

## Solution Structures of 1-Butyl-3-methylimidazolium Hexafluorophosphate Ionic Liquid Saturated with CO<sub>2</sub>: Experimental Evidence of Specific Anion–CO<sub>2</sub> Interaction

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X-ray diffraction measurements for 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid ([BMIM][PF<sub>6</sub>])–CO<sub>2</sub> systems were carried out at high pressures with a newly developed polymer cell. The intermolecular distribution functions ( $g^{\text{inter}}(r)$ ) were obtained at 25 °C for neat [BMIM][PF<sub>6</sub>] and its solutions saturated with CO<sub>2</sub> at 4 and 15 MPa, where the mole fractions ( $x$ ) of CO<sub>2</sub> correspond to 0.5 and 0.7, respectively. In  $g^{\text{inter}}(r)$  for  $x = 0.5$ , two peaks appeared at around 2.8 and 3.2 Å. These two peaks in  $g^{\text{inter}}(r)$  appreciably increased for  $x = 0.7$ ; moreover, there was another peak observed at ~3.8 Å. Only assuming the correlations between CO<sub>2</sub> and [PF<sub>6</sub>]<sup>−</sup>, it is reasonably determined that the nearest-neighbor P([PF<sub>6</sub>]<sup>−</sup>) · · · C(CO<sub>2</sub>) distances are 3.57 and 3.59 Å with the coordination numbers being 1.8 and 4.0 for  $x = 0.5$  and 0.7, respectively. It is concluded that CO<sub>2</sub> molecules are preferentially solvated to the [PF<sub>6</sub>]<sup>−</sup> anion.

### Introduction

The biphasic systems consisting of room temperature ionic liquid (IL) and supercritical (sc) CO<sub>2</sub> provide the opportunity to develop environmentally benign green chemical processes. Since Brennecke et al.<sup>1</sup> first reported the possibility of extracting solutes from ILs with scCO<sub>2</sub>, there have been a variety of attempts made such as chemical reaction, phase separation, and gas separation.<sup>2</sup> Besides the above-mentioned applications, we are interested in IL–scCO<sub>2</sub> systems from a fairly fundamental viewpoint; although a strong Coulombic field exists in ILs, why is non-dipolar CO<sub>2</sub> quite highly soluble in ILs? From the solubility measurements and molecular dynamics simulations, Maginn et al.<sup>3</sup> recently concluded that the association of CO<sub>2</sub> with the anion is of primary importance for the high solubilities. A number of researchers reported the phase behaviors in IL–scCO<sub>2</sub> systems;<sup>4</sup> however, there have been quite a few studies<sup>5,6</sup> on intermolecular interactions and structures at the microscopic level. Here, we perform X-ray diffraction measurements for [BMIM][PF<sub>6</sub>]-CO<sub>2</sub> solutions and discuss the specific interaction between CO<sub>2</sub> and anion.

### Experimental Section

The sample of [BMIM][PF<sub>6</sub>] was prepared and purified as described previously.<sup>7</sup> An appropriate amount of [BMIM][PF<sub>6</sub>] was transferred into a high-pressure X-ray diffraction cell inside a dry glovebox under an Ar atmosphere. The high-pressure cell was made of poly(etherether ketone) (PEEK) and can withstand

temperatures and pressures, at least, up to ~130 °C and ~35 MPa, respectively. The details of the polymer cell are given in the Supporting Information. In the high-pressure experiments, [BMIM][PF<sub>6</sub>] was pressurized with CO<sub>2</sub> (Showa Tansan Co., Ltd.; 99.99 vol % up) using a cooled liquid chromatography pump (JASCO, SCF-Get). The sample was mixed and allowed to equilibrate for a few hours. During each measurement, the sample pressure remained unchanged, which was monitored with a pressure gauge built in a back-pressure regulator (JASCO, SCF-Bpg).

X-ray diffraction measurements for neat [BMIM][PF<sub>6</sub>] and its solutions saturated with CO<sub>2</sub> at 4 ± 0.2 and 15 ± 1 MPa were carried out at 25 ± 3 °C with the high-pressure polymer cell. The sample of neat [BMIM][PF<sub>6</sub>] was also measured with a flat quartz tray (30 mm wide × 80 mm length × 3 mm depth) covered with a hemispherical thin polyethylene film. A  $\theta$ – $\theta$  diffractometer with Mo K $\alpha$  radiation ( $\lambda = 0.7107$  Å) manufactured by Rigaku Co. was used for the measurements. Scattered X-ray intensities were collected with a fixed counting time of 100 s over the wide angular ( $2\theta$ ) range between 3 and 150° at an interval of 0.2°, corresponding to that of the scattering vector magnitude ( $Q = 4\pi \sin \theta/\lambda$ ) between 0.5 and 17.1 Å<sup>−1</sup>. The whole angular range in each run of measurements was scanned two or four times to obtain the diffraction data with good counting statistics. It was confirmed that the diffraction data among the different runs were reproducible within the experimental errors. The maximum and minimum count numbers and statistical errors were given in the Supporting Information. The scattered intensities of the empty polymer cell were collected as the background in the same manner. Details of X-ray diffraction measurements have previously been described elsewhere.<sup>8</sup>

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## Data Reduction

The empty polymer cell showed broad diffraction peaks at  $2\theta < 15^\circ$ ; however, the background peaks were adequately corrected by comparing the interference terms ( $i(Q)$ ) and distribution functions ( $g(r)$ ) observed for [BMIM][PF<sub>6</sub>] with the polymer cell and the quartz tray at atmospheric pressure. It was confirmed that the polymer cell can provide almost the same results as the conventional quartz tray (please see the Supporting Information). The other correction and normalization procedures for the observed X-ray diffraction intensities were similar to those described in the previous paper.<sup>8a</sup>

The radial distribution function ( $g(r)$ ) can be obtained by a Fourier transform of the interference term ( $i(Q)$ ):

$$g(r) = 1 + (2\pi^2\rho r)^{-1} \int_0^{Q_{\max}} Qi(Q) \sin(Qr) dQ \quad (1)$$

Here,  $\rho$  is the number density of the stoichiometric unit and  $Q_{\max}$  is the upper limit of the integral;  $Q_{\max} = 17.1 \text{ \AA}^{-1}$  in this case.  $i(Q)$  is expressed by a sum of intra- and intermolecular interference terms:

$$i(Q) = i^{\text{intra}}(Q) + i^{\text{inter}}(Q) \quad (2)$$

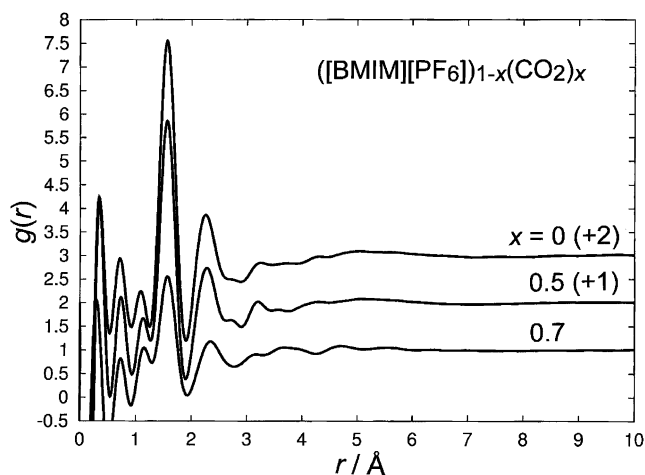
$i^{\text{intra}}(Q)$  is divided into three contributions arising from individual chemical species in ([BMIM][PF<sub>6</sub>])<sub>1-x</sub>(CO<sub>2</sub>)<sub>x</sub>:

$$i^{\text{intra}}(Q) = (1-x)i^{\text{intra}}_{[\text{BMIM}]^+}(Q) + (1-x)i^{\text{intra}}_{[\text{PF}_6]^-}(Q) + xi^{\text{intra}}_{\text{CO}_2}(Q) \quad (3)$$

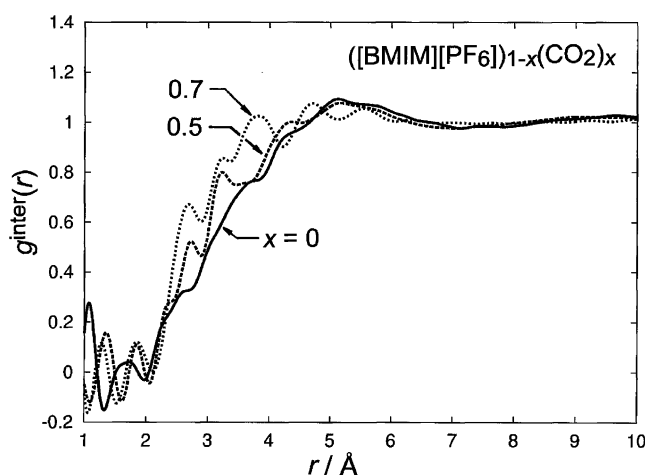
where  $x$  is the mole fraction of CO<sub>2</sub>. The values of  $x$  for the neat and sample solutions saturated with CO<sub>2</sub> at 4 MPa were evaluated from the solubility data<sup>4</sup> to be 0 and 0.5, respectively, and  $x$  at 15 MPa was assumed to be 0.7 for lack of the solubility data, of which the details will be discussed in the following section. The number density ( $\rho$ ) for each sample was calculated from  $x$  and the volume expansion data.<sup>9</sup> We estimated  $i^{\text{intra}}_{[\text{BMIM}]^+}(Q)$  from the crystal structure of [BMIM]<sup>+</sup> with [BPh<sub>4</sub>]<sup>-</sup>,<sup>10</sup>  $i^{\text{intra}}_{[\text{PF}_6]^-}(Q)$  from the crystal structure of [PF<sub>6</sub>]<sup>-</sup> in a ruthenium complex,<sup>11</sup> and  $i^{\text{intra}}_{\text{CO}_2}(Q)$  from the electron diffraction results of neat CO<sub>2</sub> gas.<sup>12</sup> Then, the intermolecular distribution function ( $g^{\text{inter}}(r)$ ) was obtained by the Fourier transform of  $i^{\text{inter}}(Q)$ .

## Results and Discussion

The observed X-ray total distribution functions ( $g(r)$ ) for the [BMIM][PF<sub>6</sub>]-CO<sub>2</sub> solutions with different compositions of  $x = 0, 0.5$ , and  $0.7$  are given in Figure 1. Several peaks observed in the low- $r$  region result from the intramolecular contributions of each chemical species. The first prominent peak at  $r \approx 1.6 \text{ \AA}$  is assigned to the P-F correlations in [PF<sub>6</sub>]<sup>-</sup>, and the second peak at  $r \approx 2.3 \text{ \AA}$  is mainly attributable to the F-F correlations in [PF<sub>6</sub>]<sup>-</sup> and to the correlations between the second-nearest atoms in the imidazolium ring of [BMIM]<sup>+</sup>. These two peaks considerably decrease with an increase in the mole fraction of CO<sub>2</sub>. Broad peaks observed in the middle range of  $r$  between  $\sim 2.5$  and  $\sim 6 \text{ \AA}$  are sensitive to the increase in  $x$ . We do not find any noticeable peaks at  $r > \sim 6 \text{ \AA}$ . In Figure 2, the intermolecular distribution functions ( $g^{\text{inter}}(r)$ ) for the three samples indicate that the dissolution of CO<sub>2</sub> brings about structural changes in the solutions. In the  $g^{\text{inter}}(r)$  of the sample with  $x = 0.5$ , two peaks appear at approximately 2.8 and 3.2  $\text{\AA}$ . The two peaks appreciably increase at  $x = 0.7$ ; moreover, there is another peak observed at  $\sim 3.8 \text{ \AA}$ . These peaks should



**Figure 1.** Observed total distribution functions ( $g(r)$ ) for [BMIM]-[PF<sub>6</sub>]-CO<sub>2</sub> solutions with different compositions of  $x = 0, 0.5$ , and  $0.7$ .



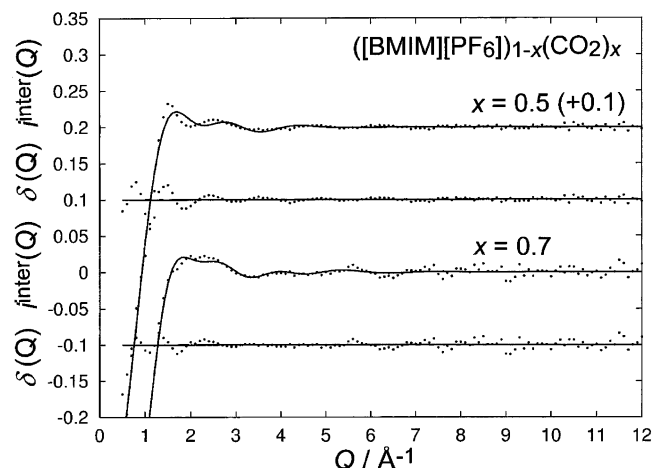
**Figure 2.** Intermolecular distribution functions ( $g^{\text{inter}}(r)$ ) for [BMIM]-[PF<sub>6</sub>]-CO<sub>2</sub> solutions with different compositions of  $x = 0, 0.5$ , and  $0.7$ .

reflect the solvation structures around CO<sub>2</sub>; however, it cannot be interpreted immediately because CO<sub>2</sub> molecules can possibly interact with the cation and anion species in the present system. Furthermore, termination ripples associated with the Fourier transform may superimpose on the observed  $g^{\text{inter}}(r)$ , which prevents detailed discussion on the intermolecular structures.

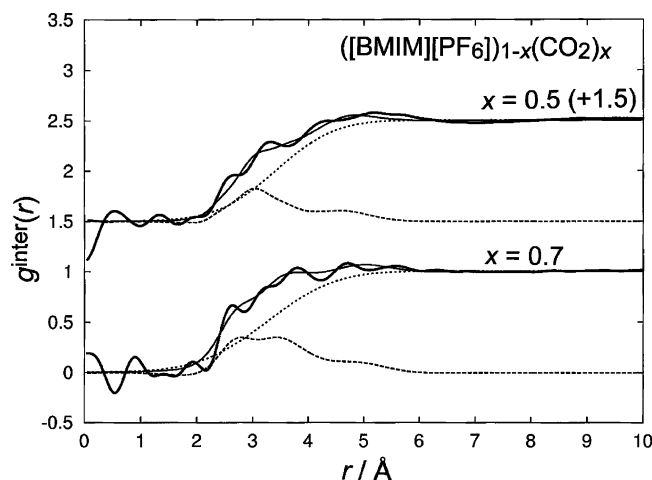
To derive information about the solution structures in [BMIM]-[PF<sub>6</sub>]-CO<sub>2</sub>, we analyze the experimental intermolecular interference terms ( $i^{\text{inter}}(Q)$ ) in the following procedure. The calculated intermolecular interference term ( $i^{\text{calcd}}(Q)$ ) is divided into the short-range contribution due to the nearest-neighbor molecules ( $i^s(Q)$ ) and the long-range one ( $i^l(Q)$ ):

$$i^{\text{calcd}}(Q) = i^s(Q) + i^l(Q) \quad (4)$$

Each term is given as a function of the interatomic distance ( $r_{ij}$ ), the root-mean-square displacement ( $l_{ij}$ ), and the coordination number ( $n_{ij}$ ) for the  $i$ - $j$  atom pair. In the calculations,  $r_{ij}$ ,  $l_{ij}$ , and  $n_{ij}$  for  $i^s(Q)$  and  $r_0$  and  $l_0$  for  $i^l(Q)$  are taken to be adjustable parameters.<sup>8</sup> The least-squares fits to the experimental interference terms were performed in the range  $0.5 \text{ \AA}^{-1} \leq Q \leq 12 \text{ \AA}^{-1}$  using the SALS program.<sup>8,13</sup> We first attempt to refine the experimental  $i^{\text{inter}}(Q)$  by taking account of only the nearest-neighbor short-range interactions between [BMIM]<sup>+</sup> and CO<sub>2</sub> because CO<sub>2</sub> molecules favorably interact with aromatic com-



**Figure 3.** Experimental intermolecular interference terms ( $i^{\text{inter}}(Q)$ , dots) for [BMIM][PF<sub>6</sub>]-CO<sub>2</sub> solutions with  $x = 0.5$  and  $0.7$  and the best-fitted results (solid lines). Residual functions ( $\delta(Q)$ ) are shown below (dots).



**Figure 4.** Experimental intermolecular distribution functions ( $g^{\text{inter}}(r)$ , thick solid line) for [BMIM][PF<sub>6</sub>]-CO<sub>2</sub> solutions with  $x = 0.5$  and  $0.7$  and the Fourier transforms of the solid lines in Figure 3 (thin solid line). The short- and long-range contributions are represented by the dashed and dotted lines, respectively.

pounds; in such cases, CO<sub>2</sub> is preferentially located in the perpendicular direction to the aromatic plane.<sup>14</sup> Although several possible geometries were considered, no reasonable solution to reproduce the experimental  $i^{\text{inter}}(Q)$  have been obtained. On the other hand, by assuming only the nearest-neighbor short-range interactions between [PF<sub>6</sub>]<sup>-</sup> and CO<sub>2</sub>, the experimental  $i^{\text{inter}}(Q)$  in each solution was successfully reproduced. These refinement results suggest that the intermolecular interaction between [BMIM]<sup>+</sup> and CO<sub>2</sub> are not so strong and may exhibit a broad distribution.

The experimental and best-fitted results of  $i^{\text{inter}}(Q)$  for [BMIM][PF<sub>6</sub>]-CO<sub>2</sub> solutions with  $x = 0.5$  and  $0.7$  are given in Figure 3, and the corresponding intermolecular distribution functions ( $g^{\text{inter}}(r)$ ) are shown in Figure 4. In both solutions, the long-range contribution seems to remain virtually the same and the dissolution of CO<sub>2</sub> brings about effective changes in the first solvation sphere at  $\sim 2.5 \text{ \AA} < r < \sim 5 \text{ \AA}$ . This implies that the long-range liquid structure may be held even in highly CO<sub>2</sub>-dissolved solutions presumably due to strong Coulombic interactions between the ionic species. The results of the least-squares refinements are summarized in Table 1, where  $r(\text{PC})$  and  $l(\text{PC})$  are the interatomic distance and the root-mean-square displacement between P([PF<sub>6</sub>]<sup>-</sup>) and C(CO<sub>2</sub>), respectively, and

**TABLE 1: Results of the Least-Squares Refinements for the Intermolecular Interference Terms ( $i^{\text{inter}}(Q)$ ) of ([BMIM][PF<sub>6</sub>])<sub>1-x</sub>(CO<sub>2</sub>)<sub>x</sub> with  $x = 0.5$  and  $0.7^a$**

interaction	parameter	$x = 0.5$	$x = 0.7$
[PF <sub>6</sub> ] <sup>-</sup> ··· CO <sub>2</sub>	$r(\text{PC})/\text{\AA}$	3.57(1)	3.59(1)
	$l(\text{PC})/\text{\AA}$	0.27(1)	0.35(1)
	$n(\text{PC})$	1.8(1)	4.0(1)
	$\theta/\text{deg}$	54(1)	46(4)
	$\phi/\text{deg}$	49(1)	24(1)
	$\tau/\text{deg}$	-74(1)	-99(4)
	$\omega/\text{deg}$	45.1(2)	0(2)
long range	$r_0/\text{\AA}$	3.61(1)	3.52(1)
	$l_0/\text{\AA}$	0.82(1)	0.93(1)

<sup>a</sup> Estimated standard deviations are given in parentheses.

$n(\text{PC})$  is the coordination number of C(CO<sub>2</sub>) around P([PF<sub>6</sub>]<sup>-</sup>). The polar angle ( $\theta$ ) and the azimuth angle ( $\phi$ ) are defined for the vector from P([PF<sub>6</sub>]<sup>-</sup>) to C(CO<sub>2</sub>), where the P atom of [PF<sub>6</sub>]<sup>-</sup> is positioned at the origin with six F atoms on the  $x$ ,  $y$ , and  $z$  axes. Similarly,  $\tau$  and  $\omega$  stand for the polar and azimuth angles in terms of the molecular axis of CO<sub>2</sub>. As mentioned in the Data Reduction section, the  $x$  value of the sample at 15 MPa was assumed to be 0.7 for lack of solubility data. One may consider that  $x = 0.7$  is overestimated; hence, the least-squares refinement has been carried out with  $x = 0.6$ , which provides quite similar results with those with  $x = 0.7$  except for a decrease in  $n(\text{PC})$  from 4.0 to 3.4 (please see the Supporting Information). Then, we proceed further discussion with  $x = 0.7$  for the sample at 15 MPa. As is seen from Table 1,  $r(\text{PC})$  remains virtually constant at  $\sim 3.6 \text{ \AA}$  independent of  $x$ , whereas  $n(\text{PC})$  increases approximately twice with an increase in  $x$  from 0.5 to 0.7. It is found, moreover, that C(CO<sub>2</sub>) is located at a position almost equivalent to three F atoms in the [PF<sub>6</sub>]<sup>-</sup> anion and the orientation of CO<sub>2</sub> relative to the [PF<sub>6</sub>]<sup>-</sup> anion would be sensitively affected by the change in  $x$ . According to the least-squares refinements, the peaks at 2.8 and 3.2  $\text{\AA}$  in  $g^{\text{inter}}(r)$  are mainly attributable to the F([PF<sub>6</sub>]<sup>-</sup>)-O(CO<sub>2</sub>) and F([PF<sub>6</sub>]<sup>-</sup>)-C(CO<sub>2</sub>) interactions and the peak at 3.8  $\text{\AA}$  is mainly attributable to the P([PF<sub>6</sub>]<sup>-</sup>)-O(CO<sub>2</sub>) and P([PF<sub>6</sub>]<sup>-</sup>)-C(CO<sub>2</sub>) interactions. The present experimental results are in good agreement with the MD simulations' results for a mixture of [BMIM][PF<sub>6</sub>]-CO<sub>2</sub> ( $x = 0.1$ ) at 25 °C as recently reported by Maginn et al.<sup>3</sup> These facts strongly suggest that CO<sub>2</sub> molecules are preferentially solvated to the [PF<sub>6</sub>]<sup>-</sup> anion rather than the [BMIM]<sup>+</sup> cation. However, a careful examination reveals somewhat different points between the present experimental results and the previous computational results. The experimental  $r(\text{PC})$  seems to be smaller than that calculated for  $g^{\text{inter}}(r)$  of P([PF<sub>6</sub>]<sup>-</sup>)-C(CO<sub>2</sub>) interactions, and the orientation of CO<sub>2</sub> might not be "tangent" to the spherical anion, as described in their paper.<sup>3</sup> Interpreting the present results straightforwardly, one can derive a picture that CO<sub>2</sub> molecules slightly penetrate into hollows of the [PF<sub>6</sub>]<sup>-</sup> anion. This finding is consistent with very small volume expansions of [BMIM][PF<sub>6</sub>] caused by the dissolution of CO<sub>2</sub>.<sup>4a,d,e</sup> The coordination numbers ( $n(\text{PC})$ ) are 1.8 and 4.0 at  $x = 0.5$  and  $0.7$ , respectively. This means that the numbers of [PF<sub>6</sub>]<sup>-</sup> anions interacting with a single CO<sub>2</sub> molecule remain almost constant at 1.8 and 1.7 at  $x = 0.5$  and  $0.7$ , respectively. Very interestingly, this is in harmony with the molecular state of water in imidazolium ionic liquids, where water molecules can form similar 1:2 type H-bonded complexes with two anions such as anion ··· HOH ··· anion.<sup>15,16</sup>

In the present work, we have experimentally determined the solvation structures in [BMIM][PF<sub>6</sub>]-CO<sub>2</sub> solutions with a newly developed high-pressure X-ray diffraction cell. It has been demonstrated that CO<sub>2</sub> molecules are preferentially solvated to

the  $[\text{PF}_6]^-$  anion. Further studies of IL– $\text{CO}_2$  systems composed of a series of cation and anion combinations, which are now in progress, can provide more reliable pictures of the solution structures that are accountable for the specific intermolecular interactions between ILs and  $\text{CO}_2$ .

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**Supporting Information Available:** Figures showing a schematic drawing of the high-pressure X-ray diffraction cell, the total interference terms ( $i(Q)$ ) and the intermolecular interference terms ( $i^{\text{inter}}(Q)$ ) of [BMIM][ $\text{PF}_6$ ] with the polymer cell and the quartz tray, and the intermolecular distribution functions ( $g^{\text{inter}}(r)$ ) of [BMIM][ $\text{PF}_6$ ] with the polymer cell and the quartz tray and tables showing the maximum and minimum count numbers and statistical errors in X-ray diffraction measurements and the least-squares refinement for ([BMIM]- $[\text{PF}_6]_{1-x}(\text{CO}_2)_x$  at 15 MPa with  $x = 0.6$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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