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# Molecular Dynamics Simulations of Ionic Liquids: Cation and Anion Dependence of Self-Diffusion Coefficients of Ions

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Molecular dynamics simulations of a series of ionic liquids [1-alkyl-3-methylimidazolium (alkyl = methyl, ethyl, butyl, hexyl, and octyl), 1-butylpyridinium, *N*-butyl-*N,N,N*-trimethylammonium and *N*-butyl-*N*-methylpyrrolidinium cations combined with a (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>−</sup> anion ([mmim][TFSA], [emim][TFSA], [bmim][TFSA], [C<sub>6</sub>mim][TFSA], [C<sub>8</sub>mim][TFSA], [bpy][TFSA], [(*n*-C<sub>4</sub>H<sub>9</sub>)(CH<sub>3</sub>)<sub>3</sub>N][TFSA], and [bmpro][TFSA]) and a 1-butyl-3-methylimidazolium combined with BF<sub>4</sub><sup>−</sup>, PF<sub>6</sub><sup>−</sup>, CF<sub>3</sub>CO<sub>2</sub><sup>−</sup>, CF<sub>3</sub>SO<sub>3</sub><sup>−</sup>, and (C<sub>2</sub>F<sub>5</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>−</sup> anions ([bmim][BF<sub>4</sub>], [bmim][PF<sub>6</sub>], [bmim][CF<sub>3</sub>CO<sub>2</sub>], [bmim][CF<sub>3</sub>SO<sub>3</sub>], and [bmim][BETA]) were carried out using the OPLS force field for ionic liquids. The force field was refined on the basis of ab initio molecular orbital calculations of isolated ions and experimental densities for four ionic liquids. The densities calculated for the 13 ionic liquids agreed with the experimental values within a 2% error. The self-diffusion coefficients calculated for the ions in the 13 ionic liquids were compared with the experimental values obtained by the NMR measurements. Although the calculated self-diffusion coefficients were about 1 order smaller than the experimental ones, the cation and anion dependence (the effects of alkyl chain length in imidazolium, cation structures, and anion species) of the experimental self-diffusion coefficients was reproduced by the simulations quite well in most cases. The translational motion of the terminal carbon atoms in the alkyl chains of the imidazolium cations on the time scale of a few nanoseconds is significantly faster than that of the atoms in the imidazolium rings and anions, which suggests that the dynamics of atoms in the polar domains of the ionic liquids is significantly different from that in the nonpolar domains. The factors determining the self-diffusion coefficients of the ions are also discussed.

## Introduction

Ionic liquids attract considerable interest, since a broad range of applications, including low-volatile solvents for green chemistry and electrolytes for electronic devices, are expected due to the negligible vapor pressure, low flammability, high ionic conductivity, and electrochemical stability of the ionic liquids.<sup>1–10</sup> The physical properties of the ionic liquid depend on the choice of the cation and anion. The melting point, density, viscosity, and ionic conductivity can vary significantly when subtle changes are made to the structure of the cation or anion. The physical properties must be known before an ionic liquid can be used in application.<sup>11</sup> Therefore, the development of a systematic method to select an ion pair for rational design of new ionic liquids is essential for the applications of the ionic liquids.

An estimation of the transport properties of the ions in the ionic liquids is important for designing new ionic liquids for electrolytes. The viscosity and ionic conductivity of the ionic liquids depend on the translational motion of the ions. The motion of the ions can be simulated by molecular dynamics

calculations. Molecular dynamics simulation will be a powerful tool for designing new ionic liquids for electrolytes if it can estimate the transport properties of the ions sufficiently accurately. Several groups calculated the self-diffusion coefficients of the ions in the ionic liquids by molecular dynamics simulations.<sup>12–30</sup> In early simulations, the self-diffusion coefficients were calculated from short simulations (1 ns or less). However, recently reported simulations show that a sufficiently long simulation (10 ns or more) is necessary to observe the diffusive behavior of the ions at room temperature, since the diffusion of the ions in the ionic liquids is very slow at room temperature.<sup>11,31</sup> The self-diffusion coefficients of the anions and cations in a few ionic liquids were calculated from sufficiently long simulations,<sup>16,24</sup> but a systematic evaluation of the performance of molecular dynamics simulations for estimating the self-diffusion coefficients of the ions in the ionic liquids has not yet been reported. It was not clear how accurately molecular dynamics simulations using a force field can predict the anion and cation dependence of the self-diffusion coefficients. In this paper we refined the OPLS force field for the ionic liquids on the basis of ab initio calculations. We calculated the self-diffusion coefficients of the ions in 13 ionic liquids from sufficiently long molecular dynamics simulations using the refined force field and compared them with the experimental

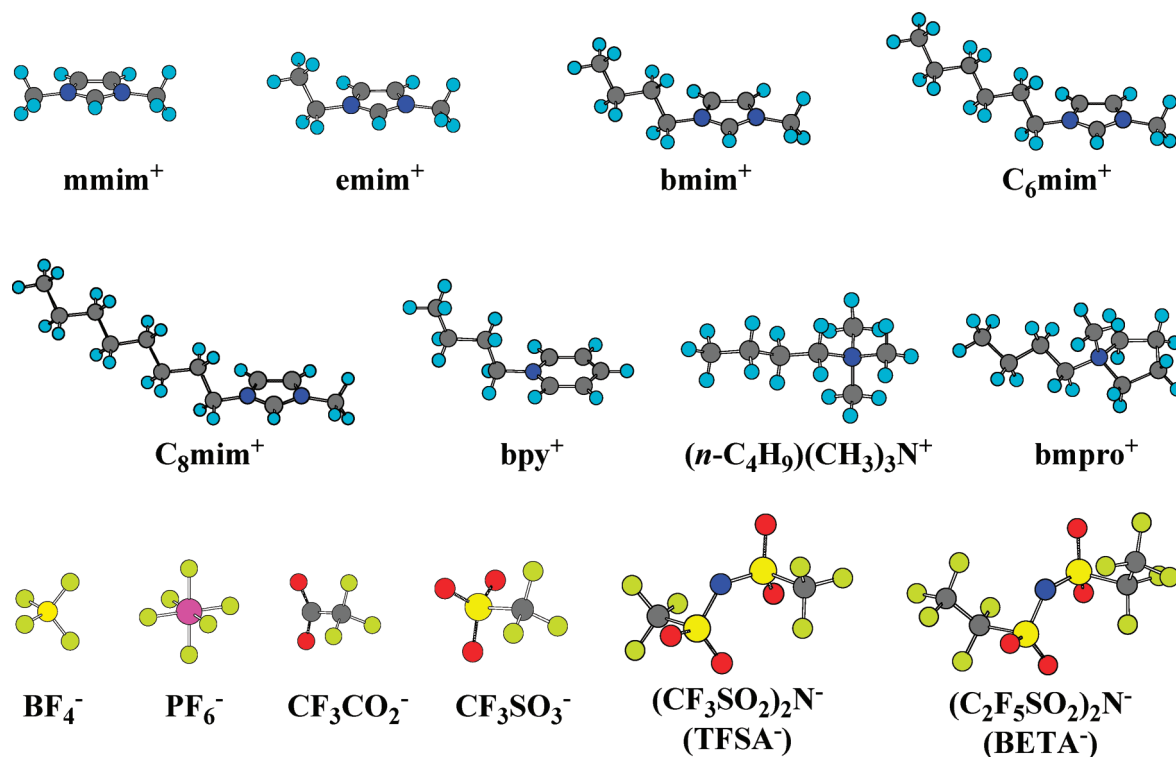
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**Figure 1.** Cations and anions used for molecular dynamics simulations. See text.

ones. We also discussed the factors determining the self-diffusion coefficients of the ions.

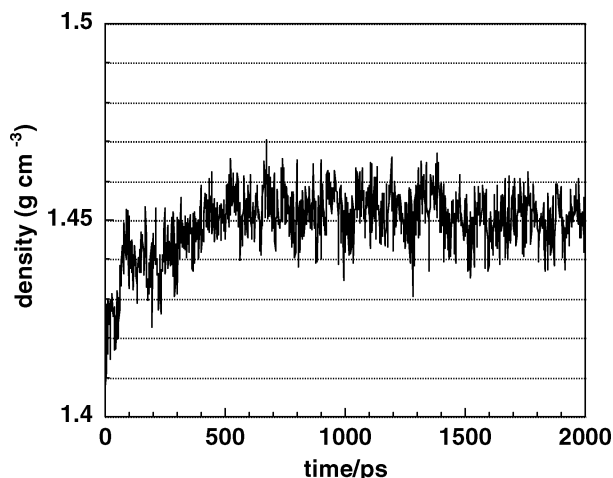
The domain segregation in the ionic liquids was observed from molecular dynamics simulations. The aggregation of the alkyl chains in the nonpolar domains and the formation of ionic channels in the polar domains were observed.<sup>32–35</sup> The detailed information on the dynamics of atoms in the two types of domains is essential for understanding the transport properties of ionic liquids. It is likely that the dynamics of atoms in the two types of domains are different. The motion of atoms in the alkyl chains will be faster than that of ring atoms in short time scale due to the greater flexibility of the chain and its lower partial charge. However, the details of the dynamics of atoms in the two types of domains were not clearly understood. We compared the translational motion of the atoms in the alkyl chains and that in the imidazolium ring by molecular dynamics simulations.

### Computational Method

The MPDYN program<sup>36</sup> was used for molecular dynamics simulations.<sup>37</sup> Molecular dynamics simulations of 125 ion pairs were carried out in the NPT ensemble.<sup>38</sup> All the C–H bonds were held rigid using the SHAKE algorithm.<sup>39</sup> Reversible RESPA was used for multiple time step integration of motion of atoms.<sup>40,41</sup> The time step size for updating interactions in the Ewald reciprocal space was 8 fs, and that for other interactions was 2 fs. Periodic boundary conditions were employed. The nonbonded forces were truncated at 12 Å, and the Coulomb interactions were computed using the Evald method.<sup>37</sup> Constant-temperature and -pressure conditions (0.1 MPa) were maintained by using the Nose–Hoover chain thermostat<sup>42</sup> and Andersen barostat.<sup>43</sup> The density of the ionic liquid was evaluated from 1 ns MD trajectories after a 2 ns MD equilibration run at 303 K. The transport properties were evaluated at higher temperature, 353 K, to obtain a better convergence of autocorrelation function. After a 2 ns equilibration run, a 12 ns production run

was made at 353 K, if not otherwise noted, to calculate the mean square displacements (MSD) of the ions. To minimize possible artifacts in the initial configurations, the system was equilibrated at 453 K starting from a low-density condition before the equilibrations at 303 and 353 K. The self-diffusion coefficients were determined by calculating the slopes of the MSDs of the ions versus time in the range between 1 and 3 ns. The 1-alkyl-3-methylimidazolium ( $\text{Rmim}^+$ , R = methyl (m), ethyl (e), butyl (b), hexyl ( $\text{C}_6$ ) and octyl ( $\text{C}_8$ )), 1-butylpyridinium ( $\text{bpy}^+$ ), *N*-butyl-*N,N,N*-trimethylammonium ( $(n\text{-C}_4\text{H}_9)(\text{CH}_3)_3\text{N}^+$ ), and *N*-butyl-*N*-methylpyrrolidinium ( $\text{bmpro}^+$ ) cations and the  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{CF}_3\text{CO}_2^-$ ,  $\text{CF}_3\text{SO}_3^-$ ,  $(\text{CF}_3\text{SO}_2)_2\text{N}^-$  (TFSA $^-$ ), and  $(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}^-$  (BETA $^-$ ) anions were used for the simulations. The structures of the cations and anions are shown in Figure 1. The ionic conductivity was calculated from the density and the self-diffusion coefficients of the cation and anion obtained by the molecular dynamics simulation at 353 K.<sup>44</sup> Details of the calculation procedure of the ionic conductivity were described elsewhere.<sup>45</sup>

Although a number of force fields for the ionic liquids were reported,<sup>11,24,26,46</sup> most of them were developed for a few ionic liquids. The OPLS force field for the ionic liquids developed by Lopes and co-workers<sup>47–50</sup> can be used for a broader range of ionic liquids. Therefore, we carried out the molecular dynamics simulations using their force field with some modifications.<sup>51</sup> The partial atomic charges of the ions were determined on the basis of the atomic charges obtained by electrostatic potential fitting using the Merz–Singh–Kollman scheme<sup>52,53</sup> from the MP2/6-311G\*\* level wave functions of the isolated ions. Some stretching and bending parameters were modified to reproduce the bond distances and the bond angles in the MP2/6-311G\*\* level optimized geometries of the isolated ions. The MP2/cc-pVTZ//MP2/6-311G\*\* level torsional potentials calculated for the isolated ions were used for the refinement of the torsional parameters. Some nonbonding parameters were modified to improve the agreement of the calculated densities



**Figure 2.** Density of [bmim][TFSA] ionic liquid at 303 K calculated by molecular dynamics simulation. The simulation is followed after equilibration at 453 K.

for the four ionic liquids ([bmim][TFSA], [bmim][BF<sub>4</sub>], [bpy]-[TFSA], and [(*n*-C<sub>4</sub>H<sub>9</sub>)(CH<sub>3</sub>)<sub>3</sub>N][TFSA]) with the experimental values.<sup>54–56</sup> Details of the force field parameters are described in the Supporting Information. The Gaussian03 program<sup>57</sup> was used for the ab initio molecular orbital calculations. The basis sets implemented in the program were used for the calculations. Electron correlation was accounted for by the second-order Møller–Plesset perturbation (MP2) method.<sup>58,59</sup>

The interaction energy ( $E_{\text{int}}$ ) for the BF<sub>4</sub><sup>−</sup> complexes with imidazolium cations ([Rmim][BF<sub>4</sub>], R = m, e, C<sub>6</sub>, and C<sub>8</sub>) were calculated at the MP2/6-311G\*\* level using the HF/6-311G\*\* level fully optimized geometries of complexes. The geometries optimized for the complexes are shown in Figure 1S in the Supporting Information. The basis set superposition error<sup>60</sup> was corrected for interaction energy calculations with the counterpoise method.<sup>61</sup> The stabilization energy ( $E_{\text{form}}$ ) by the formation of the complex was calculated as the sum of the interaction energy ( $E_{\text{int}}$ ) calculated for the complex and the deformation energies of ions ( $E_{\text{def}}$ ). The  $E_{\text{def}}$  is the sum of the increases of energies for the cation and anion by the deformations of the ions associated with the complex formation. The  $E_{\text{def}}$  was calculated at the MP2/6-311G\*\* level. Details of the calculation procedure of the stabilization energy were described elsewhere.<sup>62</sup>

## Results and Discussion

**Densities of Ionic Liquids.** The density of the [bmim][TFSA] ionic liquid obtained by the molecular dynamics simulation at 303 K is shown in Figure 2. The simulation is followed after the equilibration at 453 K. The equilibration of the density at 303 K is very slow. Figure 2 clearly shows that a sufficiently long simulation (about 1 ns) is necessary for the equilibration of the density of the ionic liquid at 303 K.

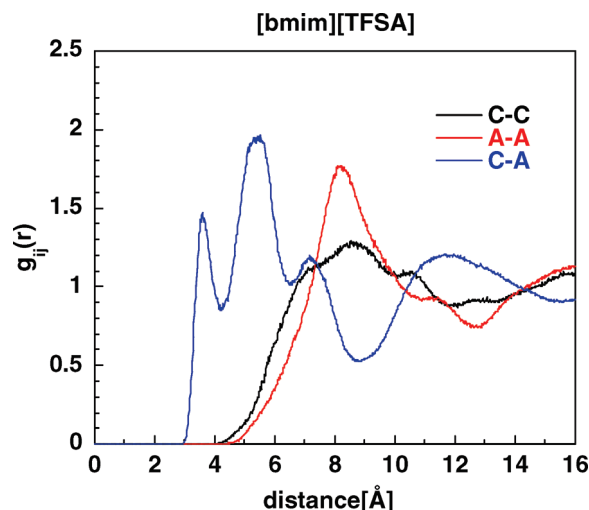
The densities calculated for the 13 ionic liquids at 303 K are compared with the experimental values as summarized in Table 1. Although only the experimental densities of the four ionic liquids were used for the refinement of the nonbonding parameters, the densities calculated for the other nine ionic liquids also agree well with the experimental values.<sup>54–56</sup> The largest error of the calculated density is 1.7%, and the average error is less than 1%.

**Structure of Ionic Liquids.** The site–site intermolecular radial distribution functions in the [bmim][TFSA] ionic liquid at 303 K were calculated as shown in Figure 3. The radial distribution functions show oscillations extending beyond 16

**TABLE 1: Experimental and Calculated Densities of Ionic Liquids at 303 K<sup>a</sup>**

	exp <sup>b</sup>	calcd	error (%) <sup>c</sup>
[mmim][TFSA]	1.565	1.572	0.4
[emim][TFSA]	1.514	1.531	1.1
[bmim][TFSA]	1.432	1.450	1.3
[C <sub>6</sub> mim][TFSA]	1.366	1.388	1.6
[C <sub>8</sub> mim][TFSA]	1.315	1.336	1.6
[bpy][TFSA]	1.444	1.448	0.3
[( <i>n</i> -C <sub>4</sub> H <sub>9</sub> )(CH <sub>3</sub> ) <sub>3</sub> N][TFSA]	1.388	1.411	1.7
[bmpro][TFSA]	1.390	1.403	0.9
[bmim][CF <sub>3</sub> SO <sub>3</sub> ]	1.294	1.291	−0.2
[bmim][CF <sub>3</sub> CO <sub>2</sub> ]	1.213	1.205	−0.7
[bmim][BETA]	1.509	1.522	0.9
[bmim][BF <sub>4</sub> ]	1.198	1.199	0.1
[bmim][PF <sub>6</sub> ]	1.365	1.374	0.7

<sup>a</sup> Density in g cm<sup>−3</sup>. <sup>b</sup> See refs 54–56. <sup>c</sup> Deviation from experimental value.



**Figure 3.** Site–site intermolecular radial distribution functions in the [bmim][TFSA] ionic liquid at 303 K. Radial distribution function between the C<sub>2</sub> carbon atoms of the bmim<sup>+</sup> cations (C–C), that between the nitrogen atoms of the TFSA<sup>−</sup> anions (A–A), and that between the C<sub>2</sub> carbon atom of the bmim<sup>+</sup> cation and the nitrogen atom of the TFSA<sup>−</sup> anion (C–A) are shown.

Å. The distribution function between the C<sub>2</sub> carbon atoms of the bmim<sup>+</sup> cations ( $g_{\text{C–C}}$ ) shows the broadest peaks, and a first maximum coincident with that between the nitrogen atoms of the TFSA<sup>−</sup> anions ( $g_{\text{A–A}}$ ) locates at about 8 Å. The distribution function between the C<sub>2</sub> carbon atom of the bmim<sup>+</sup> cation and the nitrogen atoms of the TFSA<sup>−</sup> anion ( $g_{\text{C–A}}$ ) has peaks at shorter distances (3–7 Å). The  $g_{\text{C–A}}$  is in opposition of the phase with the  $g_{\text{C–C}}$  and  $g_{\text{A–A}}$ , the typical charge-ordering structure being recovered. The radial distribution functions in the other 12 ionic liquids are shown in Figures 2S–4S in the Supporting Information. They also show the formation of similar charge-ordering structures, although the details of the radial distributions functions depend on the ions. The charge-ordering structures were also calculated for various ionic liquids by other groups.<sup>12,14,32</sup>

**MSDs of Ions.** The MSDs of the ions in the [bmim][TFSA] and [C<sub>8</sub>mim][TFSA] ionic liquids obtained from the 12 ns simulations at 353 K are shown in Figures 5S in the Supporting Information. The initial rapid increase continues until 1 ns in the simulation of highly viscous [C<sub>8</sub>mim][TFSA], which shows that a sufficiently long simulation is necessary for an accurate evaluation of the self-diffusion coefficients of the ions in the ionic liquids. The asymptotic linear region can be attributed to diffusion. The MSDs plotted on a log scale (Figure 6S in the



Supporting Information) also indicate that this region corresponds to diffusion.

**Self-Diffusion Coefficients of Ions in [bmim][TFSA].** The self-diffusion coefficients of the bmim<sup>+</sup> cation and the TFSA<sup>−</sup> anion were calculated from the MSDs of the ions over 1–3 ns (Figure 5S). The self-diffusion coefficients calculated for the bmim<sup>+</sup> cation and the TFSA<sup>−</sup> anion are 0.78 and 0.59 ( $\times 10^{-7}$  cm<sup>2</sup> s<sup>−1</sup>), respectively. To check the convergence, the MSDs of the ions were also calculated from a 100 ns-long simulation (Figure 7S in the Supporting Information). The self-diffusion coefficients obtained from the fittings of the MSD slopes over 1–3 ns are 0.81 and 0.64 ( $\times 10^{-7}$  cm<sup>2</sup> s<sup>−1</sup>) for the bmim<sup>+</sup> cation and TFSA<sup>−</sup> anion, respectively. These values are not largely different from the self-diffusion coefficients obtained from the 12 ns simulations, which suggests that the statistical errors in the calculated self-diffusion coefficients from the 12 ns simulations at 353 K are minor.

The self-diffusion coefficients of the ions were also calculated by fitting the MSDs over longer time ranges to confirm that the motion of the ions in the range of 1–3 ns corresponds to diffusion. The MSDs obtained from the 100 ns simulation were used for the fittings. The self-diffusion coefficients of the bmim<sup>+</sup> cation obtained from the fittings of the MSDs in the ranges of 3–5, 5–10, and 10–20 ns are 0.79, 0.79, and 0.73 ( $\times 10^{-7}$  cm<sup>2</sup> s<sup>−1</sup>), respectively. Those of the TFSA<sup>−</sup> anion are 0.63, 0.63, and 0.56 ( $\times 10^{-7}$  cm<sup>2</sup> s<sup>−1</sup>), respectively. These values are close to the self-diffusion coefficients of the bmim<sup>+</sup> cation and the TFSA<sup>−</sup> anion obtained from the MSDs in the range of 1–3 ns (0.81 and  $0.64 \times 10^{-7}$  cm<sup>2</sup> s<sup>−1</sup>, respectively), showing that the motion of the ions in 1–3 ns at 353 K can be attributed to diffusion. On the other hand, the self-diffusion coefficients obtained from the fittings of the MSDs in shorter time ranges are substantially larger. The self-diffusion coefficients of the bmim<sup>+</sup> cation obtained from the fittings of the MSDs in the ranges of 10–20, 20–50, 50–100, 100–200, 200–500, and 500–1000 ps are 3.22, 2.10, 1.61, 1.29, 1.01, and 0.87 ( $\times 10^{-7}$  cm<sup>2</sup> s<sup>−1</sup>), respectively. Those of TFSA<sup>−</sup> anion are 2.95, 1.88, 1.38, 1.07, 0.92, and 0.71 ( $\times 10^{-7}$  cm<sup>2</sup> s<sup>−1</sup>), respectively.

The self-diffusion coefficients calculated for the bmim<sup>+</sup> cation and the TFSA<sup>−</sup> anion at 353 K are about one order smaller than the experimental ones (15 and  $12 \times 10^{-7}$  cm<sup>2</sup> s<sup>−1</sup>, respectively). Other groups also reported similar underestimation of the self-diffusion coefficients of the ions from molecular dynamics simulations using the nonpolarized model.<sup>11,20,23</sup> Yan and co-workers studied the effects of the electronic polarization on the diffusion of the ions in the [emim][NO<sub>3</sub>] ionic liquid. They reported that the polarizable model predicts a self-diffusion coefficient that is three times higher than the nonpolarizable model and that the viscosity predicted by the polarizable model is close to the experimental one.<sup>15</sup> Borodin et al. reported that the polarizable model well reproduced the experimental self-diffusion coefficients of the ions in the *N*-methyl-*N*-propylpyrrolidinium TFSA ionic liquid.<sup>19</sup> These results suggest that the inclusion of polarization in the force field will improve the simulation results.

**Effects of Alkyl Chain Length in Imidazolium Cation on Self-Diffusion Coefficients.** The self-diffusion coefficients calculated for the ions in the 13 ionic liquids at 353 K are summarized in Table 2. The self-diffusion coefficients calculated for the ions in the [mmim][TFSA], [emim][TFSA], [bmim][TFSA], [C<sub>6</sub>mim][TFSA], and [C<sub>8</sub>mim][TFSA] ionic liquids are compared with the experimental values for evaluating the effects of alkyl chain length in the imidazolium cations as shown in Figure 4. The self-diffusion coefficients calculated for the ions

**TABLE 2: Calculated and Experimental Self-Diffusion Coefficients of Ions in Ionic Liquids<sup>a</sup>**

	exp (353 K) <sup>b</sup>		calcd (353 K) <sup>c</sup>		calcd (453 K) <sup>d</sup>	
	cation	anion	cation	anion	cation	anion
[mmim][TFSA]	22	13	1.6	0.95	18	11
[emim][TFSA]	22	14	1.7	0.78	19	10
[bmim][TFSA]	15	12	0.78	0.59	12	9.7
[C <sub>6</sub> mim][TFSA]	12	10	0.56	0.53	10	9.4
[C <sub>8</sub> mim][TFSA]	9.0	8.8	0.44	0.44	8.2	8.4
[bpy][TFSA]	14	11	0.94	0.60	12	10
[( <i>n</i> -C <sub>4</sub> H <sub>9</sub> )(CH <sub>3</sub> ) <sub>3</sub> N][TFSA]	9.3	8.4	0.22	0.21	5.8	6.7
[bmpro][TFSA]	11	9.1	0.25	0.22	6.0	5.6
[bmim][CF <sub>3</sub> SO <sub>3</sub> ]	10	9.0	0.59	0.48	10	6.8
[bmim][CF <sub>3</sub> CO <sub>2</sub> ]	12	11	1.7	1.4	21	17
[bmim][BETA]	9.8	7.3	0.86	0.74	13	8.9
[bmim][BF <sub>4</sub> ]	11	11	0.44	0.33	12	10
[bmim][PF <sub>6</sub> ]	6.7	5.7	0.35	0.33	6.4	5.1

<sup>a</sup> Self-diffusion coefficients in  $10^{-7}$  cm<sup>2</sup> s<sup>−1</sup>. <sup>b</sup> See refs 54–56.

<sup>c</sup> Obtained from 12 ns simulations. See text. <sup>d</sup> Obtained from 4 ns simulations. See text.

in the five ionic liquids accurately describe the experimental trend,<sup>55</sup> which is [mmim][TFSA]  $\sim$  [emim][TFSA] > [bmim][TFSA] > [C<sub>6</sub>mim][TFSA] > [C<sub>8</sub>mim][TFSA], although the calculated self-diffusion coefficients of the ions were about 1 order smaller than the experimental NMR values, as in the case of the [bmim][TFSA]. The NMR measurements show that the imidazolium cations have larger self-diffusion coefficients than the TFSA<sup>−</sup> anion. This tendency was also reproduced by the simulations quite well.

#### Effects of Cation Structures on Self-Diffusion Coefficients.

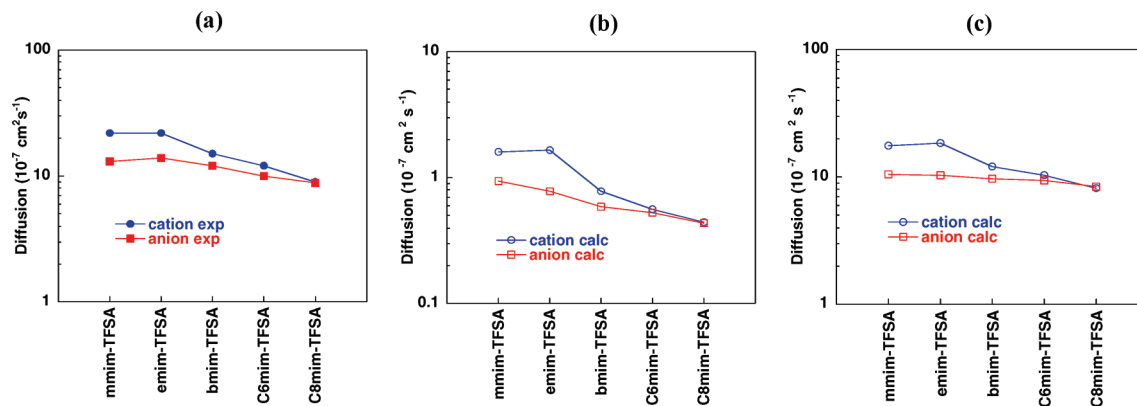
The self-diffusion coefficients calculated for the ions in the [bmim][TFSA], [bpy][TFSA], [(*n*-C<sub>4</sub>H<sub>9</sub>)(CH<sub>3</sub>)<sub>3</sub>N][TFSA], and [bmpro][TFSA] are compared with the experimental values for evaluating the effects of cation structures, as shown in Figure 5. The trends of the self-diffusion coefficients calculated for the ions in the ionic liquids again agree with the experimental trend quite well,<sup>56</sup> which is [bmim][TFSA]  $\sim$  [bpy][TFSA] > [(*n*-C<sub>4</sub>H<sub>9</sub>)(CH<sub>3</sub>)<sub>3</sub>N][TFSA]  $\sim$  [bmpro][TFSA]. The diffusion of the ions in the alkyl ammonium based ionic liquids is slower than that in the ionic liquids composed of the aromatic cations.

#### Effects of Anion Species on Self-Diffusion Coefficients.

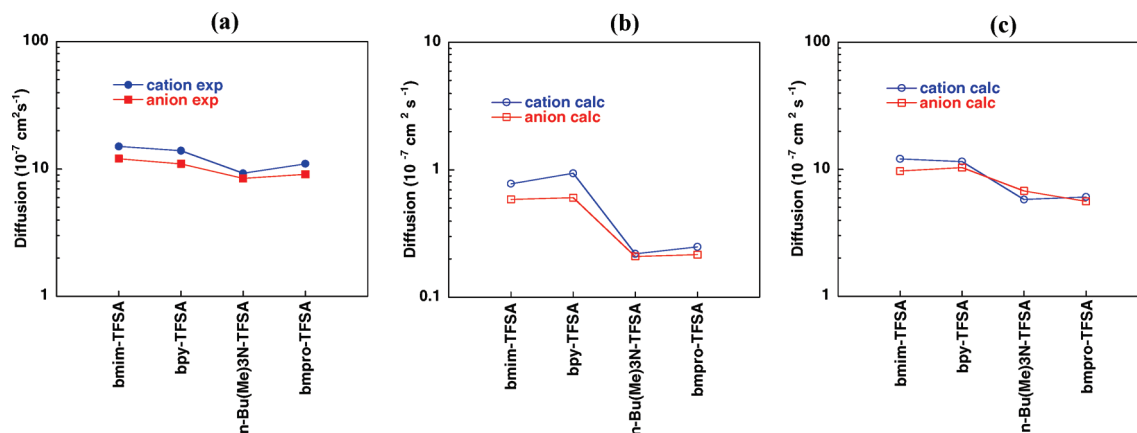
The self-diffusion coefficients of the ions in the bmim<sup>+</sup>-based ionic liquids with a variety of anions ([bmim][TFSA], [bmim][CF<sub>3</sub>SO<sub>3</sub>], [bmim][CF<sub>3</sub>CO<sub>2</sub>], [bmim][BETA], [bmim][BF<sub>4</sub>], and [bmim][PF<sub>6</sub>]) are compared for evaluating the effects of anion species, as shown in Figure 6. The experimental self-diffusion coefficients of the ions in the ionic liquids have following trends: [bmim][TFSA] > [bmim][CF<sub>3</sub>CO<sub>2</sub>]  $\sim$  [bmim][BF<sub>4</sub>] > [bmim][CF<sub>3</sub>SO<sub>3</sub>]  $\sim$  [bmim][BETA] > [bmim][PF<sub>6</sub>].<sup>54</sup> The self-diffusion coefficients calculated for the ions at 353 K have the following trends: [bmim][CF<sub>3</sub>CO<sub>2</sub>] > [bmim][BETA] > [bmim][TFSA] > [bmim][CF<sub>3</sub>SO<sub>3</sub>] > [bmim][BF<sub>4</sub>] > [bmim][PF<sub>6</sub>]. Although the simulations overestimate the diffusion of the ions in the [bmim][CF<sub>3</sub>CO<sub>2</sub>] and [bmim][BETA], the simulations well reproduced the following trends: (1) The diffusion of the ions in the [bmim][TFSA] is faster than that in the [bmim][CF<sub>3</sub>SO<sub>3</sub>]. (2) The diffusion in the [bmim][CF<sub>3</sub>CO<sub>2</sub>] is faster than that in the [bmim][CF<sub>3</sub>SO<sub>3</sub>]. (3) The diffusion in the [bmim][BF<sub>4</sub>] is faster than that in the [bmim][PF<sub>6</sub>].

#### Self-Diffusion Coefficients Calculated at Higher Temperature.

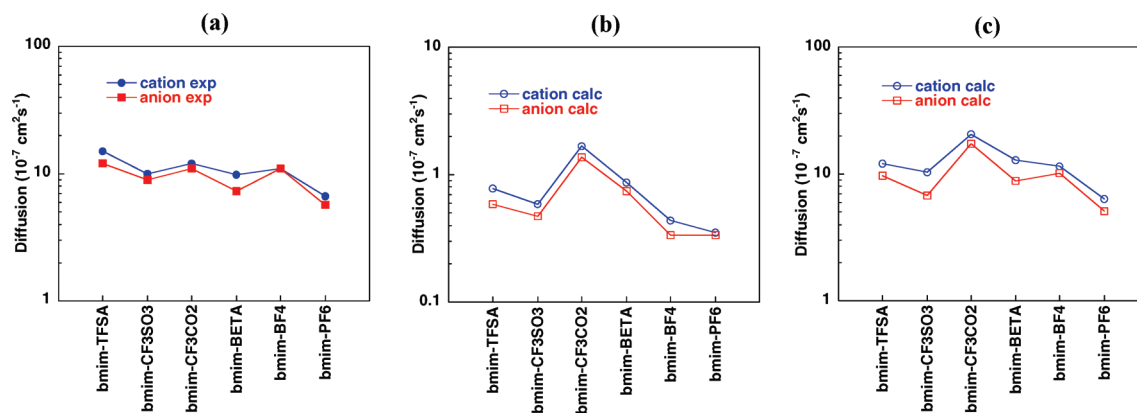
The self-diffusion coefficients of the ions in the 13 ionic liquids were also calculated at higher temperature. After 0.5 ns equilibration, a 4 ns production run was made at 453 K to



**Figure 4.** Alkyl chain length dependence of self-diffusion coefficients. Experimental values at 353 K (a), calculated values at 353 K (b), and calculated values at 453 K (c). Experimental values are taken from ref 55.



**Figure 5.** Cation dependence of self-diffusion coefficients. Experimental values at 353 K (a), calculated values at 353 K (b), and calculated values at 453 K (c). Experimental values are taken from ref 56.



**Figure 6.** Anion dependence of self-diffusion coefficients. Experimental values at 353 K (a), calculated values at 353 K (b), and calculated values at 453 K (c). Experimental values are taken from ref 54.

calculate the MSDs of the ions. The self-diffusion coefficients were obtained from the fittings of the MSD slopes over 0.5–1 ns. The self-diffusion coefficients calculated for the ions at 453 K (Table 2), which are about 1 order larger than those calculated at 353 K, are close to the experimental ones at 353 K, as shown in Figures 4–6. The cation and anion dependence of the calculated self-diffusion coefficients at 453 K is smaller than that calculated at 353 K. The experimental measurements of the self-diffusion coefficients also show that the dependence is smaller at higher temperature.<sup>54–56</sup> The cation and anion dependence of the calculated self-diffusion coefficients of ions at 453 K is very close to the experimental dependence at 353 K, whereas the dependence is emphasized in the simulations at 353 K.

**Ionic Conductivity.** The ionic conductivities calculated for the 13 ionic liquids<sup>44,45</sup> are compared with the experimental values as summarized in Table 3. The ionic conductivities obtained from the simulations are about 1 order smaller than the experimental values as in the case of the self-diffusion coefficients. Most of the experimental trends of the cation and anion dependence of the ionic conductivities are reproduced by the simulations.

**Motion of Atoms in Alkyl Chains.** The MSDs for the atoms in the  $\text{bmim}^+$  cations in the  $[\text{bmim}][\text{TFSA}]$  ionic liquid obtained from the 100 ns simulation at 353 K are shown in Figure 7. The numbering of atoms is shown in Figure 8. The slopes of the MSDs for the atoms over 10–30 ns are nearly identical, which shows that the self-diffusion coefficients of the atoms

TABLE 3: Ionic Conductivities Calculated for Ionic Liquids at 353 K<sup>a</sup>

	$D_c^a$	$D_a^b$	$\Lambda_{\text{mol}}^c$	$\rho^d$	$M^e$	$V_{\text{mol}}^f$	$\Lambda^g$	
							calcd	exp
[mmim][TFSA]	1.6	0.95	0.81	1.534	377.3	246.0	0.0033	0.032
[emim][TFSA]	1.7	0.78	0.77	1.488	391.3	263.0	0.0029	0.031
[bmim][TFSA]	0.78	0.59	0.43	1.414	419.4	296.6	0.0015	0.017
[C <sub>6</sub> mim][TFSA]	0.56	0.53	0.35	1.346	447.4	332.4	0.0010	0.012
[C <sub>8</sub> mim][TFSA]	0.44	0.44	0.28	1.293	475.5	367.7	0.0008	0.008
[bpy][TFSA]	0.94	0.60	0.49	1.410	416.4	295.3	0.0017	0.016
[( <i>n</i> -C <sub>4</sub> H <sub>9</sub> )(CH <sub>3</sub> ) <sub>3</sub> N][TFSA]	0.22	0.21	0.14	1.379	396.4	287.5	0.0005	0.012
[bmpro][TFSA]	0.25	0.22	0.15	1.366	422.4	309.2	0.0005	0.014
[bmim][CF <sub>3</sub> SO <sub>3</sub> ]	0.59	0.48	0.34	1.262	288.2	228.4	0.0015	0.016
[bmim][CF <sub>3</sub> CO <sub>2</sub> ]	1.7	1.4	0.96	1.169	252.2	215.7	0.0044	0.017
[bmim][BETA]	0.86	0.74	0.51	1.483	519.4	350.2	0.0015	0.0094
[bmim][BF <sub>4</sub> ]	0.44	0.33	0.24	1.171	226.0	193.0	0.0013	0.022
[bmim][PF <sub>6</sub> ]	0.35	0.33	0.22	1.343	284.2	211.6	0.0010	0.012

<sup>a</sup> Self-diffusion coefficient calculated for cation in  $10^{-7} \text{ cm}^2 \text{ s}^{-1}$ . <sup>b</sup> Self-diffusion coefficient calculated for anion in  $10^{-7} \text{ cm}^2 \text{ s}^{-1}$ . <sup>c</sup> Molar conductivity in  $\text{S cm}^2 \text{ mol}^{-1}$ . <sup>d</sup> Density in  $\text{g cm}^{-3}$ . <sup>e</sup> Molecular weight. <sup>f</sup> Molar volume in  $\text{cm}^3$ . <sup>g</sup> Ionic conductivity in  $\text{S cm}^{-1}$ . Experimental values were taken from refs 54–56.

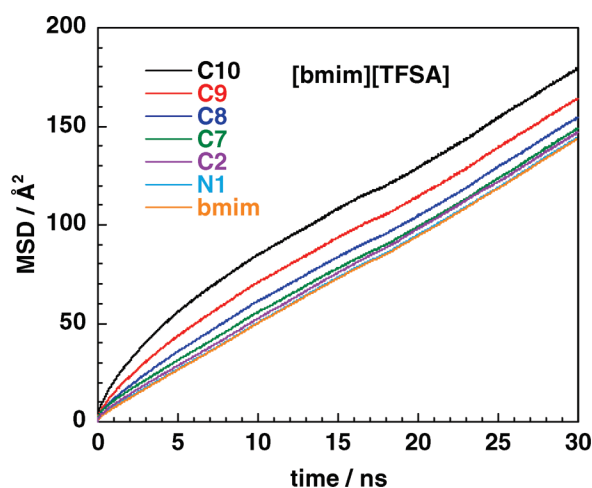


Figure 7. Mean-square displacements for atoms in imidazolium cations in [bmim][TFSA] at 353 K obtained from 100 ns simulation. Numbering of atoms is shown in Figure 8. bmim is mean-square displacement for the center of gravity of bmim<sup>+</sup> cation.

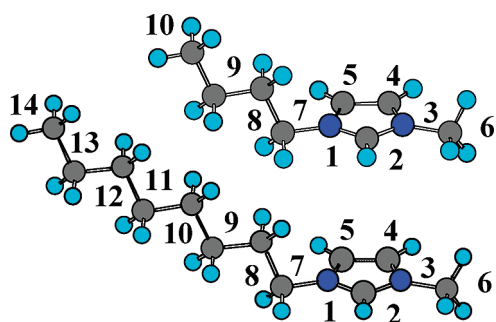


Figure 8. Numbering of atoms.

are identical. The translational dynamics of the alkyl chain and the imidazolium ring is about the same in the time scale larger than 10 ns. On the other hand, the slopes of the MSDs are significantly different over 0–5 ns. The slopes of the MSDs for the carbon atoms in the butyl group are steeper than those for the atoms in the imidazolium (N<sub>1</sub> and C<sub>2</sub>), which suggests that the motion of the carbon atoms in the alkyl chain is faster than that of the atoms in the imidazolium in the time scale of a few nanoseconds.

The MSDs for the atoms in the imidazolium cations in the [bmim][TFSA] and [C<sub>8</sub>mim][TFSA] ionic liquids at 353 K

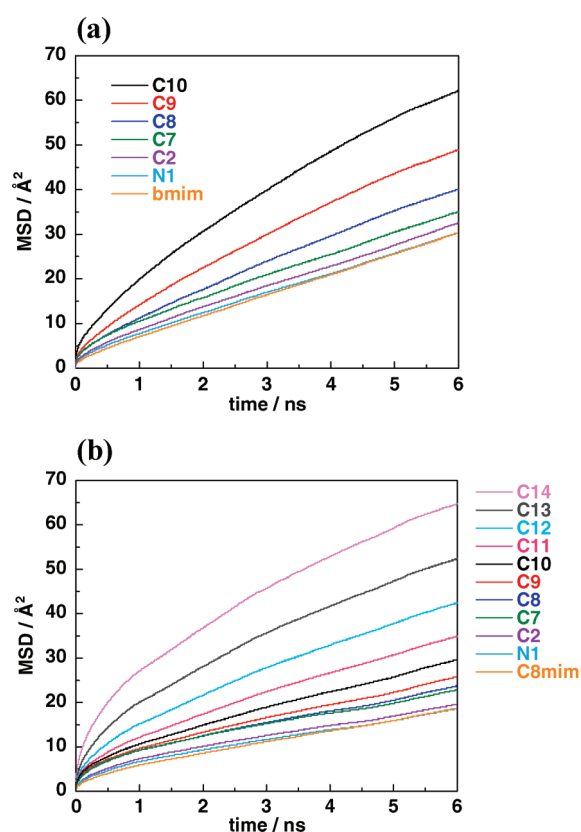


Figure 9. Mean-square displacements for atoms in imidazolium cations in [bmim][TFSA] (a) and those in [C<sub>8</sub>mim][TFSA] (b) ionic liquids at 353 K. Numbering of atoms is shown in Figure 8. bmim and C8mim are mean-square displacements for the centers of gravity of cations.

obtained from the 12 ns simulations are shown in Figure 9. The motion of the terminal carbon atoms in the alkyl chains is very fast on a time scale of a few nanoseconds. The effective diffusion coefficients for the atoms in the imidazolium cations were calculated from the MSD slopes over 1–3 ns, as summarized in Table 4. Although the effective diffusion coefficients are not the self-diffusion coefficients, they are useful for comparing the motion of the atoms in the short time scale. The effective diffusion coefficients calculated for the N<sub>1</sub> and C<sub>2</sub> in the bmim<sup>+</sup> ( $0.77$  and  $0.82 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ , respectively) are nearly identical to the self-diffusion coefficient of the center of gravity of the bmim<sup>+</sup> cation ( $0.78 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ ). The

**TABLE 4: Effective Diffusion Coefficients Calculated for Atoms in [bmim][TFSA] and [C<sub>8</sub>mim][TFSA] at 353 K<sup>a</sup>**

	bmim	C <sub>8</sub> mim
cation <sup>b</sup>	0.78	0.44
TFSA <sup>c</sup>	0.59	0.44
N1	0.77	0.41
C2	0.82	0.43
C7	0.87	0.50
C8	1.06	0.53
C9	1.31	0.58
C10	1.65	0.70
C11		0.86
C12		1.07
C13		1.32
C14		1.58

<sup>a</sup> Obtained from 12 ns simulations. Diffusion coefficients in 10<sup>-7</sup> cm<sup>2</sup> s<sup>-1</sup>. Numbering of atoms is shown in Figure 8. <sup>b</sup> Self-diffusion coefficient of center of gravity of cation. <sup>c</sup> Self-diffusion coefficient of center of gravity of TFSA anion.

effective diffusion coefficients for the N<sub>1</sub> and C<sub>2</sub> in the C<sub>8</sub>mim<sup>+</sup> (0.41 and 0.43 × 10<sup>-7</sup> cm<sup>2</sup> s<sup>-1</sup>, respectively) are also close to the self-diffusion coefficient of the C<sub>8</sub>mim<sup>+</sup> cation (0.44 × 10<sup>-7</sup> cm<sup>2</sup> s<sup>-1</sup>). The effective diffusion coefficient calculated for the terminal carbon atom (C<sub>10</sub>) in the butyl group of the bmim<sup>+</sup> cation (1.65 × 10<sup>-7</sup> cm<sup>2</sup> s<sup>-1</sup>) is 2.1 times as large as the self-diffusion coefficient for the bmim<sup>+</sup> cation. The effective diffusion coefficient for the terminal carbon atom (C<sub>14</sub>) in the octyl group of the C<sub>8</sub>mim<sup>+</sup> cation (1.58 × 10<sup>-7</sup> cm<sup>2</sup> s<sup>-1</sup>) is 3.6 times as large as the self-diffusion coefficient for the C<sub>8</sub>mim<sup>+</sup> cation. The large effective diffusion coefficients of carbon atoms in the alkyl chains show that the motion of the carbon atoms in the alkyl chains around the imidazolium ring is faster than the motion of the atoms in the imidazolium ring in the short time scale. Interestingly, the effective diffusion coefficients for the terminal carbon atoms in the bmim<sup>+</sup> and C<sub>8</sub>mim<sup>+</sup> cations (the C<sub>10</sub> in bmim<sup>+</sup> and C<sub>14</sub> in C<sub>8</sub>mim<sup>+</sup>) are nearly identical.

Lopes and co-workers observed the domain segregation in the [Rmim][PF<sub>6</sub>] and [Rmim][TFSA] ionic liquids using molecular dynamics simulations.<sup>32,33</sup> The aggregation of the alkyl chains in the nonpolar domains and the formation of tridimensional network of ionic channels in the polar domains were observed. Earlier simulations also identified similar structural features.<sup>63,64</sup> Experimental measurements also suggest the structural heterogeneities.<sup>65–67</sup> Despite the extensive studies on the domain structures in the ionic liquids, the dynamics of the atoms in the two types of domains was unclear. The molecular dynamics simulations in this work clearly show that the dynamics of the atoms in the two types of domains is significantly different in the short time scale. Although the structural inhomogeneity is not the cause of the different dynamics, the translational motion of the atoms in the imidazolium ring and anion is considerably slower than the motion of the atoms in the alkyl chains in the short time scale. The different motion of the atoms in the two types of domains will be important for understanding the transport properties of the ions and solute molecules in the ionic liquids. Lopes and co-workers found the charge ordering structure in the polar domains,<sup>32</sup> which shows that the strong attractive electrostatic interactions exist between the neighboring cation and anion. On the other hand, the attractive interactions between the alkyl chains in the nonpolar domains (mainly the dispersion interactions) are significantly weaker than the interactions between ions. Recently reported molecular dynamics simulations show that the ionic rotations take place on nanosecond time scales.<sup>13,17,68</sup>

**TABLE 5: Stabilization Energies Calculated for Formation of BF<sub>4</sub> Complexes with Imidazolium Cations and Experimental Self-Diffusion Coefficients of Ions in Ionic Liquids at 353 K**

	<i>E</i> <sub>form</sub> <sup>a</sup>	<i>D</i> <sub>cation</sub> <sup>b,c</sup>	<i>D</i> <sub>anion</sub> <sup>c,d</sup>
[dmim][BF <sub>4</sub> ]	−85.5	22	13
[emim][BF <sub>4</sub> ]	−85.2	22	14
[bmim][BF <sub>4</sub> ]	−84.7 <sup>e</sup>	15	12
[C <sub>6</sub> mim][BF <sub>4</sub> ]	−84.4	12	10
[C <sub>8</sub> mim][BF <sub>4</sub> ]	−84.3	9.0	8.8

<sup>a</sup> Stabilization energy calculated for formation of complex from isolated ions. Energy in kcal/mol. <sup>b</sup> Self-diffusion coefficient of cation in TFSA based ionic liquid; see ref 55. <sup>c</sup> Self-diffusion coefficient in 10<sup>-7</sup> cm<sup>2</sup> s<sup>-1</sup>. <sup>d</sup> Self-diffusion coefficient of anion in TFSA based ionic liquid; see ref 55. <sup>e</sup> See ref 62.

Urahata and Ribeiro reported that the motion of imidazolium has strong anisotropy.<sup>17</sup> They also reported that the time correlation functions of the velocity of the geometric center of the imidazolium and the dihedral angle of the alkyl chain, which suggests that the motion of the alkyl chain is faster than that of the imidazolium ring. Margulis reported that [bmim][PF<sub>6</sub>] ionic liquid exhibits complex dynamics with at least two different time scales of diffusion of ions.<sup>13</sup> The motion of the terminal substituent atoms will be more sensitive to the ionic rotation than the atoms in the ring. The greater flexibility of the chain and the weaker interactions between the chains are the cause of the greater freedom of movement.

#### Factors Determining Self-Diffusion Coefficients of Ions.

The relationship between the ionic structure and the transport properties of the ionic liquid is an important issue for designing new ionic liquids for many applications.<sup>69</sup> The relationship between the self-diffusion coefficients of the ions and the stabilization energies calculated for the ion pairs suggests that at least three factors play important roles in determining the magnitude of the self-diffusion coefficients of the ions. The stabilization energies calculated for the formation of the BF<sub>4</sub><sup>−</sup> complexes with imidazolium cations (Rmim<sup>+</sup>, R = m, e, b, C<sub>6</sub>, and C<sub>8</sub>) are compared with the self-diffusion coefficients of the ions in the five imidazolium based ionic liquids,<sup>55</sup> as shown in Table 5. Although the stabilization energies for the five complexes are nearly identical, the self-diffusion coefficients strongly depend on the alkyl chain length, which shows that the self-diffusion coefficients depend on the sizes of the ions. The long alkyl chain decreases the self-diffusion coefficients and increases the viscosity of the ionic liquid.<sup>55</sup> The long alkyl chain also increases the viscosity of the ionic liquids composed of other anions.<sup>70–72</sup> The radial distribution functions in the five imidazolium-based ionic liquids are nearly identical (Figures 3 and 2S), which shows that these ionic liquids have similar charge-ordering structures.

The stabilization energies calculated for the BF<sub>4</sub><sup>−</sup> complexes with emim<sup>+</sup>, 1-ethylpyridinium (epy<sup>+</sup>), *N*-ethyl-*N,N,N*-trimethylammonium ((C<sub>2</sub>H<sub>5</sub>)(CH<sub>3</sub>)<sub>3</sub>N<sup>+</sup>), and *N*-ethyl-*N*-methylpyrrolidinium (empro<sup>+</sup>)<sup>62</sup> are compared with the self-diffusion coefficients of the ions,<sup>56</sup> as shown in Table 6. The stabilization energies calculated for the four complexes are not largely different, but the self-diffusion coefficients of the ions in the imidazolium and pyridinium (aromatic cations) based ionic liquids are substantially larger than those in the alkylammonium based ionic liquids. This difference suggests that the self-diffusion coefficients also depend on the shapes of ions. The aromatic cations have board-shaped structures. The thickness of the aromatic cations is thinner than that of alkylammonium



**TABLE 6: Stabilization Energies Calculated for Formation of BF<sub>4</sub><sup>-</sup> Complexes with Cations and Experimental Self-Diffusion Coefficients of Ions in Ionic Liquids at 353 K**

	$E_{\text{form}}^a$	$D_{\text{cation}}^{b,c}$	$D_{\text{anion}}^{c,d}$
[emim][BF <sub>4</sub> ]	-85.2	15	12
[epy][BF <sub>4</sub> ]	-82.8	14	11
[(C <sub>2</sub> H <sub>5</sub> )(CH <sub>3</sub> ) <sub>3</sub> N][BF <sub>4</sub> ]	-84.6	9.3	8.4
[empro][BF <sub>4</sub> ]	-84.4	11	9.1

<sup>a</sup> Stabilization energy for formation of complex from isolated ions. Energy in kcal/mol; see ref 62. <sup>b</sup> Self-diffusion coefficient of cation in TFSA<sup>-</sup> based ionic liquid; see ref 56. <sup>c</sup> The ethyl group of the cation was replaced by an *n*-butyl group in the measurements. Self-diffusion coefficient in 10<sup>-7</sup> cm<sup>2</sup> s<sup>-1</sup>. <sup>d</sup> Self-diffusion coefficient of anion in TFSA<sup>-</sup> based ionic liquid; see ref 56.

**TABLE 7: Stabilization Energies Calculated for Formation of emim Complexes with Anions and Experimental Self-Diffusion Coefficients of Ions in Ionic Liquids at 353 K**

	$E_{\text{form}}^a$	$D_{\text{cation}}^{b,c}$	$D_{\text{anion}}^{c,d}$
[emim][BF <sub>4</sub> ]	-85.2	11	11
[emim][CF <sub>3</sub> SO <sub>3</sub> ]	-82.6	10	9
[emim][(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N]	-78.8	15	12

<sup>a</sup> Stabilization energy for formation of complex from isolated ions. Energy in kcal/mol; see ref 62. <sup>b</sup> Self-diffusion coefficient of cation in ionic liquid; see ref 54. <sup>c</sup> The ethyl group of the cation was replaced by an *n*-butyl group in the measurements. Self-diffusion coefficient in 10<sup>-7</sup> cm<sup>2</sup> s<sup>-1</sup>. <sup>d</sup> Self-diffusion coefficient of anion in ionic liquid; see ref 54.

cations, which suggests that the board-shaped structures of aromatic cations are important for the large self-diffusion coefficients.

The stabilization energies<sup>62</sup> calculated for the emim<sup>+</sup> complexes with BF<sub>4</sub><sup>-</sup>, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, and (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup> are compared with the self-diffusion coefficients of the ions<sup>54</sup> as shown in Table 7. Although the size of the (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup> anion is significantly larger than those of the BF<sub>4</sub><sup>-</sup> and CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> anions, the self-diffusion coefficients of the ions in the (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>-based ionic liquid are larger than those in the other two ionic liquids. The stabilization energy calculated for the emim<sup>+</sup> complex with (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup> is substantially smaller than those for the other two complexes, which suggests that the self-diffusion coefficients depend on the magnitude of the interaction between the anion and cation. The radial distribution functions in the [bmim][CF<sub>3</sub>SO<sub>3</sub>] ionic liquid (Figure 5S) show that the *g*<sub>C-A</sub> of [bmim][CF<sub>3</sub>SO<sub>3</sub>] has a strong peak around 4 Å. The short contact between the C<sub>2</sub> carbon atom of the bmim<sup>+</sup> cation and the SO<sub>3</sub> group of the anion also suggests the existence of the strong attraction.

## Conclusion

The molecular dynamics simulations of the 13 ionic liquids were carried out using newly refined force field based on the ab initio molecular orbital calculations of the isolated ions and the experimental densities of a few ionic liquids. The self-diffusion coefficients calculated for the ions in the ionic liquids by the molecular dynamics simulations well reproduced most of the experimental trends of the cation and anion dependence of the self-diffusion coefficients, although the calculated self-diffusion coefficients are about 1 order smaller than the experimental ones. The good performance of the molecular dynamics simulations suggests that we can predict the cation and anion dependence of the transport properties of the ionic liquids by molecular dynamics simulations if we use a carefully

refined force field. The motion of the carbon atoms close to the end of the alkyl chains of the imidazolium cations is substantially faster than the diffusion of the imidazolium ring and anion in the time scale of a few nano seconds. The dynamics of the atoms in the nonpolar domains (composed of alkyl chains) is significantly different from that in the polar domains (composed of imidazolium rings and anions). The different motion of atoms in the two types of domains will be important for understanding the transport properties of the ions and solute molecules in the ionic liquids. The relationship between the self-diffusion coefficients of the ions and the stabilization energies for the ion pairs suggests that at least three factors (size of ions, shape of ions, and magnitude of interaction energy between anion and cation) play important roles in determining the magnitude of the self-diffusion coefficients.

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**Supporting Information Available:** Geometries for [Rmim]-[TFSA] ion pairs (m, e, b, C<sub>6</sub> and C<sub>8</sub>) optimized at the HF/6-311G\*\* level, site-site intermolecular radial distribution functions of ionic liquids, mean-square displacements of ions in ionic liquids, parameter file and topology file for MPDYN program. This material is available free of charge via the Internet at <http://pubs.acs.org>

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