,

$(492.3 \pm 2.1) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, and $(493.0 \pm 2.1) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ [21], respectively. Differences in these values are not statistically significant. Therefore, the entropy at $T = 0 \text{ K}$ for all sequences is the same. It is equal to zero, as follows from the X-ray results considered below.

The entropies of the crystals for Sequences I and II are higher than that of Sequence III at all temperatures above $T = 0 \text{ K}$. At $T > 150 \text{ K}$, the differences exceed $12 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ (Figure 9). Moreover, at $T = 200 \text{ K}$, the entropy difference becomes approximately half of the entropy of fusion for crIII. This implies that the crystals for Sequences I and II are characterized by higher disorder relative to crIII at $T > 150 \text{ K}$. This is also confirmed by structural studies discussed below.

FIGURE 9. Comparison of entropies for various $[\text{C}_4\text{mim}][\text{PF}_6]$ phases: blue, Sequence I; green, Sequence II; black, Sequence III [21]; red, glass and liquid [21]

The low-temperature heat capacities of crI and crII₁ are significantly higher than that of crIII (Figure 10). Moreover, $C_{p,m}(\text{crI})$ is higher than the heat capacity of the glass reported by Kabo *et*

al. [21]. While this phenomenon has previously been observed for some ILs [31], it is still relatively rare.

FIGURE 10. Comparison of low-temperature heat capacities for various $[\text{C}_4\text{mim}][\text{PF}_6]$ phases: blue, crI; green, crII₁; black, crIII; red, glass [21].

4. Discussion

4.1 Analysis of literature data

A summary of the temperatures and enthalpies of fusion available in the literature is given in table 1. The original abbreviations for various polymorphs are presented in table 2 for convenience.

Several studies combined [7], [16], [18], [19] spectroscopic and X-ray studies with calorimetric results. However, as demonstrated below, thermodynamic and structural data are often inconsistent and should be considered separately. We will discuss the assignment of phases in calorimetric results and then in the structural data. In some cases, interpretation of the experimental results differs from that provided in the original papers.

TABLE 1 Literature data on temperatures and enthalpies of fusion for [C₄mim][PF₆]^{a,b}

$T_{\text{fus}} / \text{K}$	$\frac{\Delta_{\text{fus}} H_{\text{m}}^{\circ}}{\text{kJ} \cdot \text{mol}^{-1}}$	Method	Reference
crI			
275 ± 8	12.8 ± 0.6	AC	This work
crII ₄			
284.55 ± 0.06	12.8 ± 0.2	AC	This work
285		visual	Gomes de Azevedo <i>et al.</i> [17]
285.3^{d}	13.3	DSC	Endo <i>et al.</i> [18]
$285.8 \pm 1.4^{\text{d}}$	13.1 ± 1.4	DSC	Endo and Nishikawa [19]
286.4^{d}	12.3	DSC	Endo <i>et al.</i> [20]
crIII			
283.51 ± 0.03	19.60 ± 0.02	AC	Kabo <i>et al.</i> [21]
283.55 ± 0.03		AC	This work
$285.3 \pm 1.4^{\text{d}}$	22.6 ± 3.2	DSC	Endo and Nishikawa [19]
Unknown phase			
275.1		DSC	Choudhury <i>et al.</i> [7]
276.4	9.21 ± 0.09	DSC	Domńska and Marciniak [8]
280.0	19.91 ± 0.20	DSC	Troncoso <i>et al.</i> [9]
281.0	13.2	DSC	Fox <i>et al.</i> [10]

282 ± 2	12 ± 2 ^c	DSC	Jin <i>et al.</i> [11]
283		DSC	Huddleston <i>et al.</i> [12]
283			Tokuda <i>et al.</i> [13]
284		DSC	Fredlake <i>et al.</i> [14]
284		not specified	Dibrov and Kochi [15]
284		AC	Triolo <i>et al.</i> [16]

^a DSC, differential scanning calorimetry; AC, adiabatic calorimetry; visual, visual determination;

^b the reported uncertainties correspond to the 0.95 confidence interval for normal distribution ($k = 2$); ^c a sum of enthalpies of transition and fusion; ^d a peak maximum.

TABLE 2

Notation of crystal phases

Reference	Literature notation	This work
Triolo <i>et al.</i> [16]	crI	Sequence II or crIII ^a
	crII	crI or crIII ^b
Endo <i>et al.</i> [20], [19], [22]	α	Sequence I
Saouane <i>et al.</i> [6]	β	Sequence II
	γ	crIII
Endo <i>et al.</i> [18]	α	crI
	β	crII ₃

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^a Sequence II from calorimetric measurements, crIII from X-ray data; ^b crI was obtained after crystallization on heating starting from glass, the crystal obtained in another calorimetric experiment was crIII; ^c crII₃ from DSC measurements and crIII from spectroscopic measurements.

4.2 Calorimetry

Melting of [C₄mim][PF₆] has been studied mainly by DSC (Table 1). Adiabatic calorimetry was used by Kabo *et al.* [21] and Triolo *et al.* [16].

Triolo *et al.* [16] described a number of polymorphs for the compound based on their measurements with adiabatic calorimetry. The crystalline phase they obtained by heating the glass underwent the only solid-solid phase transition with $\Delta_{tr}H_m(252\text{ K}) \approx 1.4\text{ kJ}\cdot\text{mol}^{-1}$. This thermal behavior is similar to crI in our work. Heating of crI resulted in formation of another phase, which could also be obtained by crystallization of the liquid at $T = 260\text{ K}$. Two solid-solid phase transitions at $T_{tr} = 177\text{ K}$ ($\Delta_{tr}H_m = 0.5\text{ kJ}\cdot\text{mol}^{-1}$) and $T_{tr} = 217.5\text{ K}$ ($\Delta_{tr}H_m = 0.3\text{ kJ}\cdot\text{mol}^{-1}$) detected by Triolo *et al.* [16] for this phase can be assigned to the crII₁-to-crII₂ and crII₂-to-crII₃ transformations observed in the present work. Enthalpies of transition reported by Triolo *et al.* [16] are significantly lower than the values obtained in this work. The presence of crIII in their sample during measurements could account for the inconsistency, but this is speculation only. Triolo *et al.* [16] found that the crII₃ polymorph became unstable at $T = 246\text{ K}$ and transformed into an unknown phase. We suggest this phase to be crIII based on similar observations in our experiments. The observed phase transformations can be described as follows:

The temperature of fusion of $T_{\text{fus}} = 284 \text{ K}$ reported by Triolo *et al.* [16] for an independent run can be assigned to melting of either crII₄ or crIII.

In a study using DSC, Endo *et al.* [18] reported $T_{\text{fus}} = 285.3 \text{ K}$ for [C₄mim][PF₆]. While this value is close to that reported by Kabo *et al.* [21], it does not imply that both values should be assigned to the same polymorph. Kabo *et al.* [21] obtained the heat capacity curve from 5 K to T_{fus} and no trace of a solid-solid phase transition was found. Endo *et al.* [18] reported two solid-solid phase transitions at $T = 250 \text{ K}$ and $T = 276 \text{ K}$. The first transition corresponds to irreversible process, as reported in a subsequent paper from the same group [22]. Additionally, the enthalpy of fusion reported by Endo *et al.* [18] is 32 % lower than the value obtained by adiabatic calorimetry [21].

It is probable that Endo *et al.* [18] observed melting of crII₄ but not crIII. The crystal phase obtained below $T = 250 \text{ K}$ is then crI. A peak at $T = 276 \text{ K}$ was later observed by the authors in Sequences II and III [19]. The temperature-dependent Raman spectra had no changes that could be associated with this transformation [19]. This peak was found in the DSC curves obtained with different instruments in the same laboratory [18–20]. An anomaly with a maximum at $T = 278 \text{ K}$ was also observed by Troncoso *et al.* [9]. Therefore, the peak at $T = 276 \text{ K}$ is not a phase transition belonging to Sequence II. This peak may be caused by an unknown phase transition or fusion of crI. It is not possible to resolve this ambiguity without further research.

The reported transformations can be summarized as

Later, Endo and Nishikawa [19] noted that transformation of crII₃ into crIII occurs near $T = 255 \text{ K}$ and this process is accompanied by heat evolution. The temperatures and enthalpies of fusion for crII₃ and crIII were also reported (table 1). The enthalpies of fusion agree within the

experimental uncertainty with the results from adiabatic calorimetry. An important advantage of that work is that the instrument used allowed simultaneous spectroscopic and calorimetric measurements and provided structural information in addition to thermodynamic data. In summary, the following phase transformations were observed:

The same instrument was also used by Endo *et al.* [20], who reported somewhat different parameters of fusion for crII₄.

In a number of other works, complex phase behavior was also observed. A solid-solid phase transition at $T_{\text{tr}} = 258.0 \text{ K}$ with the enthalpy $\Delta_{\text{tr}}H_{\text{m}} = 10.67 \pm 0.11 \text{ kJ}\cdot\text{mol}^{-1}$ followed by fusion at $T_{\text{fus}} = 276.4 \text{ K}$ was observed by Domańska and Marciniak [8]. In the DSC curve obtained at a rate of $10 \text{ K}\cdot\text{min}^{-1}$, crystallization was immediately followed by the solid-solid phase transition, and the peak of fusion had a simpler shape than in later work by Choudhury *et al.* [7], who reported a DSC curve for [C₄mim][PF₆] from $T = (103 \text{ to } 313) \text{ K}$. Crystallization of the supercooled liquid started at approximately $T = 233 \text{ K}$. The authors found an irreversible solid-solid phase transition at $T_{\text{tr}} \approx 263 \text{ K}$ followed by a melting peak with complex shape. A complex melting curve was also noted by Troncoso *et al.* [9], who used a relatively low heating rate ($0.075 \text{ K}\cdot\text{min}^{-1}$) and found that the melting curve included a maximum at $T = 278 \text{ K}$. Based on the obtained DSC curve, Jin *et al.* [11] reported a transition at $T \approx 272 \text{ K}$ followed by melting of the compound. In all these works, mixtures of crystal phases were obtained, making the assignment to specific phases impossible.

4.3 Structural studies

An X-ray analysis of the crystal phase grown at $T = 243$ K by Choudhury *et al.* [7] showed that the crystal contains the $G'T$ conformer of the cation (Figure 11). A similar structure obtained by shock-induced crystallization was reported by Dibrov and Kochi [15]. Triolo *et al.* [16] noted that their X-ray powder diffraction data at $T = 190$ K agreed with the X-ray analysis by Choudhury *et al.* [7] and Dibrov and Kochi [15] recorded at $T = 180$ K and $T = 173$ K, respectively. Triolo *et al.* [16] concluded that this crystal belonged to Sequence II. If this conclusion was correct, then the diffraction patterns would be different since they corresponded to different phases crII_1 and crII_2 . Based on the procedures used for crystallization [15], [16], the obtained diffractograms should be assigned to crIII . This conclusion agrees with the results by Saouane *et al.* [6], who reported the crystal structure of crIII at $T = 263$ K. A relatively small (8 %) admixture of GT conformer observed by Saouane *et al.* [6] can be explained by pre-melting.

FIGURE 11. $[\text{C}_4\text{mim}]^+$ conformers

Saouane *et al.* [6] reported the following transformations:

Saouane *et al.* [6] are the only group to report the structure of crI and crII₂ at ambient pressure.

They noted that crI contains 100 % of the *GT* conformer of the cation at $T = 100 \text{ K}$ and 75 % *GT* + 25 % *G'T* conformer at $T = 193 \text{ K}$. This disordering is likely associated with the hump near $T = 190 \text{ K}$ in the heat capacity curve of crI (figure 2) observed in our measurements. A mixture of conformers with *TT* being the predominant component was detected in crII₂.

X-ray studies discussed above [6], [7], [15], [16] demonstrated that at low temperatures crI and crIII are ordered. Thus, the entropy of these crystals is equal to zero at $T = 0 \text{ K}$. While the X-ray data demonstrate that crII₂ is conformationally disordered, the calorimetric results from this work demonstrate that crII₁ is ordered, as evidenced by the equivalence of the entropies for the liquid calculated with all three phase sequences.

Raman spectra of the crystal phases at ambient pressure are available at several temperatures (Table 3). They confirm the major conformers of the cation in each phase identified by the X-ray diffraction. Unambiguous identification of the phases is possible only when the spectra are accompanied by simultaneous calorimetric measurements or by a well-defined thermal history. Raman spectra have not been reported for many polymorphs of [C₄mim][PF₆], and the existing spectra for crI and crIII cannot be compared in detail, as they were recorded at different temperatures.

TABLE 3 Available Raman spectra for various polymorphs of [C₄mim][PF₆]

Phase	T / K	Reference
crI	193	Endo <i>et al.</i> [18]
	229	Endo <i>et al.</i> [18]
	238	Saouane <i>et al.</i> [6]
crII ₃	234	Endo and Nishkawa [19]
	249	Saouane <i>et al.</i> [6]
crII ₃ or crII ₄	254	Endo <i>et al.</i> [18]
crIII	263	Saouane <i>et al.</i> [6]
	272	Endo and Nishkawa [19]
	280	Endo <i>et al.</i> [18]

4.4 Elevated pressure

Gomes de Azevedo *et al.* [17] studied the pressure dependence of the melting temperature for [C₄mim][PF₆] from 0.1 MPa to 89 MPa from acoustic determinations. From these data, the slope $dP/dT_{\text{fus}} = (4.83 \pm 0.33) \text{ MPa} \cdot \text{K}^{-1}$ can be found. Russina *et al.* [23] reported $dP/dT_{\text{fus}} = 5.2 \pm 0.2 \text{ MPa} \cdot \text{K}^{-1}$ over the range (285 to 373) K based on their own high-pressure Raman measurements and data by Gomes de Azevedo *et al.* [17]. The Raman spectra reported by Russina *et al.* [23] demonstrated that crII₄ was formed. Later, this conclusion was confirmed by X-ray and Raman data [6].

If pressure is further increased at $T = 293$ K, one of phases belonging to Sequence I is formed [23], [6], [24]. At $P \geq 1.2$ GPa, a new sequence of two polymorphs was detected, and their crystallographic parameters and Raman spectra were reported [24]. Surprisingly, further increase of pressure resulted in the structure becoming amorphous and the formation of either a glass or liquid.

5. Conclusion

Adiabatic calorimetry was used to detect and to fully identify phase transformations for 1-butyl-3-methylimidazolium hexafluorophosphate at ambient pressure. Three sequences of crystal phases were found and the parameters of equilibrium phase transitions were reported. Crystal structures reported in literature were assigned to the phases obtained in this work. Many inconsistencies reported in the literature were identified based on the knowledge of the relative phase stabilities and transformation sequences reported in this work. Problems that previously prevented correct interpretation of the observed phase transformations include (i) incorrect thermodynamic interpretation of the observed phase transitions, and (ii) different polymorphs obtained from the same sample for separate calorimetric and structural studies.

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imply endorsement by the National Institute of Standards and Technology. Similar products by other manufacturers may be found to work as well or better.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at

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$[\text{C}_4\text{mim}][\text{PF}_6]$