8 Ionicity in Ionic Liquids: Origin of Characteristic Properties of Ionic Liquids

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ABSTRACT

Physicochemical properties of 1-ethyl-3-methylimidazolium ionic liquids having $[CF_3CO_2]^-$, $[CH_3SO_3]^-$, $[CH_3CO_2]^-$, $[CF_3SO_3]^-$, $[BF_4]^-$, and $[N(CF_3SO_2)_2]^-$ anions were measured precisely. The ionicity, in other words the dissociativity of the ionic liquids, was estimated from the molar conductivity ratios ($\Lambda_{imp}/\Lambda_{NMR}$), where Λ_{imp} is molar conductivity from ionic conductivity measurements and Λ_{NMR} is that from ionic diffusivity by pulsed-gradient spin-echo nuclear magnetic resonance (NMR) measurements. The ionicity, $\Lambda_{imp}/\Lambda_{NMR}$, was controlled by the magnitude and balance of Coulombic forces, which were mainly altered by the anionic Lewis basicities, and van der Waals forces. The $\Lambda_{imp}/\Lambda_{NMR}$ values of the ionic liquids ranged from 0.5 to 0.8 and followed the anion-dependent order $[BF_4]^- > [N(CF_3SO_2)_2]^- > [CF_3SO_3]^- > [CF_3CO_2]^- > [CH_3SO_3]^- > [CH_3CO_2]^-$, which is the inverse order of the anionic basicities or the order of acidities of their conjugate acids. Calibration curves for the Lewis basicity–$\Lambda_{imp}/\Lambda_{NMR}$ relationship are presented for the 1-ethyl-3-methylimidazolium, $[C_2mim]^+$, and 1-butyl-3-methylimidazolium, $[C_4mim]^+$, ionic liquids, from which either $\Lambda_{imp}/\Lambda_{NMR}$ or Lewis basicity can be estimated if either of them is known. Viscosities of various $[C_2mim]^+$ and $[C_4mim]^+$ ionic liquids were correlated with the effective ionic concentration C_{eff}, which was estimated from the ionicity and molar concentration of these ionic liquids. With increasing C_{eff}, the viscosities tended to increase, although at the same C_{eff}, $[C_4mim]^+$ ionic liquids showed higher viscosities than $[C_2mim]^+$ ionic liquids because of the enhanced van der Waals forces.

8.1 INTRODUCTION

The growing interest in room temperature ionic liquids is a result of their unusual liquid properties, such as

(1) low vapour pressure and low flammability,
(2) wide liquid temperature range in conjunction with thermal stability,
(3) fast ion transport,
(4) unusual solubility, and
(5) structure-forming properties on the nanoscale.

The designability of ionic liquids by various combinations of available cations and anions, and further by preparing new cations and anions, allows significant flexibility in material design and in the optimisation of the properties of ionic liquids for specific purposes. However, the complexity of the inter-ionic interactions in ionic liquids makes the prediction of their properties difficult and, consequently, choice and design of the cations and anions are not always successful.

It is generally accepted that ionic liquids consist entirely of ions. On the basis of their high ionic conductivity, it can also be speculated that ionic liquids self-dissociate into ions (charged species) even in the absence of molecular solvents. However, the quantitative magnitude of the dissociativity was unknown prior to our studies [1–6]. Our interest lies in self-dissociativity, hereafter referred to as "ionicity," of ionic liquids [1–6] because the self-dissociative nature of ionic liquids plays a definite role in bringing about their characteristic properties. For instance, if the ionicity is low, the ionic liquid appears to have neither low vapour pressure nor high thermal stability, nor high ionic conductivity [6]. We have succeeded in the quantitative estimation of the ionicity of ionic liquids by measuring the ratio ($\Lambda_{imp}/\Lambda_{NMR}$) of the molar conductivity from ionic conductivity measurements (Λ_{imp}) to the molar conductivity (Λ_{NMR}) estimated from cationic and anionic diffusivities [1]. The Λ_{NMR} value assumes that every diffusing species detected by pulsed-gradient spin-echo (PGSE)–nuclear magnetic resonance (NMR) measurements contributes to the molar conductivity. In contrast, Λ_{imp} depends on the migration of charged species in an electric field. The ratio $\Lambda_{imp}/\Lambda_{NMR}$, thus, indicates the proportion of ions (charged species) that contribute to ionic conduction from all the diffusing species in the time- and space-averaged measurements. It has been revealed that, if the ionic charge is transported by the so-called vehicle mechanism [7], the ionicity of ionic liquids becomes lower than unity, which indicates that not all of the diffusive species in the ionic liquids give rise to ionic conduction; that is, ion aggregates or clusters are formed [1–6]. The ionicity is affected by the Lewis basicity of anions [2], and the Lewis acidity of cations [4], as well as van der Waals interactions between constituent ions [3]. The lower the Lewis

basicity and acidity and the van der Waals interaction, the higher is the ionicity of the ionic liquids [6]. Typical ionic liquids have been shown to have ionicities of *ca.* 0.5–0.8 [5].

It is known that salts of $[C_2mim]^+$ form a range of ionic liquids with different anions and that the resulting ionic liquids have relatively low viscosity. We have systematically reported the ionicity of 15 different ionic liquids [1–6]; however, reports on $[C_2mim]^+$ ionic liquids are rather limited, that is, $[C_2mim]$ $[N(CF_3SO_2)_2]$ [3] and $[C_2mim][BF_4]$ [1]. Here we add $[C_2mim][CF_3SO_3]$, $[C_2mim][CF_3CO_2]$, $[C_2mim][CH_3SO_3]$, and $[C_2mim][CH_3CO_2]$ to the entries of our ionicity study. Fundamental physicochemical properties, particularly transport properties of these ionic liquids, are presented. We also discuss how the ionicity is affected by the ionic structure of ionic liquids, and how the ionicity affects the physicochemical properties of ionic liquids by taking into account the ionicity data that we have collected.

8.2   METHODOLOGY

8.2.1   Synthesis

The ionic liquids $[C_2mim][CF_3CO_2]$, $[C_2mim][CH_3SO_3]$, and $[C_2mim][CH_3CO_2]$ were synthesised by the CO_2-releasing reactions of 1-ethyl-3-methylimidazolium-2-carboxylate with CF_3CO_2H, CH_3SO_3H, and CH_3CO_2H, respectively. 1-Ethyl-3-methylimidazolium-2-carboxylate was prepared according to the previously reported procedure [8]. 1-Ethylimidazole, dimethyl carbonate, and anhydrous methanol were put into a pressure vessel and mixed at 120 °C for 36 h. Methanol was removed from the reaction mixture under reduced pressure to yield a white solid, which was purified by recrystallisation from an ethanenitrile–tetrahydrofuran mixture. Into methanolic solutions of CF_3CO_2H, CH_3SO_3H, and CH_3CO_2H, a methanolic solution of 1-ethyl-3-methylimidazolium-2-carboxylate was added dropwise, stirred for several hours, and dried under a reduced pressure at 60 °C to remove the methanol, yielding $[C_2mim][CF_3CO_2]$, $[C_2mim][CH_3SO_3]$, and $[C_2mim][CH_3CO_2]$, respectively. $[C_2mim][CF_3SO_3]$ was prepared by a metathetic reaction of $[C_2mim]Cl$ and $Na[CF_3SO_3]$. The $[C_2mim]$ $[CF_3SO_3]$ was finally dehydrated under high vacuum with heating over 48 h. The $[C_2mim]^+$ ionic liquids obtained were stored in an argon atmosphere glovebox ($[O_2] < 1$ ppm; $[H_2O] < 1$ ppm). The structures of the ionic liquids were identified by ^1H and ^{13}C NMR spectroscopy and fast atom bombardment mass spectra (FAB-MS). Chloride content in $[C_2mim][CF_3SO_3]$ was maintained at least below the solubility limit of AgCl in water (1.4 mg l^{-1}), which was checked by adding an $AgNO_3$ solution. The water content of all of the ionic liquids, as determined by Karl–Fischer titration, was below 40 ppm. All of the data for $[C_2mim][N(CF_3SO_2)_2]$ [3] and $[C_2mim][BF_4]$ [1] were obtained from our previous work.

8.2.2 Thermal Analysis

Differential scanning calorimetry (DSC) was carried out under a dinitrogen atmosphere. The samples were tightly sealed in aluminium pans in a dry glovebox. The samples were heated up to 80 °C, and subsequently cooled to –150 °C and reheated, and cooled at a rate of 10 °C·min^{-1}, unless otherwise noted. The glass transition temperature (T_g) and melting point (T_m) were determined from the DSC thermograms during the programmed reheating steps. Thermogravimetric measurements were conducted from room temperature to 550 °C at a heating rate of 10 °C min^{-1} under a dinitrogen atmosphere.

8.2.3 Density

The density measurements were performed using a thermoregulated density metre. The measurements were conducted in the range of 15–40 °C.

8.2.4 Conductivity

The bulk ionic conductivity was measured by complex impedance measurements. The ionic liquids were introduced into a conductivity cell with platinised platinum electrodes, with a cell constant of *ca.* 1 cm^{-1}. The measurement was carried out at controlled temperatures with cooling from +100 to –10 °C.

8.2.5 Viscosity

The viscosity measurements were carried out with a cone-plate viscometer under a dinitrogen atmosphere. The temperature was controlled in the range from +80 to –10 °C.

8.2.6 Self-Diffusion Coefficients

The PGSE-NMR measurements were conducted according to our previously reported procedure [2]. The sine gradient pulse, providing a gradient strength of up to 12 T m^{-1}, was used throughout the measurements in this study. The self-diffusion coefficients were measured using a simple Hahn spin-echo sequence, (i.e., 90°–τ–180°–τ–acquisition), with a gradient pulse incorporated in each τ period. Measurements of the cationic and anionic self-diffusion coefficients in each ionic liquid were performed for either ^{1}H (399.7 MHz) or ^{19}F (376.1 MHz) nuclei. The self-diffusion coefficients of the cations and anions were calculated using the Stejskal–Tanner equation [9]. The measurements were performed in a range of temperatures with gradual cooling from 80 to –10 °C; samples were allowed to remain in thermal equilibrium at each temperature for 30 minutes prior to the measurements.

8.2.7   Solvent Polarity Parameter

The solvatochromic polarity scale of the ionic liquids was investigated using a dye, the copper(II) complex [Cu(acac)(tmen)][BPh₄] (Hacac = pentane-2,4-dione, trivially acetylacetone, tmen = N,N,N',N'-tetramethylethylenediamine, $Me_2NCH_2CH_2NMe_2$) [10]. It is well known that [Cu(acac)(tmen)][BPh₄] gives a good correlation between the donor number of a solvent and the maximum absorption wavelength (λ_{Cu}) [10]. It was confirmed that the anionic donor ability of ionic liquids strongly affected the λ_{Cu} values [5].

8.3   PHYSICOCHEMICAL, PROPERTIES OF [C₂mim]⁺-BASED IONIC LIQUIDS

Thermal properties of the [C₂mim]⁺-based ionic liquids are shown in Table 8.1, together with their formula weights. Glass transition temperatures (T_g) were observed for all ionic liquids except for [C₂mim][N(CF₃SO₂)₂] and [C₂mim][CF₃SO₃], which indicated relatively fast crystallisation kinetics of these two ionic liquids. The T_g values of [C₂mim][N(CF₃SO₂)₂] and [C₂mim][CF₃SO₃] could be obtained by means of a rapid temperature change ($50°C\,min^{-1}$). The T_g values of the ionic liquids with fluorinated anions ([N(CF₃SO₂)₂]⁻, [BF₄]⁻, [CF₃SO₃]⁻, and [CF₃CO₂]⁻) were lower than those with alkyl anions ([CH₃CO₂]⁻ and [CH₃SO₃]⁻). The T_m values of the ionic liquids with fluorinated anions, except for [C₂mim][BF₄], were lower than –10 °C. The [BF₄]⁻ anion has lower conformational flexibility than other fluorinated anions, which might explain the high T_m value. The variation of the thermal stability (T_d) of the [C₂mim]⁺ ionic liquids was largely dependent on the anionic structures, and followed the order
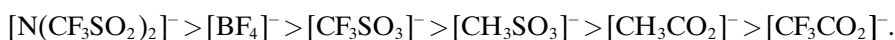
$$[N(CF_3SO_2)_2]^- > [BF_4]^- > [CF_3SO_3]^- > [CH_3SO_3]^- > [CH_3CO_2]^- > [CF_3CO_2]^-.$$

TABLE 8.1   Formula Weight (FW) and Thermal Properties of 1-Ethyl-3-Methylimidazolium Ionic Liquids

	FW/g mol⁻¹	T_g/°C[a]	T_m/°C[a]	T_d/°C[b]
[C₂mim][(CF₃SO₂)₂N]	391.3	–87[c]	–18	439
[C₂mim][CH₃COO]	170.2	–68		215
[C₂mim][BF₄]	198.0	–89	15	427
[C₂mim][CH₃SO₃]	206.3	–77	37	343
[C₂mim][CF₃COO]	224.2	–87	–14	177
[C₂mim][CF₃SO₃]	260.2	–93[c]	–10	406

[a] Onset temperature of heat capacity change (T_g) and an endothermic peak (T_m) determined by DSC.
[b] Onset temperature of mass loss (T_d).
[c] Detected by rapid cooling.

TABLE 8.2 Density Equation Parameters from Equation (8.1) and Molar Concentration at 30 °C (M_{30})

	$a/10^{-4}\,\mathrm{g\,cm^{-3}\,K^{-1}}$	$b/\mathrm{g\cdot cm^{-3}}$	$M_{30}/10^{-3}\,\mathrm{mol\,cm^{-3}}$
[C$_2$mim][N(CF$_3$SO$_2$)$_2$]	10.0	1.82	3.87
[C$_2$mim][CH$_3$COO]	6.51	1.29	6.44
[C$_2$mim][BF$_4$]	8.40	1.53	6.44
[C$_2$mim][CH$_3$SO$_3$]	6.80	1.45	6.01
[C$_2$mim][CF$_3$COO]	7.71	1.52	5.74
[C$_2$mim][CF$_3$SO$_3$]	8.46	1.64	5.30

This order is consistent with the inverse order of the Lewis basicity of the anions [5]. The exceptionally low thermal stability of [C$_2$mim][CF$_3$CO$_2$] implies thermal instability of the [CF$_3$CO$_2$]$^-$ anion.

The temperature dependence of the density of the ionic liquids showed a linear decrease with increasing temperature, which can be represented by Equation (8.1),

$$\rho = b - aT. \tag{8.1}$$

The best-fit parameters for the linear fitting are listed in Table 8.2. The observed trend indicated that the larger the formula weight of the anions, the higher is the density of the ionic liquids. Ionic liquids with fluorinated anions have higher densities than those with the corresponding non-fluorinated anions. The calculated molar concentration of the ionic liquids at 30 °C (M_{30}) increased with a decrease in the formula weight of the anions and became higher than 6.0 M for [C$_2$mim][CH$_3$SO$_3$], [C$_2$mim][BF$_4$], and [C$_2$mim][CH$_3$CO$_2$].

The temperature dependences of the viscosity (η) and conductivity (σ) of the ionic liquids are shown in Figure 8.1 and Figure 8.2, respectively. The profiles fitted to the Vogel–Fulcher–Tammann (VFT) equations are also depicted in Figure 8.1 and Figure 8.2, and the corresponding VFT equations are Equation (8.2) and Equation (8.3),

$$\eta = \eta_0 \exp[B/(T - T_0)], \tag{8.2}$$

$$\sigma = \sigma_0 \exp[-B/(T - T_0)], \tag{8.3}$$

where the constants η_0 (mPa s), σ_0 (S cm^{-1}), B (K), and T_0 (K) are also adjustable parameters. The best-fit parameters for the viscosities and conductivities are listed in Table 8.3 and Table 8.4, respectively.

The viscosity values (Figure 8.1) showed a marked dependence on whether or not the ionic liquids comprised fluorinated anions, with the observed trend that the ionic liquids of fluorinated anions had lower viscosity. The conductivity values (Figure 8.2), on the other hand, were affected not only by the viscosity values but also by the molar concentrations (Table 8.2). The ionic
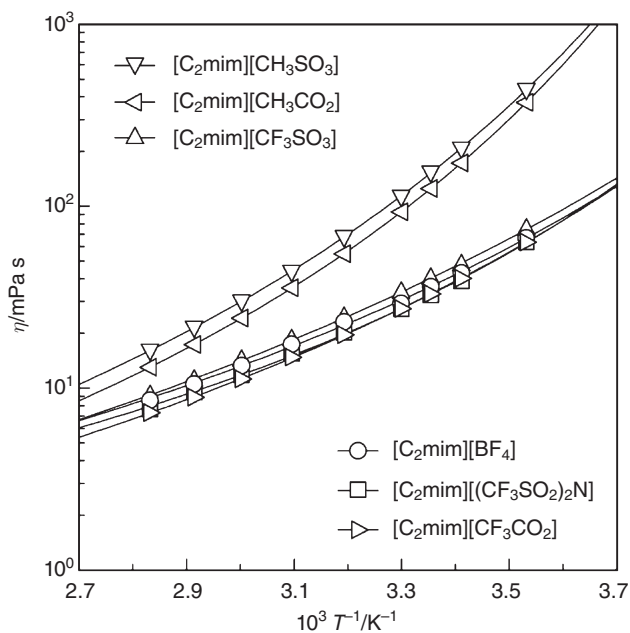
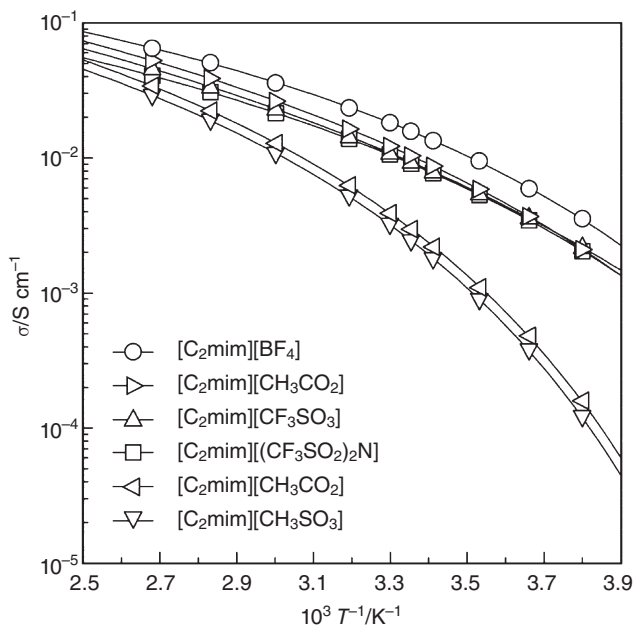**Figure 8.1** Temperature dependence of viscosity for [C$_2$mim]$^+$ ionic liquids.

Figure 8.2 Temperature dependence of ionic conductivity for [C$_2$mim]$^+$ ionic liquids.

TABLE 8.3 VFT Parameters of Viscosity Data

	$\eta_0/10^{-1}\,mPa\,s$	$B/10^2\,K$	T_0/K
$[C_2mim][(CF_3SO_2)_2N]$	4.0 ± 1.3	5.09 ± 0.81	182 ± 10
$[C_2mim][CH_3COO]$	1.7 ± 0.1	6.98 ± 0.09	192 ± 1
$[C_2mim][BF_4]$	2.5 ± 0.9	6.82 ± 1.00	161 ± 10
$[C_2mim][CH_3SO_3]$	1.7 ± 0.1	7.55 ± 0.20	187 ± 2
$[C_2mim][CF_3COO]$	1.9 ± 0.3	6.89 ± 0.52	165 ± 5
$[C_2mim][CF_3SO_3]$	1.8 ± 0.5	7.98 ± 0.81	151 ± 8

TABLE 8.4 VFT Equation Parameters of Ionic Conductivity Data

	$\sigma_0/10^{-1}\,S\,cm^{-1}$	$B/10^2\,K$	T_0/K
$[C_2mim][(CF_3SO_2)_2N]$	5.8 ± 0.2	5.54 ± 0.13	165 ± 2
$[C_2mim][CH_3COO]$	10.1 ± 0.4	6.07 ± 0.09	194 ± 1
$[C_2mim][BF_4]$	6.6 ± 0.4	4.55 ± 0.18	176 ± 3
$[C_2mim][CH_3SO_3]$	8.7 ± 0.4	6.06 ± 0.12	195 ± 1
$[C_2mim][CF_3COO]$	9.8 ± 0.3	6.12 ± 0.08	163 ± 1
$[C_2mim][CF_3SO_3]$	11.0 ± 0.3	7.16 ± 0.10	148 ± 1

liquids with lower viscosity and higher molar concentrations exhibited higher conductivity.

The PGSE-NMR method for the determination of the self-diffusion coefficient allows the evaluation of the diffusivity of NMR-sensitive nuclei. Since the ionic liquids used in this study include NMR-sensitive ^1H and ^{19}F (or ^1H) nuclei in the cation and anion, respectively, each self-diffusion coefficient could be independently determined and was defined as self-diffusion coefficients of the cation (D_{cation}) and anion (D_{anion}). The temperature dependence of the diffusion coefficients in each case exhibited convex, curved profiles; therefore, experimental data were fitted with the VFT equation for diffusivity, Equation (8.4),

$$D = D_0 \exp[-B/(T - T_0)], \tag{8.4}$$

where the constants D_0 ($cm^2\,s^{-1}$), B (K), and T_0 (K) are adjustable parameters. The best-fit parameters of the ionic diffusivity are summarised in Table 8.5. The simple sum of the cationic and anionic self-diffusion coefficients ($D_{cation} + D_{anion}$) for these ionic liquids at each temperature was calculated and the best-fit parameters for the VFT equation were estimated. The results are also listed in Table 8.5. The ($D_{cation} + D_{anion}$) values for the $[C_2mim]^+$ ionic liquids followed the order

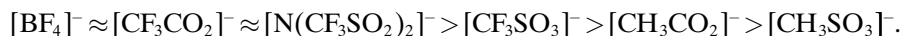$$[BF_4]^- \approx [CF_3CO_2]^- \approx [N(CF_3SO_2)_2]^- > [CF_3SO_3]^- > [CH_3CO_2]^- > [CH_3SO_3]^-.$$

TABLE 8.5   VFT Equation Parameters of Self-Diffusion Coefficient Data

	$D_0/10^{-4}\,cm^2\,s^{-1}$	$B/10^2\,K$	T_0/K
[C₂mim][N(CF₃SO₂)₂]			
Cation	1.1 ± 0.1	8.16 ± 0.41	147 ± 4
Anion	0.9 ± 0.1	8.57 ± 0.30	147 ± 3
Cation + anion	2.1 ± 0.2	8.36 ± 0.35	146 ± 3
[C₂mim][CH₃COO]			
Cation	1.6 ± 0.3	8.88 ± 0.47	174 ± 4
Anion	2.0 ± 0.4	9.65 ± 0.56	170 ± 4
Cation + anion	3.6 ± 0.6	9.24 ± 0.50	172 ± 4
[C₂mim][BF₄]			
Cation	1.2 ± 0.1	8.56 ± 0.40	144 ± 4
Anion	1.4 ± 0.2	9.34 ± 0.50	141 ± 4
Cation + anion	2.6 ± 0.3	8.93 ± 0.42	143 ± 4
[C₂mim][CH₃SO₃]			
Cation	1.4 ± 0.4	8.96 ± 0.85	174 ± 7
Anion	1.1 ± 0.2	8.59 ± 0.62	180 ± 5
Cation + anion	2.5 ± 0.6	8.80 ± 0.74	177 ± 6
[C₂mim][CF₃COO]			
Cation	0.9 ± 0.2	7.25 ± 0.64	159 ± 7
Anion	0.9 ± 0.2	7.59 ± 0.63	159 ± 6
Cation + anion	1.7 ± 0.4	7.41 ± 0.62	159 ± 6
[C₂mim][CF₃SO₃]			
Cation	2.0 ± 0.4	10.62 ± 0.71	126 ± 6
Anion	1.9 ± 0.4	11.36 ± 0.72	126 ± 6
Cation + anion	3.9 ± 0.7	10.97 ± 0.63	125 ± 5

This order is roughly consistent with the inverse order of the magnitude of the viscosity, which indicates that the translational dynamics of each ion is governed by the macroscopic viscosity.

Since the molar concentration of these ionic liquids is strongly dependent on the formula weight (anionic structures) (Table 8.2), the molar conductivity was calculated from the ionic conductivity and molar concentration. The VFT equation for the molar conductivity is given in Equation (8.5),

$$\Lambda = \Lambda_0 \exp[-B / (T - T_0)], \qquad (8.5)$$

where Λ_0 ($S\,cm^2\,mol^{-1}$), B (K), and T_0 (K) are constants.

The best-fit parameters for the temperature dependence (Λ_{imp}) are shown in Table 8.6. The molar conductivity of the ionic liquids can also be calculated from the self-diffusion coefficients (Λ_{NMR}), as determined by the PGSE-NMR measurements, using the Nernst–Einstein equation, Equation (8.6),

$$\Lambda_{NMR} = N_A e^2 (D_{cation} + D_{anion}) / kT = F^2 (D_{cation} + D_{anion}) / RT, \qquad (8.6)$$

TABLE 8.6 VFT Parameters of Molar Conductivity Data Based on Impedance Measurements (Λ_{imp})

	$\Lambda_0/10^2\,S\,cm^2\,mol^{-1}$	$B/10^2\,K$	T_0/K
[C$_2$mim][(CF$_3$SO$_2$)$_2$N]	1.9 ± 0.1	6.04 ± 0.15	161 ± 2
[C$_2$mim][CH$_3$COO]	1.8 ± 0.1	6.36 ± 0.09	192 ± 1
[C$_2$mim][BF$_4$]	1.3 ± 0.1	4.86 ± 0.18	172 ± 3
[C$_2$mim][CH$_3$SO$_3$]	1.7 ± 0.1	6.33 ± 0.12	193 ± 1
[C$_2$mim][CF$_3$COO]	2.1 ± 0.1	6.57 ± 0.09	160 ± 1
[C$_2$mim][CF$_3$SO$_3$]	2.6 ± 0.1	7.70 ± 0.10	144 ± 1

TABLE 8.7 VFT Parameter of Molar Conductivity Based on Diffusivity Measurements (Λ_{NMR})

|	$\Lambda_0/10^2\,S\,cm^2\,mol^{-1}$	$B/10^2\,K$	T_0/K
[C$_2$mim][N(CF$_3$SO$_2$)$_2$]	3.1 ± 0.3	6.41 ± 0.25	159 ± 3
[C$_2$mim][CH$_3$COO]	5.6 ± 0.8	7.60 ± 0.39	180 ± 4
[C$_2$mim][BF$_4$]	3.9 ± 0.3	6.90 ± 0.27	155 ± 3
[C$_2$mim][CH$_3$SO$_3$]	4.0 ± 0.8	7.22 ± 0.55	185 ± 5
[C$_2$mim][CF$_3$COO]	2.8 ± 0.5	5.78 ± 0.49	169 ± 6
[C$_2$mim][CF$_3$SO$_3$]	5.3 ± 0.7	8.51 ± 0.46	138 ± 5

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 best-fit parameters of the VFT equation for the temperature dependence of the molar conductivity calculated from the ionic diffusion coefficient and Equation (8.6) are listed in Table 8.7.

The data and parameters in Table 8.1, Table 8.2, Table 8.3, Table 8.4, Table 8.5, Table 8.6, and Table 8.7 represent a precise and reliable compilation of the physicochemical properties, particularly transport properties, of these 1-ethyl-3-methylimidazolium ionic liquids.

8.4 TRANSFERENCE NUMBER AND IONICITY

Figure 8.3 shows the apparent cationic transference number, $D_{cation}/(D_{cation} + D_{anion})$, for each of the 1-ethyl-3-methylimidazolium ionic liquids, calculated from the PGSE-NMR diffusivity data as a function of temperature. The cationic transference number represents the relative diffusivity of the cation. The transference numbers followed the approximate order
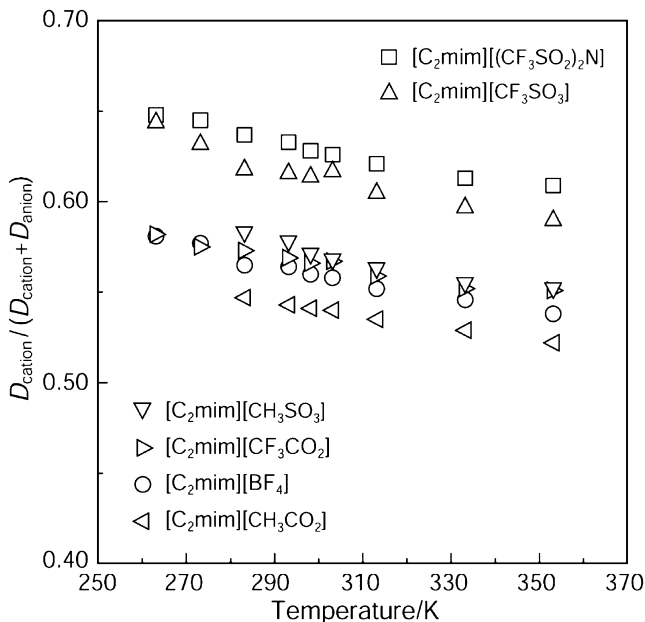
$$[N(CF_3SO_2)_2]^- > [CF_3SO_3]^- > [CH_3SO_3]^- > [CF_3CO_2]^- > [BF_4]^- > [CH_3CO_2]^-,$$
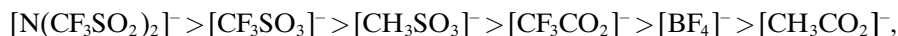
Figure 8.3 Cationic transference numbers for 1-ethyl-3-methylimidazolium ionic liquids determined from PGSE-NMR diffusivity measurements as a function of temperature.

which clearly indicates that the relative diffusivity of the cations decreases with a decrease in the size of the anions.

However, the cationic self-diffusion coefficient was larger than the anionic diffusion coefficient, even for small anions such as $[BF_4]^-$ and $[CH_3CO_2]^-$. The cationic and anionic radii of $[C_2mim][BF_4]$ have been reported to be 0.303 nm and 0.227 nm, respectively [11, 12]. Nonetheless, the cationic transference number of $[C_2mim][BF_4]$ was estimated to be 0.55–0.58. It should be noted that all of the ionic liquids that we have reported exhibit cationic transference numbers higher than 0.5, irrespective of the ionic sizes [1–4]. There appears to be a certain electrostatic effect that causes faster diffusivity of the cations than of the anions in these ionic liquids. A recent molecular dynamics simulation of the self-diffusion coefficients of 1,3-dialkylimidazolium ionic liquids also demonstrates higher diffusivity of the cations than of the anions [13]. In this study, the cationic transference number decreased almost linearly with increasing temperature in all the ionic liquids, indicating the higher thermal acceleration of the anionic diffusion than the $[C_2mim]^+$ diffusion. This is consistent with the previously observed tendency in the $[C_4mim]^+$ ionic liquids [1–4].

For all the ionic liquids over the entire temperature range considered, the electrochemical molar conductivity (Λ_{imp}) was lower than the calculated molar conductivity (Λ_{NMR}; obtained from the PGSE-NMR diffusivity data and
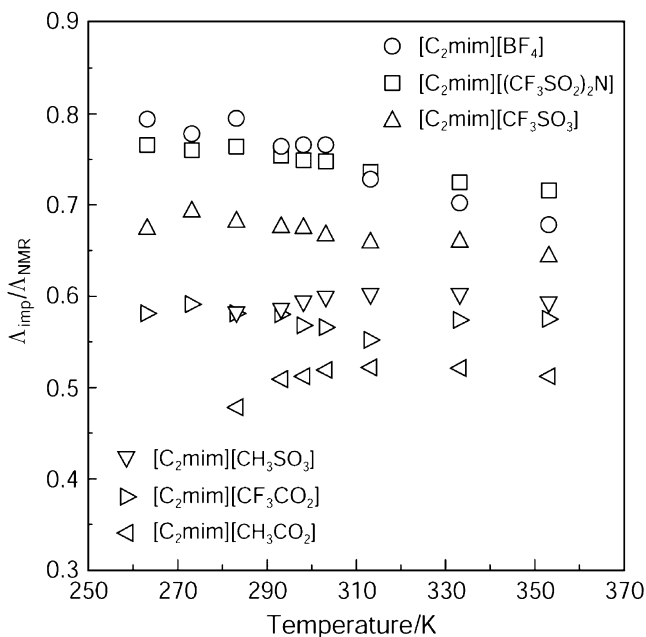
Figure 8.4 $\Lambda_{imp}/\Lambda_{NMR}$ (ionicity, dissociativity) of 1-ethyl-3-methylimidazolium ionic liquids as a function of temperature.

Equation (8.6)). Thus, the ratio $\Lambda_{imp}/\Lambda_{NMR}$ (ionicity) was lower than unity (Figure 8.4), which is consistent with observations reported in our series of previous studies [1–4], in which the observed ratios were shown to correlate with the ionic nature of the ionic liquids [5, 6]. It is clear that not all of the diffusive species in the ionic liquids lead to ionic conduction; that is, ion aggregates or clusters are formed. The NMR measurements could not distinguish between associated non-charged species and charged ionic species on the NMR timescale. The timescales for any association or dissociation of the ionic species are much shorter than those of dc conductivity measurements. In the conductivity measurements, an individual charged ionic species migrates in an electric field for a characteristic time during which it exists as a charged species, but it may associate with other ions to form a neutral aggregate for another characteristic length of time. When the ions exist in such a neutral form, they do not contribute to conduction.

The variation of the anions in the 1-ethyl-3-methylimidazolium ionic liquids led to the different $\Lambda_{imp}/\Lambda_{NMR}$ values, and the ionicity followed the order

$$[BF_4]^- > [N(CF_3SO_2)_2]^- > [CF_3SO_3]^- > [CF_3CO_2]^- > [CH_3SO_3]^-$$
$$> [CH_3CO_2]^- \text{ at } 30°C,$$
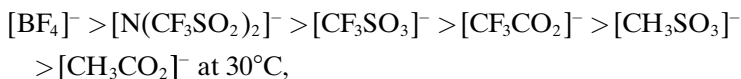
and ranged from 0.5 to 0.8. Since the cationic structure is fixed as $[C_2mim]^+$, the order of $\Lambda_{imp}/\Lambda_{NMR}$ depends entirely on the nature of the anion, which we will discuss in the following section. It was rather surprising for us that even $[C_2mim][CH_3CO_2]$, consisting of the strongly Lewis basic $[CH_3CO_2]^-$ anion, exhibited an ionicity value higher than 0.5.

8.5 CORRELATION OF IONICITY WITH IONIC STRUCTURES AND PHYSICOCHEMICAL PROPERTIES

The ionicity of the ionic liquids should be controlled by the types, magnitudes, and balances of the inter-ionic forces, which vary depending on the cationic and anionic structures. Figure 8.5 shows the relationship between λ_{Cu} and $\Lambda_{imp}/\Lambda_{NMR}$ for the 1-ethyl-3-methylimidazolium and 1-butyl-3-methylimidazolium ionic liquids with different anionic structures.

It can be seen from Figure 8.5 that the relationships between λ_{Cu} and $\Lambda_{imp}/\Lambda_{NMR}$ for $[C_2mim]^+$ and $[C_4mim]^+$ ionic liquids give two different lines and that a decrease in λ_{Cu}, that is, a decrease in the donor ability of the ionic liquids, induces an increase in $\Lambda_{imp}/\Lambda_{NMR}$. Since the cation was kept constant for each series of ionic liquids, the difference in λ_{Cu} is a function of the donor ability of the anions. Insensitivity of λ_{Cu} towards the cationic structures was also confirmed by observation of the same λ_{Cu} values for the $[C_2mim]^+$ and $[C_4mim]^+$ ionic liquids when the anion was kept constant. It should be noted that when
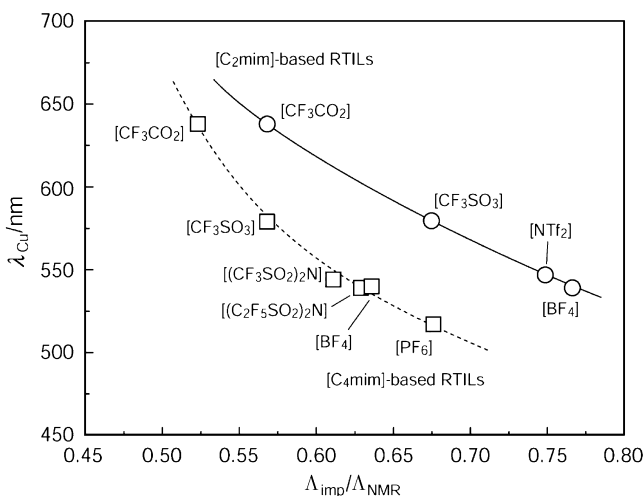

Figure 8.5 The relationship between λ_{Cu} and $\Lambda_{imp}/\Lambda_{NMR}$ (ionicity, dissociativity) for $[C_2mim]^+$ and $[C_4mim]^+$ ionic liquids with different anionic structures at 30 °C. The solid and broken lines in the plots are guides for the eyes.

the donor ability of the anion is the same, $[C_4mim]^+$ ionic liquids show lower ionicity values than $[C_2mim]^+$ ionic liquids. We have demonstrated that the ionicity values are controlled not only by the Lewis basicity and acidity of anions and cations, respectively [2, 4], but also by van der Waals interaction [3] between ions, including inductive and dispersion forces. Higher Lewis basicity and acidity and stronger van der Waals interactions result in lower ionicity [6]. The two independent lines in Figure 8.5 are attributed to stronger van der Waals interaction for the 1-butyl-3-methylimidazolium ionic liquids owing to the longer alkyl chain length. Although it was impossible to measure λ_{Cu} for $[C_2mim][CH_3CO_2]$ and $[C_2mim][CH_3SO_3]$ because of a shortage of the obtained samples, we could estimate the Lewis basicity (donor ability) of these anions from the $\lambda_{Cu}-\Lambda_{imp}/\Lambda_{NMR}$ relationship for the $[C_2mim]^+$ ionic liquids and the $\Lambda_{imp}/\Lambda_{NMR}$ values of $[C_2mim][CH_3CO_2]$ and $[C_2mim][CH_3SO_3]$. The obtained Lewis basicity order is as follows:

$$[CH_3CO_2]^- > [CF_3CO_2]^- > [CH_3SO_3]^- > [CF_3SO_3]^- > [N(CF_3SO_2)_2]^- > [BF_4]^-.$$
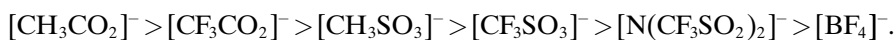
The pK_a values of the conjugated acids of $[CH_3CO_2]^-$, $[CF_3CO_2]^-$, and $[CH_3SO_3]^-$ are 4.8, 0.5, and –2.0, respectively, and they confirm the order mentioned earlier. If we use these $\lambda_{Cu}-\Lambda_{imp}/\Lambda_{NMR}$ relationships as calibration curves, we can estimate either λ_{Cu} or $\Lambda_{imp}/\Lambda_{NMR}$ when either of them is known. The λ_{Cu} values of $[C_2mim][N(CN)_2]$ and $[C_2mim][SCN]$ were measured at 652 nm and 702 nm, respectively, which gave the respective ionicity values of 0.55 and 0.50 from the calibration curve. $[C_2mim][PF_6]$ is a solid at room temperature; however, its ionicity is roughly estimated as 0.8, assuming that it gives the same λ_{Cu} as $[C_4mim][PF_6]$.

It is interesting to note that the order of ionicity of the 1-ethyl-3-methylimidazolium ionic liquids corresponds well with the observed trend for T_d (Table 8.1). This correlation indicates that the more dissociative ionic liquids exhibit the higher thermal stability. The decomposition or pyrolysis of the 1,3-dialkylimidazolium salts was reported to proceed via an S_N2 mechanism [14, 15], which indicates that an increase in the Lewis basicity (nucleophilicity) of the anions accelerates the S_N2 decomposition reactions of the ionic liquids. The observed variation of T_d in response to the change in the nucleophilicity of the anions in this study is therefore understandable and is in agreement with the literature [14, 15].

From the results presented in Figure 8.5, it is clear that the ionicity is affected not only by the Lewis basicity of the anions but also by van der Waals interactions between the ions. It has also been clarified, from *ab initio* calculations [16], that the difference in the former parameter mainly influences the Coulombic interaction between cations and anions. Therefore, simply put, ionicity is determined by a subtle balance between Coulombic and van der Waals interactions between ions. As we proposed earlier [5], values of the effective ionic concentration $C_{eff} = M_{30} \times \Lambda_{imp}/\Lambda_{NMR}$ become a useful indicator of the strength of Coulombic interactions since $(C_{eff})^{-1/3}$ is a measure of
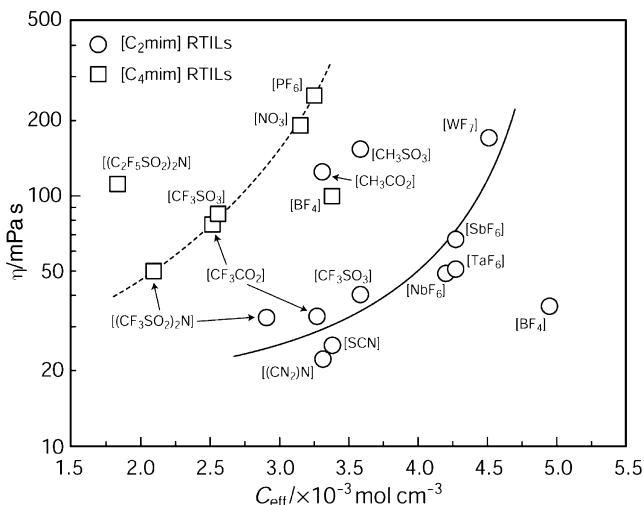
Figure 8.6 C_{eff} dependency of viscosity for 1-ethyl-3-methylimidazolium and 1-butyl-3-methylimidazolium ionic liquids with different anionic structures at 30 °C. The solid and broken lines are guides for the eyes.

the average inter-ionic distance. Figure 8.6 shows the C_{eff} dependence of the η values at 30 °C for the 1-ethyl-3-methylimidazolium and 1-butyl-3-methylimidazolium ionic liquids with different anionic structures. C_{eff} of [C$_4$mim][NO$_3$] was calculated using an estimate of $\Lambda_{imp}/\Lambda_{NMR}$ (0.55) and the reported density data at 30 °C (1.1497 g cm^{-3}) [17]. The reported data for η [17] was then plotted against the calculated value of C_{eff}. For [C$_2$mim][N(CN)$_2$] and [C$_2$mim][SCN], C_{eff} was similarly estimated from $\Lambda_{imp}/\Lambda_{NMR}$ obtained from Figure 8.5 and their densities [18, 19]. The literature value of η for [C$_2$mim][SCN] at 25 °C [19] was used in Figure 8.6 because of lack of data at 30 °C. Since conjugated acids of [NbF$_6$]$^-$, [SbF$_6$]$^-$, [TaF$_6$]$^-$, and [WF$_7$]$^-$ are super-strong acids, and their strengths appear to be similar to or stronger than that of HPF$_6$, the $\Lambda_{imp}/\Lambda_{NMR}$ values of these ionic liquids were assumed to be 0.8, except for [C$_2$mim][WF$_7$], for which a value of 0.85 was used. The reported η values [20] of these ionic liquids were plotted against the estimated C_{eff} values.

From Figure 8.6, it is apparent that the η–C_{eff} relationships for the 1-ethyl-3-methylimidazolium and 1-butyl-3-methylimidazolium ionic liquids are different. The [C$_4$mim]$^+$ ionic liquids exhibited a higher η value at constant C_{eff}. Although some amount of scatter of data was observed, the η values generally tended to increase with increasing C_{eff} for each series of the ionic liquids. Since η reflects inter-ionic frictions, an increase in the Coulombic or van der Waals interaction induces an increase in η. If similar van der Waals interactions can be assumed in the 1-ethyl-3-methylimidazolium and 1-butyl-3-methylimidazolium ionic liquids, an increase in C_{eff} induces an increase in the

Coulombic interaction, thereby resulting in an increase in the η values. When the anions were the same ($[N(CF_3SO_2)_2]^-$, $[CF_3CO_2]^-$, and $[CF_3SO_3]^-$), 1-butyl-3-methylimidazolium ionic liquids gave higher η values than 1-ethyl-3-methylimidazolium and ionic liquids, which again confirms stronger van der Waals interaction in the 1-butyl-3-methylimidazolium ionic liquids. The η–C_{eff} relationship for the 1-butyl-3-methylimidazolium ionic liquids showed an increase in η values as C_{eff} increased, the exceptions being $[C_4mim][N(C_2F_5SO_2)_2]$ and $[C_4mim][BF_4]$. $[C_4mim][N(C_2F_5SO_2)_2]$ exhibited a high η value, despite low C_{eff}, which appeared to be because of the enhanced van der Waals interaction originating from $[N(C_2F_5SO_2)_2]^-$, as seen in $[C_nmim][N(CF_3SO_2)_2]$, whose η values increase with the alkyl chain length [3]. The exceptionally low η–value for $[BF_4]^-$ ionic liquids was also observed in the η–C_{eff} relationship for the 1-ethyl-3-methylimidazolium ionic liquids. It is noteworthy that a change in the anionic structure from $[CF_3CO_2]^-$ to $[CH_3CO_2]^-$ and from $[CF_3SO_3]^-$ to $[CH_3SO_3]^-$ brought about a large increase in the η values in spite of the similar C_{eff} values. The perfluorinated anionic structures appeared to have a viscosity-lowering effect.

8.6   CONCLUSIONS

The major conclusions of this study can be summarised as follows:

1. By the neutralisation of 1-ethyl-3-methylimidazolium-2-carboxylate with protic acids, which have higher acidity than carbonic acid, ionic liquids having the conjugated bases of the protic acids as counteranions could be easily prepared via CO_2-releasing reactions. Special purification procedures were not necessary for the obtained ionic liquids. This method was successfully applied to the preparation of $[C_2mim][CF_3CO_2]$, $[C_2mim][CH_3SO_3]$, and $[C_2mim][CH_3CO_2]$.

2. Physicochemical properties, particularly transport properties, of 1-ethyl-3-methylimidazolium ionic liquids having $[CF_3CO_2]^-$, $[CH_3SO_3]^-$, $[CH_3CO_2]^-$, $[CF_3SO_3]^-$, $[BF_4]^-$, and $[N(CF_3SO_2)_2]^-$ anions were precisely measured. The data for the former four ionic liquids are presented for the first time in this study.

3. The ionicity of the ionic liquids was controlled by the magnitude and balance of Coulombic forces, which, in this study, were mainly altered by the anionic Lewis basicities, and the van der Waals forces. The ionicity, $\Lambda_{imp}/\Lambda_{NMR}$, of the ionic liquids ranged from 0.5 to 0.8 and followed the anion-dependent order $[BF_4]^- > [N(CF_3SO_2)_2]^- > [CF_3SO_3]^- > [CF_3CO_2]^- > [CH_3SO_3]^- > [CH_3CO_2]^-$, which is the inverse order of the anionic donor ability or the order of acidity of the conjugated acids.

4. Calibration curves for the $\lambda_{Cu}-\Lambda_{imp}/\Lambda_{NMR}$ relationship were obtained for the 1-ethyl-3-methylimidazolium and 1-butyl-3-methylimidazolium ionic

liquids, from which either $\Lambda_{imp}/\Lambda_{NMR}$ or λ_{Cu} can be estimated if either of them is known.

5. Viscosities of various 1-ethyl-3-methylimidazolium and 1-butyl-3-methylimidazolium ionic liquids were correlated with the effective ionic concentration C_{eff}, which was estimated from the ionicity and molar concentration of these ionic liquids. With increasing C_{eff}, the viscosities tended to increase, although at the same C_{eff} values, 1-butyl-3-methylimidazolium ionic liquids showed higher viscosities than 1-ethyl-3-methylimidazolium ionic liquids because of the enhanced van der Waals force effect.

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