## **Physicochemical Properties and Structures of Room Temperature Ionic Liquids. 1.** Variation of Anionic Species

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Room-temperature ionic liquids (RTILs) based on 1-butyl-3-methylimidazolium ([bmim]) with a variety of fluorinated anions were prepared, and the thermal behavior, density, viscosity, self-diffusion coefficients of the cations and anions, and ionic conductivity were measured over a wide temperature range. The temperature dependencies of the self-diffusion coefficient, viscosity, ionic conductivity, and molar conductivity have been fitted to the Vogel–Fulcher–Tamman equation, and the best-fit parameters for the self-diffusion coefficient, viscosity, ionic conductivity, and molar conductivity have been estimated, together with the linear fitting parameters for the density. The self-diffusion coefficients determined for the individual ions by pulsed-fieldgradient spin-echo NMR method exhibit higher values for the cation compared with the anion over a wide temperature range, even if its radius is larger than that of the anionic radii. The summation of the cationic and anionic diffusion coefficients for the RTILs follows the order  $[bmim][(CF_3SO_2)_2N] > [bmim][CF_3CO_2]$ > [bmim][CF<sub>3</sub>SO<sub>3</sub>] > [bmim][BF<sub>4</sub>] > [bmim][(C<sub>2</sub>F<sub>5</sub>SO<sub>2</sub>)<sub>2</sub>N] > [bmim][PF<sub>6</sub>] at 30 °C, and the order of the diffusion coefficients greatly contrasts to the viscosity data. The ionic association is proposed from the results of the ratios of molar conductivity obtained from impedance measurements to that calculated by the ionic diffusivity using the Nernst–Einstein equation. The ratio for the ionic liquids follows the order  $[bmim][PF_6]$  $> [bmim][BF_4] > [bmim][(C_{F_5}SO_2)_2N] > [bmim][(CF_3SO_2)_2N] > [bmim][CF_3SO_3] > [bmim][CF_3CO_2] at$ 30 °C and provides quantitative information on the active ions contributing to ionic conduction in the diffusion components.

#### Introduction

Air- and water-stable room temperature ionic liquids (RTILs) are comprised entirely of ions and are liquids at ambient or far below ambient temperature. They possess unique physicochemical properties, such as negligible vapor pressure, nonflammability, high ionic conductivity, and high thermal, chemical, and electrochemical stability, which make them so distinct from conventional molecular liquids.<sup>1</sup> It is not surprising that ionic liquids, while attracting significant attention of academicians in multidisciplinary areas, have been considered as new solvents and materials for practical applications. The low volatility, together with the ease of handling and high ionic concentration, have led the RTILs to be used as novel organic and inorganic reaction media and separation solvents.<sup>2</sup> Since the ionic liquids are essentially ionic conductors, their utilization as novel electrolytes for electrochemical devices, such as lithium secondary batteries, electric double layer capacitors, dye-sensitized solar cells, fuel cells, and actuators, has also been the subject of intense study.<sup>3-10</sup> These developments also include hybrid materials based on the RTILs with polymers and nanocarbons.11-15

The RTILs are typically comprised of combinations of organic cations, such as imidazolium, pyridinium, pyrroli-

dinium, ammonium, sulfonium and phosphonium derivatives, and bulky and soft anions, such as [BF<sub>4</sub>], [PF<sub>6</sub>], [CF<sub>3</sub>SO<sub>3</sub>], and [(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N].<sup>2b,16-21</sup> Since numerous combinations of the cationic and anionic structures are possible, physicochemical properties of the ionic liquids can be easily tuned simply by changing the structure of the component ions. Proper design of the ionic liquids has, thus, been the most fascinating domain of the current research. For the design, however, it is necessary to accumulate data on the basic physical and chemical properties. The high ionic concentration, resulting in the high Coulombic interactions, implies that the differences in the ionic state and ion dynamics significantly contribute to the difference in the physicochemical properties of RTILs. However, microscopic information about the ionic state and ion dynamics has been insufficient. It has only been recently recognized that pulsedfield-gradient spin-echo (PGSE) nuclear magnetic resonance (NMR) method can be applied for the measurement of the selfdiffusion coefficients of the individual ionic species.<sup>22-24</sup> We have successfully applied the technique for the determination of the cationic and anionic self-diffusion coefficients of certain RTILs of 1-ethyl-3-methylimidazolium ([emim]) and 1-butylpyridinium ([bpy]) cations with [BF<sub>4</sub>] and [(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N] anions.<sup>25</sup> On the basis of the analysis of the ionic diffusivity, viscosity, and conductivity, we were able to obtain useful information on the diffusion mechanism and ion transport, which further indicated the ion association/dissociation in the ionic liquids. However, since the study involved ionic liquids only from two different cationic and anionic species, a clear correlation between the physicochemical properties and the structural difference

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could not be made. This necessitates a comprehensive study on the effect of the ionic structures on the physicochemical characteristics of a wide variety of ionic liquids.

The present studies have been initiated to present reliable data for the physicochemical properties of a series of ionic liquids, which include thermal behavior, density, self-diffusion coefficient of the cation and anion, viscosity, and ionic conductivity over a wide temperature range. The ultimate goal is, however, to know the relationship between the ionic structures and the physicochemical properties, in order to establish principles for the molecular design of the RTILs having desirable properties. In this study, a series of RTILs with a fixed cation, 1-butyl-3-methylimidazolium ([bmim]), with different anions, [(C<sub>2</sub>F<sub>5</sub>SO<sub>2</sub>)<sub>2</sub>N], [(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N], [CF<sub>3</sub>SO<sub>3</sub>], [PF<sub>6</sub>], [CF<sub>3</sub>-CO<sub>2</sub>], and [BF<sub>4</sub>], were prepared. The physicochemical properties were investigated, with focusing on the ion transport properties depending on the change in the anionic structures, to know the relationships between the ionic diffusivity, viscosity, and molar conductivity.

#### **Experimental Section**

Synthesis. The syntheses of the RTILs used in this study were based on a metathesis reaction of 1-butyl-3-methylimidazolium chloride ([bmim][Cl]) and alkali metal or silver salts with different anions, following a slight modification of the procedure reported by Welton and co-workers.<sup>26</sup> The [bmim]-[Cl] was prepared by reacting 1-methylimidazole with 1-chlorobutane in cyclohexane under a reflux condition, and the product was purified by recrystallization from acetonitrile/ethyl acetate solution to yield a white crystalline solid. For the preparation of [bmim][(C<sub>2</sub>F<sub>5</sub>SO<sub>2</sub>)<sub>2</sub>N] and [bmim][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N], the anion exchange reaction of [bmim][Cl] was made by adding 1.2 equivalent amount of LiN(SO<sub>2</sub>C<sub>2</sub>F<sub>5</sub>)<sub>2</sub> and LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> in water, followed by repeatedly washing with water. For [bmim]-[CF<sub>3</sub>SO<sub>3</sub>], [bmim][PF<sub>6</sub>] and [bmim][BF<sub>4</sub>], 1.2 equivalent amount of sodium salts of the corresponding anions and [bmim][Cl] were reacted in dichloromethane and filtered off, and then the organic solutions were extracted several times with a small amount of water to remove [bmim][Cl], as already described. The ionic liquid,  $[bmim][CF_3CO_2]$ , was prepared by the reaction of equimolar amounts of [bmim][Cl] and CF<sub>3</sub>CO<sub>2</sub>Ag in water. The precipitate, AgCl, was filtered off, and the filtrate was concentrated and passed through a silica gel column to completely remove AgCl. All of the ionic liquids were finally dehydrated under high vacuum with heating over 48 h and were stored in an argon atmosphere glovebox (VAC,  $[O_2] < 1$  ppm,  $[H_2O] < 1$  ppm). The structures of the ionic liquids were identified by <sup>1</sup>H and <sup>13</sup>C NMR and fast atom bombardment mass spectra (FAB-MS) using a JEOL JMS-AX500 mass spectrometer. Chloride content in the hydrophilic [bmim][CF3SO3], [bmim][CF<sub>3</sub>CO<sub>2</sub>], and [bmim][BF<sub>4</sub>] was maintained at least below the solubility limit of AgCl in water (1.4 mgL<sup>-1</sup>), as checked by adding an AgNO<sub>3</sub> solution. For the hydrophobic ionic liquids, [bmim][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N], [bmim][(C<sub>2</sub>F<sub>5</sub>SO<sub>2</sub>)<sub>2</sub>N], and  $[bmim][PF_6]$ , which are not miscible with water, chloride in the aqueous phases in contact with the ionic liquids could not be detected by using the AgNO<sub>3</sub> solution. Water content of all of the RTILs, determined by Karl Fischer titration, was below 40 ppm. For none of the RTILs, any other impurities such as alkali metal and silver derived from the starting materials or byproducts could be detected in the FAB-MS measurements.

**Thermal Analysis.** Differential scanning calorimetry (DSC) was carried out on a Seiko Instruments DSC 220C under nitrogen atmosphere. The samples were tightly sealed in

aluminum pans in the dry glovebox. The samples were heated to 80 °C followed by cooling to -150 °C and then heated at a cooling and heating rate of 10 °C min<sup>-1</sup>. The glass transition temperature ( $T_g$ ) and the melting point ( $T_m$ ) were determined from the DSC thermograms during the programmed reheating steps. Thermogravimetric measurements were conducted on a Seiko Instruments thermo-gravimetry/differential thermal analyzer (TG-DTA 6200) from room temperature to 550 °C at a heating rate of 10 K min<sup>-1</sup>, unless otherwise noted, under nitrogen atmosphere with open alumina (Al<sub>2</sub>O<sub>3</sub>) pans, and for some cases also with aluminum (Al) pans.

**Density.** The density measurement was performed using a thermo-regulated density/specific gravity meter DA-100 (Kyoto Electronics Manufacturing Co. Ltd.). The measurements were conducted in the range of 15 to 40  $^{\circ}$ C.

**Self-Diffusion Coefficients.** The PGSE-NMR measurements were conducted by using a JEOL JNM-AL 400 spectrometer with a 9.4 T narrow-bore superconducting magnet equipped with a JEOL pulse field gradient probe and a current amplifier. The sine gradient pulse, providing gradient strength up to 12 Tm<sup>-1</sup>, was used throughout the measurements in this study. The selfdiffusion coefficients were measured using a simple Hahn spin echo sequence, (i.e., 90°- $\tau$ -180°- $\tau$ -Acquisition), incorporating a gradient pulse in each  $\tau$  period. The free diffusion echo signal attenuation, *E*, is related to the experimental parameters by<sup>27</sup>

$$\ln(E) = \ln(S/S_{g=0}) = -\gamma^2 g^2 D \delta^2 (4\Delta - \delta) / \pi^2$$
 (1)

where S is the spin-echo signal intensity,  $\delta$  is the duration of the field gradient with magnitude  $g, \gamma$  is the gyromagnetic ratio, D is the self-diffusion coefficient, and  $\Delta$  is the interval between two gradient pulses. Unless otherwise noted, the measurements were conducted with  $\Delta = 50$  ms. A recycle delay sufficient in allowing full relaxation (i.e.,  $>5T_1$ ) was used between each transition. The measurements for the cationic and anionic selfdiffusion coefficients in each RTIL were made by <sup>1</sup>H (399.7 MHz) and <sup>19</sup>F (376.1 MHz) nuclei, respectively. The measurement was performed at a range of temperatures with gradual cooling from +80 to -10 °C with the samples thermally equilibrated at each temperature for 30 min prior to the measurements. The samples were inserted into a 5 mm (o.d.) NMR microtube (BMS-005J, Shigemi, Tokyo) in the glovebox to a height of 5 mm. The sample height of some of the ionic liquids, which were susceptible to convection due to their low viscosities, was maintained at 2 mm, so that the relatively small sample volume could minimize the deleterious effect of convection in the diffusion measurements.<sup>28</sup> The reliability of the selfdiffusion coefficients for some RTILs was crosschecked by replicate measurements by using a different system, a JEOL GSH-200 spectrometer with a 4.7 T wide-bore magnet controlled by TecMag Apollo.24,28

**Viscosity.** The viscosity measurement was carried out with a Toki RE80 cone-plate viscometer under nitrogen atmosphere. The temperature was controlled in the range of +80 to -10 °C by a Thomas TRL-108H circulation-type thermo-regulated water bath.

**Electrochemical Measurements.** The bulk ionic conductivity was measured by complex impedance measurements, using a computer-controlled Hewlett-Packard 4192A LF impedance analyzer over the frequency range from 5 Hz to 13 MHz. The RTILs were filled in a conductivity cell constructed with platinized platinum electrode cells (TOA Electronics, CG-511B) with the cell constants of ca. 1 cm<sup>-1</sup> determined by a standard KCl aqueous solution. The measurement was carried out at controlled temperatures with cooling from +100 to -10 °C.

**TABLE 1:** Molecular Weight and Thermal Properties

	$MW/gmol^{-1}$	$T_{\rm g}/^{\rm o}{\rm C}^a$	$T_{\rm m}/^{\rm o}{\rm C}^a$	$T_{\rm d}/^{\rm o}{\rm C}^b$
$[bmim][(C_2F_5SO_2)_2N]$	519.4	-84		402
$[bmim][(CF_3SO_2)_2N]$	419.4	-87	-3	423
[bmim][CF <sub>3</sub> SO <sub>3</sub> ]	288.2		17	409
[bmim][PF <sub>6</sub> ]	284.2	-77	10	433
[bmim][CF <sub>3</sub> CO <sub>2</sub> ]	252.2	-78		176
[bmim][BF <sub>4</sub> ]	226.0	-83		425

<sup>*a*</sup> Onset temperatures of a heat capacity change  $(T_g)$ , and an endothermic peak  $(T_m)$  determined by differential scanning calorimetry. <sup>*b*</sup> Onset temperatures of mass loss  $(T_d)$ .

For the temperature range between 40 and 10 °C, the measurement was conducted using a Lauda RE104 thermo-regulated water bath, whereas the other measurements were conducted in a Tabai Espec SU-220 temperature chamber.

#### Results

Thermal Property and Density. Impurities in the RTILs may significantly affect their properties, such as thermal property, viscosity, conductivity, and diffusivity.<sup>29</sup> However, chloride and water content in the system were in the acceptable limits, and no other impurities could be detected; therefore, the physicochemical properties of the ionic liquids in this study have no considerable influence from the impurities. The DSC results during reheating scans are listed in Table 1. At the scanning rate of 10 °C min<sup>-1</sup>, each RTIL in this study exhibits a heat capacity change in the DSC thermogram, corresponding to a glass transition temperature  $(T_g)$ , with the exception of [bmim]-[CF<sub>3</sub>SO<sub>3</sub>]. No endothermic peak, corresponding to a melting point  $(T_m)$ , was observed for  $[bmim][(C_2F_5SO_2)_2N]$ , [bmim]-[CF<sub>3</sub>CO<sub>2</sub>], and [bmim][BF<sub>4</sub>] in the cycle of the measurements. Although [bmim][CF<sub>3</sub>SO<sub>3</sub>] did not exhibit the  $T_g$  at the scan rate of the measurement, the crystallization exotherm in the cooling scan was found to be significantly lower than the  $T_{\rm m}$ (by ca. 40 °C). These results indicate the very slow crystallization rate and the fairly stable supercooling state for the ionic liquids. Thermogravimetric results show that most of the ionic liquids have excellent short-term thermal stability up to 400 °C at a scan rate of 10 °C min<sup>-1</sup>, except for [bmim][CF<sub>3</sub>CO<sub>2</sub>] at 176 °C (Table 1). However, the thermal stability shows scan rate dependency, and a faster heating scan has been found to give higher thermal stability. For instance, the onset temperatures of mass loss (T<sub>d</sub>) of [bmim][PF<sub>6</sub>] and [bmim][CF<sub>3</sub>CO<sub>2</sub>] at a scan rate of 10 °C min<sup>-1</sup> are higher by about 30 and 10 °C, respectively, compared to those of 3 °C min<sup>-1</sup>. Similary, the thermal stability of [bmim][BF4] and [bmim][PF6] showed strong dependence on the type of the used sample pans by about 50 and 80 °C, respectively, where the  $T_{\rm d}$  using an alumina pan was higher than those using an aluminum pan (data not shown). This can be attributed to enhanced thermal decomposition catalyzed by aluminum metal.<sup>30</sup> The  $T_d$  for the RTILs apparently follows the order of  $[PF_6] > [BF_4] \approx [(CF_3SO_2)_2N] > [CF_3 SO_3$  >  $[(C_2F_5SO_2)_2N] \gg [CF_3CO_2]$ . The thermal stability of the RTILs, therefore, depends on the anionic species. The pyrolysis of the imidazolium based salts have been reported to proceed most likely via S<sub>N</sub>2 process, and therefore, change in the basicity and/or nucleophilicity of the anions is likely to bring about a change in the thermal stability of the RTILs.<sup>31</sup> The different  $T_{d}$  for the variation in the nucelophilicity of the RTILs in this study is, therefore, reasonable and in agreement with literature.

Temperature dependency of density for the RTILs, as depicted in Figure 1, shows linear decrease with increasing temperature. The best-fit parameters for the linear fitting are listed in Table



Figure 1. Density of [bmim] based ionic liquids as a function of temperature.

TABLE 2: Density Equation Parameters and Molar Concentration at 30 °C ( $M_{30}$ ) Density Equation

$\rho = b - aT$				
	$a/10^{-4}$ g cm <sup>-3</sup> K <sup>-1</sup>	<i>b</i> / g cm <sup>-3</sup>	$R^{2/}$ $10^{-1}$	$M_{30}/10^{-3}$ mol cm <sup>-3</sup>
$[bmim][(C_2F_5SO_2)_2N]$	10.3	1.81	9.99	2.91
$[\text{bmim}][(CF_3SO_2)_2N]$ $[\text{bmim}][CF_3SO_3]$	9.40 8.00	1.54	9.99	3.42 4.49
[bmim][PF <sub>6</sub> ] [bmim][CF <sub>3</sub> CO <sub>2</sub> ]	8.69 7.54	1.63 1.44	9.96 9.98	4.80 4.81
[bmim][BF <sub>4</sub> ]	7.26	1.42	9.98	5.30

2. The difference in the anions with the same [bmim] cation in the ionic liquids leads to different density, and the order of density approximately follows the decreasing order of the molecular weight of the anions. The calculated molar concentration of the RTILs at 30 °C ( $M_{30}$ ) based on the density value and molecular weight is also tabulated in Table 2. The molar concentration increases with decrease in the molecular weight of the anions, and the values range from 2.91 to 5.30 mol L<sup>-1</sup>.

Self-Diffusion Coefficient and Viscosity. The PGSE-NMR method for the determination of the self-diffusion coefficient allows evaluation of the diffusivity of ions without the use of any additional probe molecules, which might affect the diffusion of the ions. Since the RTILs used in this study include NMRsensitive <sup>1</sup>H and <sup>19</sup>F nuclei in the cation and anion, respectively, each of the cationic and anionic self-diffusion coefficients could be independently determined. Figure 2 shows the temperature dependency of self-diffusion coefficients of the cation  $(D_{\text{cation}})$ and anion (*D*<sub>anion</sub>) for [bmim][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N], [bmim][CF<sub>3</sub>SO<sub>3</sub>], and [bmim][(C<sub>2</sub>F<sub>5</sub>SO<sub>2</sub>)<sub>2</sub>N] (Figure 2a) and [bmim][CF<sub>3</sub>CO<sub>2</sub>], [bmim][BF<sub>4</sub>], and [bmim][PF<sub>6</sub>] (Figure 2b). The measuring time ( $\Delta$  in eq 1) dependency of the self-diffusion coefficients for some of the ionic liquids was checked, and in the range of  $\Delta$ from 20 to 100 ms, the self-diffusion coefficients did not show any notable dependency for [bmim][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N], [bmim][PF<sub>6</sub>], and [bmim][BF<sub>4</sub>], which suggests that the ion diffusion is the Fickian diffusion in the homogeneous fluid and the convection effects can be disregarded in the temperature range studied under the experimental conditions. The temperature dependency of the diffusion coefficients in each case exhibits convex curvedprofiles; therefore, experimental data were fitted with the Vogel-Fulcher-Tamman (VFT) equation<sup>32</sup> for diffusivity

$$D = D_0 \exp[-B/(T - T_0)]$$
(2)



**Figure 2.** Temperature dependence of self-diffusion coefficients of the cation and anion for (a)  $[bmim][(C_F_3SO_2)_2N]$ ,  $[bmim][(CF_3SO_2)_2N]$ , and  $[bmim][CF_3SO_3]$  and (b)  $[bmim][PF_6]$ ,  $[bmim][CF_3CO_2]$ , and  $[bmim][BF_4]$ .

where the constants  $D_0$  (cm<sup>2</sup> s<sup>-1</sup>), B (K), and  $T_0$  (K) are adjustable parameters. The best-fit parameters of the ionic diffusivity are summarized in Table 3. The dashed and solid lines in Figure 2 are the calculated curves by using the best-fit parameters and eq 2. It is worthwhile to describe that the  $D_0$ and the *B* parameters of the anion are larger than those of the cation for all of the RTILs. The experimental ionic self-diffusion coefficients for [bmim] and [PF<sub>6</sub>] in the [bmim][PF<sub>6</sub>] at 25 °C, evaluated from the data using the best-fit parameters of the VFT equation (eq 2), are 6.8 and  $4.0 \times 10^{-8}$  cm<sup>2</sup> s<sup>-1</sup>, respectively. The simulated values for the self-diffusion coefficients at 25 °C, reported by Morrow et al.<sup>33</sup> by a molecular dynamic (MD) study, are  $9.7 \pm 4.1$  and  $8.8 \pm 4.2 \times 10^{-8}$  cm<sup>2</sup> s<sup>-1</sup>, respectively, which are fairly close to our experimental results.

The simple sum of the cationic and anionic self-diffusion coefficients ( $D_{\text{cation}} + D_{\text{anion}}$ ) for these RTILs is shown in Figure 3, and the best-fit parameters of the VFT equation are also listed in Table 3. The sum of the cationic and anionic diffusion coefficients for the ionic liquids follows the order [bmim][(CF<sub>3</sub>-SO<sub>2</sub>)<sub>2</sub>N] > [bmim][CF<sub>3</sub>CO<sub>2</sub>] > [bmim][CF<sub>3</sub>SO<sub>3</sub>] > [bmim]-[BF<sub>4</sub>] > [bmim][(C<sub>2</sub>F<sub>5</sub>SO<sub>2</sub>)<sub>2</sub>N] > [bmim][PF<sub>6</sub>] at 30 °C.

The temperature dependency of the viscosity  $(\eta)$  for the RTILs and the profiles fitted to the VFT equation are depicted in Figure 4. The corresponding VFT equation is

$$\eta = \eta_0 \exp[B/(T - T_0)] \tag{3}$$



Figure 3. Temperature dependence of simple summation of the cationic and anionic self-diffusion coefficients  $(D_{\text{cation}} + D_{\text{anion}})$  for [bmim] based ionic liquids.

L	$D = D_0 \exp[-B/(T - T_0)]$			
	$D_0/10^{-4} \mathrm{~cm}^{-2} \mathrm{~s}^{-1}$	<i>B</i> /10 <sup>2</sup> K	$T_0/K$	
$[bmim][(C_2F_5SO_2)_2N]$				
cation	$1.7 \pm 0.2$	$9.95\pm0.43$	$160 \pm 3$	
anion	$1.9 \pm 0.1$	$11.09\pm0.17$	$154 \pm 1$	
cation+anion	$3.5 \pm 0.3$	$10.43\pm0.27$	$157 \pm 2$	
[bmim][(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N]				
cation	$1.1 \pm 0.1$	$8.45\pm0.37$	$157 \pm 3$	
anion	$1.3 \pm 0.3$	$9.33\pm0.67$	$152\pm 6$	
cation+anion	$2.3 \pm 0.3$	$8.84\pm0.45$	$155 \pm 4$	
[bmim][CF <sub>3</sub> SO <sub>3</sub> ]				
cation	$0.80 \pm 0.01$	$8.29\pm0.43$	$163 \pm 4$	
anion	$1.8 \pm 0.2$	$10.95\pm0.34$	$147 \pm 3$	
cation+anion	$2.3 \pm 0.2$	$9.42\pm0.23$	$156 \pm 2$	
[bmim][PF <sub>6</sub> ]				
cation	$1.5 \pm 0.3$	$9.87 \pm 0.54$	$169 \pm 4$	
anion	$1.8 \pm 0.3$	$10.84\pm0.54$	$165 \pm 4$	
cation+anion	$3.2 \pm 0.5$	$10.32\pm0.44$	$167 \pm 3$	
[bmim][CF <sub>3</sub> CO <sub>2</sub> ]				
cation	$1.4 \pm 0.1$	$9.19\pm0.29$	$160 \pm 2$	
anion	$1.9 \pm 0.2$	$10.28\pm0.40$	$155\pm3$	
cation+anion	$3.3 \pm 0.3$	$9.70\pm0.29$	$158 \pm 2$	
[bmim][BF <sub>4</sub> ]				
cation	$1.4 \pm 0.1$	$9.35\pm0.28$	$162 \pm 3$	
anion	$2.8 \pm 0.4$	$11.08\pm0.47$	$153\pm3$	
cation+anion	$4.0 \pm 0.4$	$10.21\pm0.31$	$158 \pm 2$	

where  $\eta_0$  (mPas), *B* (K), and  $T_0$  (K) are constants. The best-fit parameters for viscosity are tabulated in Table 4. The macroscopic viscosity values at 30 °C follows the order [bmim][PF<sub>6</sub>] > [bmim][(C<sub>2</sub>F<sub>5</sub>SO<sub>2</sub>)<sub>2</sub>N] > [bmim][BF<sub>4</sub>] > [bmim][CF<sub>3</sub>SO<sub>3</sub>] > [bmim][CF<sub>3</sub>CO<sub>2</sub>] > [bmim][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N], which well contrasts with that of the ionic self-diffusion coefficients.

**Conductivity.** All of the six [bmim]-based ionic liquids have relatively high ionic conductivities ( $\sigma$ ), which exhibit temperature dependency, as shown in Figure 5. The VFT equation for conductivity is

$$\sigma = \sigma_0 \exp[-B/(T - T_0)] \tag{4}$$

where  $\sigma_0$  (Scm<sup>-1</sup>), *B* (K), and  $T_0$  (K) are constants. The best-fit parameters are shown in Table 5. Since the molar concentration of these RTILs is strongly dependent on the anionic structure (Table 2), the molar conductivity has also been calculated from



Figure 4. Viscosities of [bmim] based room-temperature ionic liquids as a function of temperature.



Figure 5. Temperature dependence of ionic conductivity for [bmim] based ionic liquids.

**TABLE 4: VFT Equation Parameters of Viscosity Data** 

$\eta = \eta_0 \exp[B/(T - T_0)]$			
	$\eta_0/10^{-1}$ mPas	$B/10^2 \mathrm{K}$	$T_0/K$
$[bmim][(C_2F_5SO_2)_2N]$	$1.7\pm0.2$	$7.63\pm0.38$	$180\pm3$
[bmim][(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N]	$2.5 \pm 0.2$	$6.25 \pm 0.22$	$180 \pm 2$
[bmim][CF <sub>3</sub> SO <sub>3</sub> ]	$3.7 \pm 0.6$	$5.70 \pm 0.37$	$193 \pm 4$
[bmim][PF <sub>6</sub> ]	$3.6 \pm 0.5$	$6.39 \pm 0.25$	$201 \pm 2$
[bmim][CF <sub>3</sub> CO <sub>2</sub> ]	$1.1 \pm 0.2$	$7.88 \pm 0.53$	$177 \pm 4$
[bmim][BF <sub>4</sub> ]	$2.1 \pm 0.1$	$6.97 \pm 0.69$	$185 \pm 6$

 TABLE 5: VFT Equation Parameters of Ionic Conductivity

 Data

$\sigma = \sigma_0 \exp[-B/(T - T_0)]$			
	$\sigma_0/10^{-1}$ mPas	$B/10^2 \mathrm{K}$	$T_0/\mathrm{K}$
$[bmim][(C_2F_5SO_2)_2N]$	$7.1 \pm 0.5$	$7.96\pm0.22$	$169 \pm 2$
$[bmim][(CF_3SO_2)_2N]$	$4.3 \pm 0.2$	$5.65\pm0.14$	$178 \pm 2$
[bmim][CF <sub>3</sub> SO <sub>3</sub> ]	$9.8 \pm 0.8$	$7.93\pm0.26$	$162 \pm 3$
[bmim][PF <sub>6</sub> ]	$14.7 \pm 1.0$	$8.55\pm0.20$	$174 \pm 2$
[bmim][CF <sub>3</sub> CO <sub>2</sub> ]	$9.2 \pm 0.4$	$7.19\pm0.13$	$172 \pm 1$
[bmim][BF <sub>4</sub> ]	$13.8\pm0.6$	$7.41\pm0.13$	$174 \pm 1$

the ionic conductivity and the molar concentration. The VFT equation for the molar conductivity is

$$\Lambda = \Lambda_0 \exp[-B/(T - T_0)]$$
<sup>(5)</sup>

where  $\Lambda_0$  (Scm<sup>2</sup> mol<sup>-1</sup>), *B* (K), and  $T_0$  (K) are constants. The temperature dependency of the molar conductivity ( $\Lambda_{imp}$ ) and



**Figure 6.** Molar conductivity of [bmim] based ionic liquids: (a) obtained from ionic conductivity and molar concentration; (b) calculated from ionic self-diffusion coefficients and the Nernst–Einstein equation.

 TABLE 6: VFT Equation Parameters of Molar

 Conductivity Data

	$\Lambda_0/10^2$		
	$\mathrm{Scm}^2\mathrm{mol}^{-1}$	$B/10^{2} { m K}$	$T_0/K$
$\overline{\Lambda_{\rm imp}} = \Lambda_0 \exp[-B/(T - T_0)]$			
$[bmim][(C_2F_5SO_2)_2N]$	$3.0 \pm 0.2$	$8.43\pm0.24$	$166 \pm 2$
$[bmim][(CF_3SO_2)_2N]$	$1.5 \pm 0.1$	$6.05 \pm 0.13$	$175 \pm 1$
[bmim][CF <sub>3</sub> SO <sub>3</sub> ]	$2.7 \pm 0.2$	$8.41\pm0.29$	$159 \pm 3$
[bmim][PF <sub>6</sub> ]	$3.8 \pm 0.2$	$8.97\pm0.20$	$172 \pm 2$
[bmim][CF <sub>3</sub> CO <sub>2</sub> ]	$2.3 \pm 0.1$	$7.61\pm0.13$	$169 \pm 1$
[bmim][BF <sub>4</sub> ]	$3.2 \pm 0.1$	$7.80\pm0.12$	$171 \pm 1$
$\Lambda_{\rm NMR} = \Lambda_0 \exp[-B/(T-T_0)]$			
$[bmim][(C_2F_5SO_2)_2N]$	$5.6 \pm 0.5$	$8.69\pm0.28$	$165 \pm 2$
$[bmim][(CF_3SO_2)_2N]$	$3.6 \pm 0.4$	$7.03\pm0.33$	$165 \pm 3$
[bmim][CF <sub>3</sub> SO <sub>3</sub> ]	$3.5 \pm 0.3$	$7.67\pm0.23$	$165 \pm 2$
[bmim][PF <sub>6</sub> ]	$5.2 \pm 0.8$	$8.73\pm0.43$	$174 \pm 3$
[bmim][CF <sub>3</sub> CO <sub>2</sub> ]	$5.1 \pm 0.4$	$7.94 \pm 0.22$	$166 \pm 2$
[bmim][BF <sub>4</sub> ]	$6.2 \pm 0.5$	$8.44\pm0.25$	$166 \pm 2$

their VFT fitting curves are shown in Figure 6a, with the bestfit parameters listed in Table 6. The molar conductivity of the RTILs can also be calculated from the self-diffusion coefficients ( $\Lambda_{NMR}$ ), determined by the PGSE-NMR measurements, using the Nernst–Einstein equation

$$\Lambda_{\rm NMR} = N_{\rm A} e^2 (D_{\rm cation} + D_{\rm anion}) / kT = F^2 (D_{\rm cation} + D_{\rm anion}) / RT$$
(6)

where  $N_A$  is the Avogadro number, e is the electric charge on each ionic carrier, k is the Boltzmann constant, F is the Faraday

constant, and *R* is the universal gas constant. The temperature dependency of the molar conductivity calculated from the ionic diffusion coefficient and eq 6 is shown in Figure 6b and the best-fit parameters of the VFT equation are listed in Table 6. The experimental molar conductivity value ( $\Lambda_{imp}$ ) is lower than that of the calculated molar conductivity ( $\Lambda_{NMR}$ ) in the whole temperature range, which has been established as one of the important phenomena associated with ionic liquids (vide infra).

#### Discussion

**Ion Diffusion Mechanisms of [bmim]-Based RTILs.** The sum of the cationic and anionic diffusion coefficients determined for the RTILs ranges from 1.6 to  $6.0 \times 10^{-7}$  cm<sup>2</sup> s<sup>-1</sup> at 30 °C and is relatively low. The viscosity and self-diffusion coefficient of a typical polar organic solvent, propylene carbonate (PC), have been reported as 2.5 mPas at 25 °C and  $5.8 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup> at 30 °C, respectively.<sup>22,34</sup> The low ionic diffusivity of the ionic liquids is therefore well justified in terms of their high viscosity (from 40 to 182 mPas at 30 °C). The much lower ion diffusion coefficients and higher viscosity for the ionic liquids may be attributable to the very strong Coulombic forces among each ionic species in the ionic liquids.

As mentioned above, the sum of cationic and anionic selfdiffusion coefficients and viscosities for the RTILs differs depending on the anionic structures. In general, the diffusivity is correlated to the fluidity  $(1/\eta)$  by the Stokes–Einstein equation

$$D = \frac{kT}{c\pi\eta r_s} \tag{7}$$

where k is the Boltzmann constant, T is the absolute temperature, c is a constant, and  $r_s$  is the effective hydrodynamic (Stokes) radius. Figure 7a,b illustrates the relationship between the  $T\eta^{-1}$ and the self-diffusion coefficient of the cation and anion, respectively. All of the ionic liquids give approximately straight lines passing through the origin (regression factor:  $R^2 > 0.988$ ), indicating that the ionic diffusivity in the ionic liquids basically obeys eq 7. However, it should be noted that the slopes of the straight lines are not identical, even for the identical cationic relationships (Figure 7a). The Stokes law is based on the assumption of a rigid solute sphere diffusing in a continuum of solvent, and in the case of a large solute in a small solvent, the factor, c, can attain the value of 6. However, if the ratio of the solute size to solvent is increased, especially for highly viscous media, the correlation breaks down, and the value of c in eq 7 is reduced to ca.  $4.^{35}$  Thus, the factor *c* may help to understand the microscopic ion dynamics in the RTILs. The reported van der Waals radius from MM2 and ab initio molecular orbital calculations is 0.330, 0.362, 0.326, 0.267, 0.254, and 0.227 nm for [bmim], [(C<sub>2</sub>F<sub>5</sub>SO<sub>2</sub>)<sub>2</sub>N], [(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N], [CF<sub>3</sub>SO<sub>3</sub>], [PF<sub>6</sub>], and [BF<sub>4</sub>], respectively.<sup>36,37</sup> By using the experimental slopes in Figure 7a and the van der Waals radius of [bmim], the factor c for [bmim] based ionic liquids with [(C2F5SO2)2N], [(CF3-SO<sub>2</sub>)<sub>2</sub>N], [CF<sub>3</sub>SO<sub>3</sub>], [PF<sub>6</sub>], [CF<sub>3</sub>CO<sub>2</sub>], and [BF<sub>4</sub>] can be obtained as 3.3, 3.4, 3.4, 3.0, 3.8, and 3.3, respectively. Similarly, the c values for the anionic diffusivity from Figure 7b are 4.1, 4.3, 5.0, 4.6, and 4.6 for [(C<sub>2</sub>F<sub>5</sub>SO<sub>2</sub>)<sub>2</sub>N], [(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N], [CF<sub>3</sub>SO<sub>3</sub>], [PF<sub>6</sub>], and [BF<sub>4</sub>], respectively. Although the van der Waals radius of [CF<sub>3</sub>CO<sub>2</sub>] is not available in the literature, the factor c can be approximated in the range from 5.4 to 6.0, by using the radii of  $[PF_6]$  and  $[BF_4]$ . The results of smaller c values of the cation than those of anions suggest that the anions in the ionic liquids diffuse slower than the cation if they have the same van der Waals radii.



**Figure 7.** Relationship between  $T \eta^{-1}(T)$ , absolute temperature; and  $\eta$ , viscosity) and self-diffusion coefficients of (a) the cation and (b) anion for [bmim] based ionic liquids.



**Figure 8.** Apparent cationic transference number,  $D_{\text{cation}}/(D_{\text{cation}} + D_{\text{anion}})$ , for [bmim] based ionic liquids plotted against temperature.

Figure 8 depicts the apparent cationic transference number  $(D_{\text{cation}}/(D_{\text{cation}} + D_{\text{anion}}))$  for each RTIL as a function of temperature. Interestingly, the cationic self-diffusion coefficient is larger than the anionic diffusion coefficient at all of the temperatures of the measurements, except for [bmim][BF4] at 80 °C. The transference number approximately follows the order  $[(C_2F_5SO_2)_2N] \ge [(CF_3SO_2)_2N] \ge [CF_3SO_3] \ge [PF_6] \ge [CF_3-CO_2] \ge [BF_4]$ . The order is likely to be influenced by the size



Figure 9. Molar conductivity ratios  $(\Lambda_{imp}/\Lambda_{NMR})$  for [bmim] based ionic liquids plotted against temperature.

of the anions. It should be mentioned here that, despite a large disparity of the cationic (0.330 nm) and anionic (0.227 nm) radii, the transference number of [bmim][BF<sub>4</sub>] is estimated to be higher than 0.5 at room temperature. These results also indicate that the cation can diffuse faster than the anions, even if the cationic radius is larger than the anionic radii. The apparent cationic transference number decreases almost linearly with increasing temperature in all RTILs indicating the relatively higher thermal acceleration of the anionic diffusion compared with the [bmim] diffusion, which is supported by the larger *B* values, in other words, the activation energies for the diffusivity of the anions than those for the cations (Table 3) for the individual ionic liquids.

Ionic Association and Ion Transport Behavior. The <sup>1</sup>H and the <sup>19</sup>F NMR signals were always single lines for each assigned nucleus without multiple signals, indicating that, even if there are dissociated, paired, and/or aggregated ionic species, the rate of exchange for the chemical equilibrium between the dissociated and associated ions in the ionic liquids is faster than the time scale of NMR measurements. The data on the ionic diffusivity and the molar conductivity makes it possible to compare the ratio of the molar conductivity obtained from the impedance measurement ( $\Lambda_{imp}$ ) to that calculated from the ionic diffusivity ( $\Lambda_{\rm NMR}$ ). The application of the Nernst-Einstein equation for the interpretation of the experimental results of PGSE-NMR self-diffusion coefficients has been proved useful by Aihara et al. for electrolyte solutions including lithium salts, wherein they have shown that the  $\Lambda_{imp}/\Lambda_{NMR}$  approaches unity for complete dissociation of the electrolytes at the infinite dilution.<sup>23</sup> The  $\Lambda_{imp}/\Lambda_{NMR}$  can provide useful information about the ionic dissociation/association under equilibrium in the RTILs, as it serves as an indicator of the percentages of ions contributing to the ionic conduction within the diffusing component.

The  $\Lambda_{imp}/\Lambda_{NMR}$  is plotted against temperature in Figure 9 and is found to be relatively insensitive to the temperature. It is clear that the ratios for all of the RTILs in this study are lower than unity, indicating that not all of the diffusive species in ionic liquids contribute to the ionic conduction. It indicates that ionic association occurs in the liquids. The variation of the anions in the [bmim]-based RTILs leads to the different  $\Lambda_{imp}/\Lambda_{NMR}$  values, and the ratio follows the order [PF<sub>6</sub>] > [BF<sub>4</sub>] > [(C<sub>2</sub>F<sub>5</sub>SO<sub>2</sub>)<sub>2</sub>N] > [(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N] > [CF<sub>3</sub>SO<sub>3</sub>] > [CF<sub>3</sub>CO<sub>2</sub>] at 30 °C. Since the cationic structure is fixed to [bmim], the order of the  $\Lambda_{imp}/\Lambda_{NMR}$  depends merely on the anionic character. In the [PF<sub>6</sub>], [BF<sub>4</sub>], [(C<sub>2</sub>F<sub>5</sub>SO<sub>2</sub>)<sub>2</sub>N], and [(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N], the highly



Figure 10. FAB-MS spectra of [bmim][PF<sub>6</sub>] for (a) positive FAB and (b) negative FAB.

electronegative fluorine atom and electron-withdrawing perfluorosulfonyl groups contribute to the distribution of the anionic charge of phosphate, borate, and imide, respectively. In addition to the anionic charge distribution, the effect of the surfacecovering of the anion backbone by fluorine atoms may be a significant factor for weak interaction with the [bmim] cation. On the other hand, the more pronounced anionic charge localization in the anionic structures of [CF<sub>3</sub>SO<sub>3</sub>] and [CF<sub>3</sub>CO<sub>2</sub>], compared to other anions, makes them interacting sites with the [bmim]. Consequently, the interaction gives relatively lower  $\Lambda_{\text{imp}}/\Lambda_{\text{NMR}}$  values for [bmim][CF<sub>3</sub>SO<sub>3</sub>] and [bmim][CF<sub>3</sub>CO<sub>2</sub>]. The  $\Lambda_{imp}/\Lambda_{NMR}$  results are in good agreement with the previous report by Linert et al.,<sup>38</sup> wherein the donor number of [BF<sub>4</sub>] has been estimated to be lower than that of [CF<sub>3</sub>SO<sub>3</sub>] by solvatochromic study. Thus, the electron-donor ability (or Lewis basicity) determines the order of the ratios in the ionic liquids. It should be mentioned here that the molecular and quasimolecular ion peaks could be observed by the FAB-MS measurements without use of any matrixes. A typical example of the FAB-MS spectra for [bmim][PF<sub>6</sub>] is shown in Figure 10. The mass-to-charge ratio, m/z = 139, and 423 in the positive FAB spectrum (Figure 10a) can be assigned by [bmim] and [bmim]<sub>2</sub>[PF<sub>6</sub>], respectively. Similarly, the values of m/z = 145, 429, and 713 in the negative FAB spectrum (Figure 10b) are attributed to [PF<sub>6</sub>], [bmim][PF<sub>6</sub>]<sub>2</sub>, and [bmim]<sub>2</sub>[PF<sub>6</sub>]<sub>3</sub>, respectively. The observation of such ion aggregates and/or clusters of imidazolium salts in a liquid matrix has also been reported.12b,39 Interestingly, the highest molecular ions in the same measured condition, corresponding to [bmim]<sub>3</sub>[CF<sub>3</sub>CO<sub>2</sub>]<sub>4</sub>, could be detected for the [bmim][CF<sub>3</sub>CO<sub>2</sub>] ionic liquid, which gave the lowest  $\Lambda_{imp}/\Lambda_{NMR}$  values.

### **Concluding Remarks**

In this study, we propose that the ratio  $\Lambda_{imp}/\Lambda_{NMR}$  is a useful parameter to characterize various properties of the RTILs with varying anionic species. In other words, the  $\Lambda_{imp}/\Lambda_{NMR}$  represents "ionicity" of the ionic liquids, and the significant physical and chemical properties of RTILs may be determined by this parameter. Although this study is only concerned with anionic effects on the ion dynamics and ionicity, it is equally important to establish a correlation between the cationic structures and the physicochemical properties of RTILs. Further studies would be focused on the elucidation of such a correlation.

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