Ionization State and Ion Migration Mechanism of Room Temperature Molten Dialkylimidazolium Fluorohydrogenates

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Received: September 10, 2004; In Final Form: October 19, 2004

The ionization state of room temperature molten salts, alkylimidazolium fluorohydrogenates (RMIm-(HF)_{2.3}F: R = alkyl group, M =methyl group), was evaluated from the observed diffusion coefficient and viscosity, using the Stokes–Einstein relation. Assuming that the dissociation degree of the salt is acceptable for representation of the ionic state of the molten salts, the larger the cation size with elongation of the alkyl chain was, the higher the dissociation degree of the salt. Further, we proposed that an idea of the "degree of ordering of cations and anions" was more suitable to represent the ionization state without solvent species. On the basis of this idea, the smaller the cation size of RMIm(HF)_{2.3}F salt was, the higher the ordering of the ion, indicating formation of domain particles of aggregated ions as a unit of mobile species such as A(AX)_m⁺ and X(AX)_n⁻ for A⁺X⁻ salt. It was found that highly ordered particles, with large numbers for *m* and *n*, showed a high diffusion coefficient.

Introduction

The development of new types of electrolytes applicable for electrochemical devises is promoted to improve the safety and performance of energy preservation devices. The room temperature molten salt (RTMS) is one of the candidates for the electrolyte of electrochemical devices due to the highly ionic conductivity and nonvolatility.

Since the report of 1-ethyl-3-methylimidazorium tetrafluoroborate by Wilkes et al.,¹ many kinds of RTMS of alkylimidazolium cations with a fluoroanion have been investigated from the viewpoint of academic interest and application to practical usage such as solvents for synthesis and electrochemical devices. We have prepared a new series of alkylimidazolium fluorohydrogenates (RMIm(HF)_{2.3}F: R = alkyl group, M = methyl group).^{2,3} This series is composed of an imidazolium cation with two alkyl chains and mixed anions of (HF)₂F⁻ and (HF)₃F⁻. One of them, 1-ethyl-3-methylimidazolium salt (EMIm(HF)_{2.3}F), has a wide liquid temperature range above and below room temperature (-60 to +100 °C) and a high conductivity of 100 mS cm⁻¹ at 298 K, which is the highest value of any RTMS at present.

The cause of prominent low viscosity and high conductivity, which follow Walden's rule, of EMIm(HF)_{2.3}F has been controversial since its discovery. This is essentially attributed to the more significant subject of "what dominates the dynamic property of RTMS"? To answer that question, we have investigated structural features of RMIm(HF)_{2.3}F salts using the high-energy X-ray diffraction technique combined with ab initio

molecular orbital calculation.^{4,5} In that study, we found that $RMIm(HF)_{2.3}F$ exhibits an ordering of flat molecular cations similar to solid EMImF•HF in which cations and anions form a layered structure. Low viscosity leading to high conductivity of this series might be correlated with the semioriented structure, which permits ions to move connected with each other in a certain direction with a small amount friction.⁵

Another point that must be addressed to realize the dynamic feature of RTMS is the ionization condition. In practice, there is a report that the idea of "dissociation degree of the salt" was simply applied to RTMS to interpret the conductivity and diffusion coefficient results.⁶ However, the applicability should be considered seriously because the concept of the dissociation degree originates from the solvation effect of the solvent species on the ions promoting the salt dissociation in solutions. However, it is also a fact that the viscosity and conductivity of RTMS cover a wide range depending on the combination of the cation and anion. This reveals that the ionization condition of RTMS is correlated with the structure of the ions and dominates the dynamic properties of the ionic species.

One characteristic feature of RTMS dynamics is represented by Walden's rule in which plots of molar conductivity with a reciprocal of viscosity are roughly on a line independent of the kind of salt.⁷ This empirical rule is associated with the Stokes— Einstein relation in which the diffusion coefficient of a fluid particle in the solution is inversely proportional to solution viscosity.⁸ Therefore, if we can directly obtain the diffusion coefficients of the cation and anion individually, evaluation of the Stokes—Einstein relation would be more effective to investigate the properties of mobile species because the conductivity includes mobility and carrier concentration of all charged species. It is possible to elucidate the ionization condition of RTMS by the application of observed

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diffusion coefficients which are responsible for mobility of each probed species.

We have used the pulsed gradient spin—echo NMR technique to measure the diffusion coefficient of the ionic species. This approach has the advantage that the diffusion coefficient of the individual nuclear species can be detected: cation species probed by ¹H and anion species probed by ¹H and ¹⁹F for RMIm-(HF)_{2.3}F. It should be noted that the observed diffusion coefficient of electrolyte materials from NMR spectroscopy reflects the dissociation condition of the salt. For example, in the case of a dissolved lithium salt in a solvent, the observed diffusion coefficient probed by ⁷Li can be denoted as

$$D_{\rm Li}^{\rm obs} = xD_{\rm cation} + (1-x)D_{\rm pair} \tag{1}$$

where D_{cation} and D_{pair} are inherent diffusion coefficients of the coexisting cation and ion pair, respectively, with the degree of dissociation, *x*, at the equilibrium condition.⁹ By analogy with this situation, the diffusion coefficient of RTMS reflects the ionization state in which the ion and ion pair coexist exchanging quickly with each other according to their thermal motion.

In this research, we intend to interpret the state of ions in RMIm(HF)_{2.3}F from the analysis of the observed diffusion coefficient using the Stokes–Einstein relation to realize the cause of high conductivity. This elucidation would give evidence of determining factors of ionic mobility in molten salts, leading to significant information for the design of RTMS applicable to electrochemical devices.

Experimental Section

A series of RMImCl (RMIm = 1,3-dimethylidazolium (DMIm), 1-ethyl-3-methylimidazolium (EMIm), 1-propyl-3methylimidazolium (PrMIm), 1-butyl-3-methylimidazolium (BMIm), 1-pentyl-3-methylimidazolium (PeMIm), and 1-hexyl-3-methylimidazolium (HMIm)) was prepared by reaction of 1-methylimidazole and an alkyl chloride. The salt was dissolved in acetonitrile, dried over molecular sieves, and then precipitated from the solution by adding ethyl acetate to purify the chloride. Chlorides were weighed and charged on a plastic reaction tube and interacted with a large excess of anhydrous HF at 273– 298 K. Volatile gases were eliminated by nitrogen gas purge and successive pumping with a rotary pump. We measured the composition of the evacuated salt by elemental analysis and gravimetry and confirmed the chemical formula of RMIm-(HF)_{2.3}F.

The viscosity of the molten salts was determined with the aid of Ubbelohde-type glass viscometers or a Brookfield Engineering Laboratories DV-III cone and plate rheometer.¹⁰ Ionic conductivity was measured by using the complex impedance technique in the temperature range of -20 to 50 °C.

We measured diffusion coefficients of the ionic species using the pulsed gradient spin—echo NMR (PGSE-NMR) technique with a JNM-ECP300W spectrometer and wide-bore probe units adjusting the probed nuclear species, ¹H (300.5 MHz) and ¹⁹F (282.7 MHz).¹¹ The NMR spectrum of ¹H comprises several peaks attributed to protons of the cation and anion. Comparing the spectra among the series of RMIm(HF)_{2.3}F, five peaks located >12 ppm were assigned to the cation and a peak at ca. 10 ppm was assigned to the anion by using TMS reference. For the ¹⁹F spectrum, one peak appeared that was attributed to the anion. Therefore, the diffusion coefficient of the cation species denoted by $D_{H(cation)}$ was estimated by averaging the evaluated diffusion values from each attenuation of the five peaks. And the anion diffusion coefficients obtained from ¹H



Figure 1. Temperature dependence of the diffusion coefficient of cation species detected by ¹H ($D_{\text{H(cation)}}$) and anion species detected by ¹H ($D_{\text{H(anion)}}$) and by ¹⁹F ($D_{\text{F(anion)}}$) for (a) EMIm(HF)_{2.3}F, (b) BMIm(HF)_{2.3}F, and (c) HMIm(HF)_{2.3}F.

and ¹⁹F were represented as $D_{\text{H(anion)}}$ and $D_{\text{F(anion)}}$, respectively. In this study, the stimulated echo sequence was used at measurement.⁹ The half-sine-shaped gradient pulse was applied twice in sequence after the first and third 90° pulses to detect attenuation of echo intensity according to the migration property of the probed species.¹² Typical values of the field gradient pulse parameters were g = 0.17-0.62 T/m for pulse strength, $\delta = 0-3$ ms for pulse width, and $\Delta = 80$ ms for the interval between the two gradient pulses. The diffusion coefficient was measured in the temperature range -10 to 50 °C.

Ab initio molecular orbital calculations were carried out to optimize geometries of ions by using the B3LYP method¹³ with the 6-31+G(d,p) basis set in the Gaussion 94 program. The van der Waals (vdW) volumes of the ions were calculated on optimized geometries by using the Connolly surface calculation method¹⁴ in the Cerius (version 3.8) program.

Results and Discussion

1. Diffusion Behavior of the Contributing Species of RMIm(**HF**)_{2.3}**F.** NMR spin—echo signal intensities of ¹H assigned to protons of the cation ($I_{\text{H(cation)}}$) and of ¹H and ¹⁹F

from the anion (I_{H(anion)}, I_{F(anion)}) of RMIm(HF)_{2.3}F exhibited an exponential decay with δ^2 , indicating random walk migration of the species in the molten salts.¹¹ Therefore, apparent diffusion coefficients $D_{H(cation)}$, $D_{H(anion)}$, and $D_{F(anion)}$ were estimated from the slope of log plots of $I_{H(cation)}$, $I_{H(anion)}$, and $I_{F(anion)}$, respectively, against $\gamma^2 g^2 \delta^2 (4\Delta - \delta) / \pi^2$.¹⁵ Figure 1 shows the temperature dependence of apparent diffusion coefficients $(D_{\rm H(cation)}, D_{\rm H(anion)}, D_{\rm F(anion)})$ of the cation and anion species of EMIm(HF)₂ ₃F, BMIm(HF)₂ ₃F, and HMIm(HF)₂ ₃F molten salts. These results demonstrate several characteristic features. One is that, in each salt, activation energies (E_a) of diffusion estimated from the slopes are almost the same independent of the cation, anion, and probed nuclei. This indicates that the carrier migration mechanism is essentially the same between the cation and anion of RMIm(HF)_{2.3}F. Cation and anion species would migrate randomly by colliding and exchanging positions with each other. This result explicitly rules out the possibility of another peculiar migration mechanism such as proton hopping represented by Grotthus proton transfer among anion species.¹⁶ The larger value of $D_{\text{H(anion)}}$ or $D_{\text{F(anion)}}$ compared with $D_{\text{H(cation)}}$ for all salts reflects the greater size of the cation than that of the anion. That is, the smaller the size of the species, the faster it could migrate according to the Stokes-Einstein relation when weight and charge densities are constant.^{17,18} It is also anomalous that $D_{H(anion)}$ and $D_{F(anion)}$ did not necessarily agree with each other because the observed diffusion coefficient should be independent of the probed nucleus if the observed species are identical. This result is consistent with the observation of the IR spectra that $(HF)_2F^-$ and $(HF)_3F^-$ coexist as the anion species in the salts.⁵ The difference in the composition ratio of H to F between $(HF)_2F^-$ (2:3) and $(HF)_3F^-$ (3:4) and the fast exchange between the two species through HF resulted in independent observed values of $D_{H(anion)}$ and $D_{F(anion)}$. Taking into account the order of magnitude of the inherent diffusion coefficient, $D_{(\text{HF})_2\text{F}^-} > D_{(\text{HF})_3\text{F}^-}$, that is expected from the order of the anion size, $r_{(HF)_2F^-} < r_{(HF)_3F^-}$, the observed $D_{F(anion)}$ should be larger than $D_{\mathrm{H(anion)}}$ on the assumption of that only the two species, $(HF)_2F^-$ and $(HF)_3F^-$, contribute to the observed diffusion values. This is because $D_{H(anion)}$ and $D_{F(anion)}$, under the situation of two anion species coexisting, can be represented explicitly as

$$D_{\rm H(anion)} = \frac{3a}{3a+2b} D_{\rm (HF)_3F^-} + \frac{2b}{3a+2b} D_{\rm (HF)_2F^-}$$
$$D_{\rm F(anion)} = \frac{4a}{4a+3b} D_{\rm (HF)_3F^-} + \frac{3b}{4a+3b} D_{\rm (HF)_2F^-}$$
(2)

where *a* and *b* (=1 - *a*) are the molar fraction of (HF)₃F⁻ and (HF)₂F⁻ in the salt, respectively. This relation leads to

$$D_{\text{F(anion)}} - D_{\text{H(anion)}} = \frac{ab}{(4a+3b)(3a+2b)} (D_{(\text{HF})_2\text{F}^-} - D_{(\text{HF})_3\text{F}^-}) (3)$$

Considering the situation of $D_{(HF)_2F} > D_{(HF)_3F}$ mentioned above, eq 3 has to be greater than 0. The opposite experimental result of $D_{H(anion)} \ge D_{F(anion)}$, independent of the kind of cation, suggests the existence of another fast diffusive species. Considering the situation of anion species, $(HF)_2F^-$ and $(HF)_3F^-$, coexisting under the equilibrium condition, the exchanging species, HF, between the two anions can be a candidate as the third diffusive component of the diffusion values. In this case, eq 2 can be modified by using the molar fraction of *a*, *b*, and c (a + b + c = 1) for (HF)₃F⁻, (HF)₂F⁻, and HF, respectively, as

$$D_{\mathrm{H(anion)}} = \frac{3a}{3a+2b+c} D_{(\mathrm{HF})_{3}\mathrm{F}^{-}} + \frac{2b}{3a+2b+c} D_{(\mathrm{HF})_{2}\mathrm{F}^{-}} + \frac{c}{3a+2b+c} D_{\mathrm{HF}}$$
$$D_{\mathrm{F(anion)}} = \frac{4a}{4a+3b+c} D_{\mathrm{(HF)}_{3}\mathrm{F}^{-}} + \frac{3b}{4a+3b+c} D_{\mathrm{(HF)}_{2}\mathrm{F}^{-}} + \frac{c}{4a+3b+c} D_{\mathrm{$$

As a result,

$$D_{\rm H(anion)} - D_{\rm F(anion)} \propto a(b-c)D_{\rm (HF)_3F^-} - b(a+c)D_{\rm (HF)_2F^-} + c(a+b)D_{\rm HF}$$
 (5)

Considering the atomic fraction of H:F = 2.3:3.3, which was confirmed by the chemical analyses for this type of salt, $0 \le a \le 0.3$, $0 \le b \le 0.77$, $0 \le c \le 0.23$ (10/13 $\le a + b \le 1$) are held simultaneously. The contribution of D_{HF} , which is expected to be larger than $D_{(\text{HF})_2\text{F}^-}$, leads to $D_{\text{H(anion)}} > D_{\text{F(anion)}}$ consistent with the observed results in Figure 1. IR spectroscopy did not give the evidence of HF except for two independent species, (HF)₂F⁻ and (HF)₃F⁻. Furthermore, this kind of salt is chemically stable without any volatility and corrosive action to glass. These results indicate that the lifetime (probability of existence) of HF, corresponding to the pre-factor of D_{HF} in eq 4, is too small to be confirmed in the IR spectra which represent the equilibrium state, but the inherent diffusion coefficient, D_{HF} , is fairly large enough to affect the observed diffusion values under the condition of $D_{\text{H(anion)}} > D_{\text{F(anion)}}$.

2. Interpretation of Ionic State Based on the Dissociation Degree of the Salt. *a. Validity of the Haven Ratio* ($\Lambda_{imp}/\Lambda_{NMR}$) *for Evaluation of the Dissociation Degree of the Salt.* Table 1 lists electrical conductivity, viscosity, and observed and estimated diffusion coefficients of each ionic species and several physical parameters of RMIm(HF)_{2.3}F at 25 °C. With increasing molecular weight of the salt caused by extension of the side chain of the cation, Λ_{imp} and D_{total} decreased almost monotonically although the reverse order was observed between DMIm-(HF)_{2.3}F and EMIm(HF)_{2.3}F. This general feature is attributed to the fact that an increase in cation size leads to the viscosity increase of the molten salts.

The ratio of molar conductivities estimated from impedance technique (Λ_{imp}) to diffusion coefficient from PGSE-NMR (Λ_{NMR}), which is called the Haven ratio,¹⁹ was not unity and depended on the sample shown in Table 1. This indicates that the salt does not completely dissociate to isolated ions.¹⁹ It is expected that the ionization state depends on the structure and combination of the cation and anion species. We then first speculate the static feature of ions of the molten salts before evaluating the ionic migration mechanism.

One of the ways of representing the ionization state in RTMS is to apply the idea of "degree of dissociation of the salt" that is conventional for the dissolved salt in a solvent. We here assume that at any moment a molten salt is, in some degree, dissociated into ions and partially maintains the associated condition between the cation and anion forming ion pairs. This situation could be characterized by the degree of dissociation, x, that represents a fraction of ions in the total (ions and ion-pairs) species in the salt. Under the equilibrium condition, the ion and ion pair exchange with each other very fast compared with the time taken for a diffusion measurement.⁹ As a result,

 TABLE 1: Ionic Conductivity, Observed and Estimated Diffusion Coefficients, and Several Physical Parameters of

 Alkylimidazolium Fluorohydrogenates, $RMIm(HF)_{2.3}F^{a,b}$

| | DMIm | EMIm | PrMIm | BMIm | PeMIm | HMIm |
|---|------|------|-------|------|-------|------|
| MW | 162 | 176 | 190 | 204 | 218 | 232 |
| $\sigma/\mathrm{mS~cm}^{-1}$ | 110 | 100 | 61 | 33 | 27 | 16 |
| η/cP | 5.1 | 4.9 | 7.0 | 19.6 | 26.7 | 25.8 |
| density/g cm ⁻³ | 1.17 | 1.13 | 1.11 | 1.08 | 1.05 | 1.00 |
| $\Lambda_{\rm imp}/{ m S~cm^2mol^{-1}}$ | 15.2 | 15.6 | 10.4 | 6.2 | 5.6 | 3.7 |
| $D_{\rm H(cation)}/10^{-6}{\rm cm}^2{\rm s}^{-1}$ | 2.3 | 3.0 | 1.4 | 0.94 | 0.97 | 0.74 |
| $D_{\rm H(anion)}/10^{-6}~{\rm cm}^2{\rm s}^{-1}$ | 3.0 | 4.5 | 2.0 | 1.5 | 1.7 | 1.6 |
| $D_{\rm F(anion)}/10^{-6}~{\rm cm}^2{\rm s}^{-1}$ | 2.9 | 3.8 | 2.1 | 1.3 | 1.4 | 1.6 |
| $D_{\rm av(anion)}^{c}/10^{-6}~{\rm cm}^2{\rm s}^{-1}$ | 3.0 | 4.1 | 2.0 | 1.4 | 1.5 | 1.6 |
| $D_{\text{total(anion)}}^{d}/10^{-6} \text{ cm}^2 \text{ s}^{-1}$ | 5.3 | 7.1 | 3.4 | 2.4 | 2.5 | 2.3 |
| $\Lambda_{\rm NMR}/{ m S~cm^2~mol^{-1}}$ | 19.8 | 26.7 | 12.8 | 8.9 | 9.4 | 8.7 |
| $\Lambda_{ m imp}/\Lambda_{ m NMR}$ | 0.77 | 0.58 | 0.82 | 0.70 | 0.60 | 0.43 |

^{*a*} R:D for 1,3-dimethylidazolium, E for 1-ethyl-3-methylimidazolium, Pr for 1-propyl-3-methylimidazolium, B for 1-butyl-3-methylimidazolium, Pe for 1-pentyl-3-methylimidazolium and H for 1-hexyl-3-methylimidazolium. ^{*b*} σ , η , and *D* were *o*bserved at 25 °C. ^{*c*} $D_{av(anion)} = (2.3/5.6)D_{H(anion)} + (3.3/5.6)D_{F(anion)}$ due to the atomic fraction of H:F = 2.3:3.3. ^{*d*} $D_{total} = D_{H(cation)} + D_{av(anion)}$.

the observed diffusion coefficient probed by ¹H assigned to the anion, for example, can be expressed by using x as

$$D_{\rm H}^{\rm obs} = x D_{\rm anion} + (1-x) D_{\rm pair} \tag{6}$$

As mentioned above, $\Lambda_{imp}/\Lambda_{NMR}$ seems to characterize the dissociation condition of the salt.⁶ This idea is qualitatively acceptable because the impedance data reflect only charged ion migration in contrast to the NMR diffusion coefficient attributed to the transport behavior of both the ion and ion pair. Considering eq 6, we here represent $\Lambda_{imp}/\Lambda_{NMR}$ explicitly for quantitative evaluation using the inherent diffusion value, D_{cation} , D_{anion} , or D_{pair} , of each species.¹⁹

$$\frac{\Lambda_{\rm imp}}{\Lambda_{\rm NMR}} = \frac{x(D_{\rm cation} + D_{\rm anion})}{x(D_{\rm cation} + D_{\rm anion}) + 2(1 - x)D_{\rm pair}} = \frac{1}{1 + 2\left(\frac{1 - x}{x}\right)\frac{D_{\rm pair}}{D_{\rm cation} + D_{\rm anion}}}$$
(7)

It is proved that the Haven ratio is approximated to x in the case of $D_{\text{cation}} + D_{\text{anion}} \approx 2D_{\text{pair}}$ or $x \approx 1.^{20}$ What is the situation in other cases? We here assume two different samples denoted by subscripts 1 and 2, under the situation of

$$\left(\frac{\Lambda_{\rm imp}}{\Lambda_{\rm NMR}}\right)_2 > \left(\frac{\Lambda_{\rm imp}}{\Lambda_{\rm NMR}}\right)_1 \tag{8}$$

Then, the ratio of the dissociation degree of the two samples, x_2/x_1 , could be derived from eqs 6 and 7 as

$$\frac{x_2}{x_1} > \frac{D_{\rm H(cation)}^2 + D_{\rm av(anion)}^2}{D_{\rm H(cation)}^1 + D_{\rm av(anion)}^1} \times \frac{D_{\rm cation}^1 + D_{\rm anion}^1}{D_{\rm cation}^2 + D_{\rm anion}^2}$$
(9)

in which $D_{\text{H(cation)}}$ and $D_{\text{av(anion)}}$ are observed and averaged observed values, respectively, represented by

$$D_{\text{H(cation)}} = xD_{\text{cation}} + (1-x)D_{\text{pair}}$$
$$D_{\text{av(anion)}} = \frac{2.3}{5.6}D_{\text{H(anion)}} + \frac{3.3}{5.6}D_{\text{F(anion)}} = xD_{\text{anion}} + (1-x)D_{\text{pair}} (10)$$

It is easy to understand the real situation by assuming that samples 1 and 2 correspond to $HMIm(HF)_{2.3}F$ and $EMIm(HF)_{2.3}F$, respectively. We find that the salts satisfy eq 8 from



Figure 2. Walden's plot, log Λ vs log $1/\eta$ of EMIm(HF)_{2.3}F (\bigcirc), BMIm(HF)_{2.3}F (\triangle), and HMIm(HF)_{2.3}F (\square).

Table 1. The first fraction of the right-hand side of eq 9 concerning the observed values is greater than unity from Table 1. On the other hand, the second fraction of the side comprising the inherent diffusion values of the cation and anion is expected to be less than unity due to the size effect, the EMIm cation being smaller in size than the HMIm cation, indicating $D_{\text{cation}}^1 < D_{\text{cation}}^2$. As a result, the descending degree of magnitude of x_1 and x_2 is not determined uniquely. This is because only the case of both fractions being greater than unity guarantees $x_2 > x_1$. That is, the ordering of magnitude of $\Lambda_{\text{imp}}/\Lambda_{\text{NMR}}$ is not necessarily consistent with the ordering of the dissociation degree of the salt. This indicates that the dissociation condition of the salt has to be interpreted by another approach for quantitative evaluation.

b. Application of the Stokes-Einstein Relation for Evaluation of the Dissociation Degree of the Salt. The empirical Walden's rule has been applied to RTMS materials in several reports to categorize the dynamic feature compared with glass and inorganic electrolytes.^{21,22} Walden's rule originally states that the product of molar conductivity and viscosity of hydrodynamic materials having moving entities in conduction is a constant at a given temperature. In practice, the behavior of plots of $\log \Lambda$ vs log $1/\eta$ has been elucidated in detail for many electrolyte materials. It is explained that the magnitude of the slope and the position of the plot relative to the ideal line extrapolated from 1 M KCl solution indicate the characteristics of the ionic state and ion transport mechanism.^{21,22} Figure 2 represents the Walden's plot of RMIm(HF)_{2.3}F with different cations. It is characteristic that the slope of the plot of EMIm(HF)2.3F was almost unity, parallel to the ideal line, and, on the other hand, the plots of BMIm(HF)2.3F and HMIm(HF)2.3F showed slopes of less than unity. The difference in slope may reflect the difference in ionization state and ion transport mechanism among the salts. To investigate the situation systematically, it is more appropriate to apply the Stokes–Einstein equation, which gives the dynamic feature of individual species with the diffusion coefficient⁸ according to the form of

$$D = kT/6\pi\eta r \tag{11}$$

where *D* is the diffusion coefficient of the species, *k* is the Boltzmann constant, η is the solution viscosity, and *r* is the hydrodynamic radius of the mobile species. The advantage of the Stokes–Einstein equation compared with the Walden rule is that it deals with the individual species that is characterized by the inherent diffusion coefficient. The validity of the application of the Stokes–Einstein relation to ionic liquids has been under debate.^{21,23} The most serious arguement against the application is that the mobile species cannot be assumed to be in macroscopic sphere continuum fluid. Despite this fact, however, a fairly good fit of the cation species of molten salts to the Stokes–Einstein relation is pointed out by Bockris and Reddy.²³ Furthermore, the Reynolds number (*Re*)²⁴ defined by

$$Re = \nu d \frac{\rho}{\eta} \tag{12}$$

where ν is the velocity, d is the diameter of the moving sphere, η is the viscosity, and ρ is the density of the medium, is much smaller than unity ($Re \approx 10^{-11}$) by substituting the typical values of RMIm(HF)_{2.3}F, for $d_{\rm ion} \approx 10^{-8}$ cm, $\nu_{\rm ion} \approx 10^{-5}$ cm s⁻¹, $\eta \approx$ 10^{-2} poise, $\rho \approx 1$ g cm⁻³. This reveals that Stokes' relation is fairly satisfied under this situation.²⁴ These considerations support that the application of the Stokes–Einstein relation is not necessarily extraordinary and is rather effective to survey the dynamic feature of individual species as long as the Stokes– Einstein relation is discussed by analogy with Walden's rule.

Figure 3 represents the observed diffusion coefficients, $D_{\text{H(cation)}}$, $D_{\text{H(anion)}}$, and $D_{\text{F(anion)}}$ of RMIm(HF)_{2.3}F (R = E, B, H) as a function of T/η according to eq 11. In the case of EMIm-(HF)_{2.3}F, the plots showed a linear change in the observed region. On the other hand, the plots of BMIm(HF)2.3F and HMIm(HF)_{2.3}F showed a slight change in slope, that is, a decrease in slope with an increase in T/η . This means that the ion migration mechanism in BMIm(HF)_{2.3}F and HMIm(HF)_{2.3}F, with a large difference in size between the cation and anion, would deviate from the ideal Stokes-Einstein relation. This deviation is fundamentally the same as the phenomena of Walden plots of log Λ vs log $1/\eta$ with the slope of less than unity, and would be attributed to the imbalanced size of the cation and anion, preventing the random collision between them for random walk migration especially at higher temperature. To compare the ionization state between the salts, we drew approximate lines for the data following the Stokes-Einstein relation in Figure 3. Table 2 lists the relative value of the slope of each observed species for three samples. EMIm(HF)2.3F showed the lowest values in the three samples for both the cation and anion species.

We here evaluate the meaning of the difference in slope of the Stokes-Einstein plot of the observed diffusion values, $D_{\rm H(cation)}$, $D_{\rm H(anion)}$, and $D_{\rm F(anion)}$. If the individual species in molten salts, characterized by the respective diffusion values, $D_{\rm cation}$, $D_{\rm anion}$, and $D_{\rm pair}$, obey the Stokes-Einstein relation, they can be denoted as,

$$D_{\rm ion} = \frac{kT}{6\pi\eta r_{\rm ion}}, \qquad D_{\rm pair} = \frac{kT}{6\pi\eta r_{\rm pair}}$$
 (13)



Figure 3. Diffusion coefficient of cation species detected by ¹H ($D_{\text{H(cation)}}$) and anion species detected by ¹H ($D_{\text{H(anion)}}$) and by ¹⁹F ($D_{\text{F(anion)}}$) vs $\eta^{-1}T$ for (a) EMIm(HF)_{2.3}F, (b) BMIm(HF)_{2.3}F, and (c) HMIm(HF)_{2.3}F.

TABLE 2: Relative Value of the Slope of the Plots of $D_{\text{H(cation)}}$ vs T/η , $D_{\text{H(anion)}}$ vs T/η , and $D_{\text{F(anion)}}$ vs T/η for EMIm(HF)_{2.3}F, BMIm(HF)_{2.3}F, and HMIm(HF)_{2.3}F

| | EMIm(HF) _{2.3} F | BMIm(HF) _{2.3} F | HMIm(HF) _{2.3} F |
|---------------------|---------------------------|---------------------------|---------------------------|
| $D_{\rm H(cation)}$ | 0.048 | 0.068 | 0.071 |
| $D_{\rm H(anion)}$ | 0.072 | 0.113 | 0.208 |
| $D_{\rm F(cation)}$ | 0.060 | 0.113 | 0.132 |

As a result, observed diffusion values can be summarized by using eq 6 as

$$D_{\rm obs} = \frac{kT}{6\pi\eta} \left(\frac{x}{r_{\rm ion}} + \frac{1-x}{r_{\rm pair}} \right) \tag{14}$$

Then, the slope, s, of the plot of D_{obs} vs T/η listed in Table 2 is denoted as

$$s = \frac{k}{6\pi} \left(\frac{x}{r_{\rm ion}} + \frac{1-x}{r_{\rm pair}} \right) \tag{15}$$

Here, we add subscripts 1 and 2 for distinction of the two samples having different cations such as $HMIm(HF)_{2,3}F$ and

EMIm(HF)_{2.3}F, respectively, in order to realize the concrete meaning of *s* values. We can also assume $r_1 = hr_2$ (h > 1) where r_1 and r_2 are hydrodynamic radii of the ion pairs of HMIm(HF)_{2.3}F and EMIm(HF)_{2.3}F, respectively. The descending degree of the magnitude of slope between them can be evaluated from eq 15 as

$$s_{1} - s_{2} \propto \frac{x_{1}}{r_{\text{anion}}} + \frac{1 - x_{1}}{r_{1}} - \frac{x_{2}}{r_{\text{anion}}} - \frac{1 - x_{2}}{r_{2}} = \frac{x_{1} - x_{2}}{r_{\text{anion}}} + \frac{1}{r_{2}} \left(\frac{1 - x_{1}}{h} - (1 - x_{2})\right) < \frac{x_{1} - x_{2}}{r_{\text{anion}}} + \frac{1}{r_{2}} \left((1 - x_{1}) - (1 - x_{2})\right) = (x_{1} - x_{2}) \left(\frac{1}{r_{\text{anion}}} - \frac{1}{r_{2}}\right) (16)$$

As $s_1 > s_2$ from Table 2, the right-hand side of eq 16 is greater than 0. As a result, due to the relation of $r_{anion} < r_2$, $x_1 > x_2$ is induced. That is, the relative magnitude of the slope, *s*, agrees with that of the dissociation degree, *x*, when the larger salt shows higher values of the slope in the Stokes–Einstein plot.

On the basis of this consideration, the dissociation degree of the salt becomes lower with decreasing cation size. This result conflicts with the general recognition that a higher dissociation degree of the salt leads to a higher conductivity due to the enhanced ion concentration. This may be due to the fact that the contribution from mobility is more effective compared with the carrier content to the conductivity of this type of molten salt. To realize the ion transport mechanism responsible for high mobility, we tried to use a new interpretation in the next section.

3. Interpretation of Ionic State Based on the "Degree of Ordering of Ions". As we mentioned previously, it is not necessarily appropriate for molten salts to apply the concept of the dissociation degree of the salt. This is because molten salts do not contain solvent species which play the part of solvation for ions and initiate separation of the cation and anion. We rather propose to take into account a more reasonable idea of the "degree of approach between the cation and anion" or the "degree of ordering of ions" to represent the ionization state in molten salts. Ordered ions prepare a domain which is a unit particle of the migration species. With an increase in the degree of ionic orientation, the size of the domain increases. The slope of the plot in Table 2 would directly reflect the size of the domain particle according to this interpretation. It is well-known from eq 11 that the larger the size of the mobile species, the more gentle the slope becomes. The fact that the plot of EMIm-(HF)_{2.3}F showed the smallest value of the slope for both the cation and anion species indicates that the cations and anions are most highly oriented in the salt forming the largest domain particles compared with those of BMIm(HF)2.3F and HMIm-(HF)_{2,3}F despite the smallest cation, EMIm. The comparison of the unit ion size among the salts is shown in Figure 4. The highest ordering of the ions of EMIm(HF)2.3F may be due to the steric matching of the cation and anion. As a result, when we simplify the indications of the cation and anion of the salts as A^+ and X^- , respectively, domain particles responsible for the observed diffusion coefficient could be denoted as $A(AX)_m^+$ and $(AX)_n X^-$. EMIm(HF)_{2.3}F would have the largest numbers for *m* and *n* in the salts.

Finally, discussion must address why the larger particle composed of several oriented ions showed a faster diffusion coefficient because the result essentially opposes the size effect on diffusivity predicted from the Stokes–Einstein relation. This can be explained as follows. With an increase in the particle size in proportional to the number *m* of $A(AX)_m^+$, for example,



Figure 4. Ionic structure and size of cations, EMIm^+ , BMIm^+ , and HMIm^+ , and anions, $(\text{HF})_2\text{F}^-$ and $(\text{HF})_3\text{F}^-$, of $\text{RMIm}(\text{HF})_{2.3}\text{F}$ obtained from ab initio molecular orbital calculation.

the charge density of the particle is reduced. In molten salts, Coulombic interactions and the geometry of the mobile species are dominant factors of carrier mobility by affecting the strength and the frequency of confliction among the species. It is expected that the dispersion of charge density of a mobile particle with the size enlargement is effective to reduce the frictional resistance in migration.

Ion orientation in molten salts would be analogous to the ordered structure of ionic crystals. In practice, high-energy X-ray diffraction measurements of RMIm(HF)_{2.3}F suggest the possibility of a highly ordering structure consistent with the crystal structure of EMImFHF.^{4,5} Among the observed salts, EMIm-(HF)_{2.3}F demonstrated the most oriented structure from the diffusion measurements. It seems that the size balance between the cation and anion is significant to prepare the oriented structure as shown in Figure 4.

Summary

We elucidated the dynamic feature of the room temperature molten salts, RMIm(HF)_{2.3}F (R = arkyl group), to interpret the ionization state based on both the ideas of the "dissociation degree of the salt", which assumes two coexisting states, ion and ion pair, and the "degree of ordering", which assumes a mobile particle composed of several ions in orientation. In the liquid of molten salts without any solvent species, the ions change their position and migrate conflicting with each other influenced by their Coulombic force. In this situation, it is more realistic that the aggregates of ordered ions, $A(AX)_m^+$ and $(AX)_nX^-$, frequently changing their form and size by inserting and extracting some mono-ions at the surface, are responsible for ion diffusion, rather than that the isolated ions $(A^+ \text{ and } X^-)$ and ion pair (AX) coexist under the dissociation equilibrium state. Designing a highly ordered structure is effective for the preparation of room temperature molten salts with high mobility because the domain composed of several oriented ions would experience lower frictional resistance in migration due to the lower charge density compared with that of the isolated ions.

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