Structural and Spectroscopic Characteristics of a Proton-Conductive Ionic Liquid Diethylmethylammonium Trifluoromethanesulfonate [dema][TfOH]

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Structural specificity including dynamic behavior and stable conformations in the bulk phase of diethylmethylammonium trifluoromethanesulfonate [dema][TfOH], which is assumed to be a prominent ionic liquid electrolyte for non-humidified intermediate temperature fuel cells, have been investigated by ^{1}H NMR, IR spectroscopic analyses, and molecular dynamics (MD) simulation. It is found that an N–H proton in [dema][TfOH] is an exchangeable mobile proton which can be substituted by D_2O, and free rotation around the N–C bond in the ethyl side chain of the ammonium cation is retarded by ionic interactions between the cations and anions, therefore the methylene protons in the ethyl side chain are unisochronous. In addition, the rotational barrier of this N–C bond was observed to be 71 kJ mol^{-1}, comparable to the barrier height of the amide N–C bond (which is well-known to have partial double bond character) from temperature-dependent NMR experiments by monitoring the peak-shape changes of methylene protons in the ethyl side chain of the ammonium cation. The bulk-phase structure of [dema][TfOH] was calculated by MD simulations on the basis of the OPLS-AA force field, and the evaluated structure was consistent with those of experimental results. Thus, IR spectrum frequency of the N–H proton, and the ^{1}H NMR chemical shift values could be rationally assigned on the basis of the theoretically evaluated structures in the bulk phase.

Polymer electrolyte fuel cells (PEFCs)[1,2] are a promising energy conversion system for an ecologically sustainable economy. Though much effort has been taken to establish the technology by using perfluoroalkyl ionomer, Nafion,[1] and hydrocarbon ionomers,[3] fuel cell technology has not been as widely applied as lithium ion batteries.[4] One of the critical drawbacks of the general PEFC system using sulfonated membranes such as Nafion is that the PEFC system requires water for proton conduction, since hydronium ion which is generated from the reaction of water with sulfonic acid group protons works as proton carrier.[5] Therefore, such a PEFC system cannot be operated at higher than the boiling point of water, resulting in low utilization of exhaust heat and low Pt activity.[6] Recently, Watanabe et al. have developed a protic ionic liquid (IL) diethylmethylammonium trifluoromethanesulfonate [dema][TfOH],[7] which can be used as a superb electrolyte for fuel cells that can be operated under non-humidified conditions at elevated temperature (non-humidified intermediate temperature fuel cell). The [dema][TfOH] has splendid electrochemical properties for non-humidified intermediate temperature fuel cells as follows: $T_{\mathrm{m}} = -13\,°\mathrm{C}$, $T_{\mathrm{d}} = 360\,°\mathrm{C}$, and $\sigma = 53\,\mathrm{mS\,cm^{-1}}$ at 150 °C under anhydrous conditions. Open circuit potential (OCP): 1.03 V under anhydrous conditions at 150 °C. Why can [dema][TfOH] work as a superb electrolyte for the fuel cell? First of all, it is requisite to make clear the bulk-phase structure of this ionic liquid to get an essential knowledge to enable to exert splendid electrochemical properties. Therefore, experimental structural studies of [dema][TfOH] have been carried out by using NMR and IR spectroscopy. By combining these experimental results with theoretical molecular modeling simulation, a more detailed microscopic picture of how ionic liquid can function as a good electrolyte for fuel cells may be provided. In this paper, we will show a detailed atomic image with regard to structural characteristics of proton-conductive [dema][TfOH] derived from physical organic experiments and theoretical MD simulations.

Results and Discussion

Structural Aspects Obtained from Spectral Analyses. NMR and IR spectrum measurements have been carried out on [dema][TfOH] to obtain structural data intrinsic to this proton-conductive IL. ^{1}H NMR spectrum of neat [dema][TfOH] at an ambient temperature ($T = 30\,°\mathrm{C}$) in a coaxial double sample tube is shown in Figure 1. A broad N–H proton believed to be the origin of conductive protons is observed at 7.33 ppm, and alkyl protons in ammonium cation are found in the region of 0.5–3.0 ppm. The noteworthy points to be mentioned are that the N–H proton is coupled with its neighboring methyl and methylene protons in the alkyl side chains, and each methylene proton is unisochronous (i.e., has different chemical shift value), and therefore appears as a multiplet. Each of these methylene protons are observed at 2.80 and 2.68 ppm, respectively. Why are these methylene protons unisochronous? One reasonable explanation is that free rotation around the N–C bond in the alkyl side chain is rather restricted due to steric hindrance in [dema][TfOH]. Therefore, we have monitored NMR spectral changes by raising the probe temperature from 30 to 120 °C. As shown in Figure 1, the unisochronous methylene protons coalesce at 70 °C (343 K), and finally are

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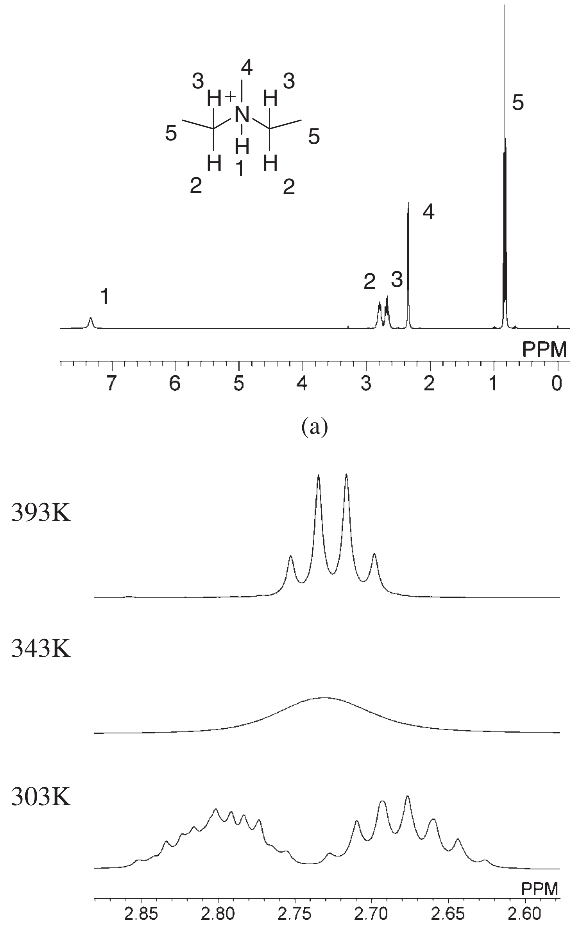

(a)

(b)

Figure 1. (a) ^{1}H NMR spectrum ($T = 303$ K, neat, in co-axial double sample tube) of [dema][TfOH]. (b) ^{1}H NMR spectral peak shape changes of unisochronous methylene protons (2.60–2.85 ppm) by raising probe temperature from 303 to 393 K with enlarged scale.

isochronous at 120 °C (393 K) (same chemical shift) to represent a typical methylene quartet signal (intensity ratio: 1:3:3:1) as seen for those located next to methyl protons. The chemical shift of the center of the methylene protons (proton 2 and 3) was almost the same during the temperature increase. This experimental result supports our assumption that the motion of alkyl side chains in [dema][TfOH] is hindered at ambient temperature. By applying standard dynamic NMR[8] to derive the rotational barrier around the σ bond from this temperature-dependent NMR experiment, the rotational barrier of the C–N bond (T_c (coalescence temperature) $= 343$ K) has been evaluated to be 71 kJ mol^{-1}. The rotational barrier $\Delta G^{\#}$ can be calculated from the observed chemical shift difference ($\Delta\nu$: Hz) between the unisochronous methylene protons ($\Delta\nu = 50.9$ Hz in this case) at the coalescence temperature (T_c) from eqs 1 and 2.

$$k = \pi\Delta\nu/2^{0.5} \tag{1}$$

$$\Delta G^{\#} = 2.303RT_c\{10.32 + \log(T_c/k)\} \tag{2}$$

where, k represents the rate constant for rotation around the corresponding σ-bond (N–C), and R is the gas constant.

Table 1. ^{1}H NMR Spectrum Assignment of [dema][TfOH] at 30 °C (Neat)

Assignment	Chemical shift /ppm	Peak shape	Coupling constant /Hz
1	7.33	broad (1H)	$J_{25} = 7.32$, $J_{35} = 7.32$
2	2.80	m (2H)	$J_{23} = 13.17$
3	2.68	m (2H)	$J_{12} = 3.70$
4	2.34	d (3H)	$J_{13} = 7.07$
5	0.82	t (6H)	$J_{14} = 5.12$

The obtained rotational barrier (71 kJ mol^{-1}) around the N–C bond is comparable to those of the amide N–C bond. The reported rotational barriers of the N–C bond[9] for *N*,*N*-dimethylformamide (DMF) and *N*,*N*-dimethylacetamide (DMA) are 87.6 kJ mol^{-1} ($T_c = 392$ K) and 72.5 kJ mol^{-1} ($T_c = 298$ K), respectively. This observed rotational barrier (71 kJ mol^{-1}) in [dema][TfOH] signifies hindered rotation of the N–C bond in this IL. We are assuming that this hindered rotation around the N–C bond comes from rather strong intra- and/or intermolecular ionic interactions leading to the steric hindrance against free rotation in [dema][TfOH]. With regard to the magnitude and conformational characteristics of these ionic interactions between cations and anions, theoretical consideration will be carried out later on the basis of the bulk-phase structure of [dema][TfOH] evaluated by MD simulations. A complete assignment of these unisochronous methylene protons and their related coupling constants ($^3J_{\text{H–H}}$: vicinal and $^2J_{\text{H–H}}$: geminal) has been accomplished by decoupling the N–H proton leading to a simplified NMR spectrum. The determined chemical shift values of each unisochronous methylene protons and relevant coupling constants (J) are summarized in Table 1. As shown in Table 1, an unisochronous methylene proton located cis to the N–H proton is found at 2.80 ppm (lower field), and a trans methylene proton stands at 2.68 ppm. The geminal coupling ($^2J_{\text{H–H}}$) between unisochronous methylene protons is 13.17 Hz. It is interesting to note that the vicinal coupling constant between the N–H proton and cis methylene proton ($^3J_{\text{NH–H(cis)}} = 3.70$ Hz) is smaller (about half) than the corresponding trans vicinal coupling constant between the N–H proton and trans methylene proton ($^3J_{\text{NH–H(trans)}} = 7.07$ Hz). This specific configurationally dependent change of vicinal $^3J_{\text{H–H}}$ values remind us of the well-known relation for olefinic protons $^3J_{\text{H–H}}$ ($^3J_{\text{H–H(trans)}}/{}^3J_{\text{H–H(cis)}} \approx 2.0$). Thus, the experimentally determined vicinal $^3J_{\text{NH–H}}$ of [dema][TfOH] stated above also suggests hindered bond rotation around the N–C bond as shown from the temperature-dependent ^{1}H NMR spectral changes of unisochronous methylene protons.

The next intriguing aspect of the NMR spectrum of [dema][TfOH] is the N–H proton mobility. The fact that the N–H proton couples with neighboring methyl and methylene protons at 30 °C signifies slower exchange compared to more mobile OH protons found in H_2O and carboxylic acids. On the time scale of our NMR experiments (400 MHz, ^{1}H NMR), proton exchange occurring faster than 10^{-3} s cannot be observed due to the Heisenberg uncertainty principle. Therefore, at ambient temperature the N–H proton in [dema][TfOH]

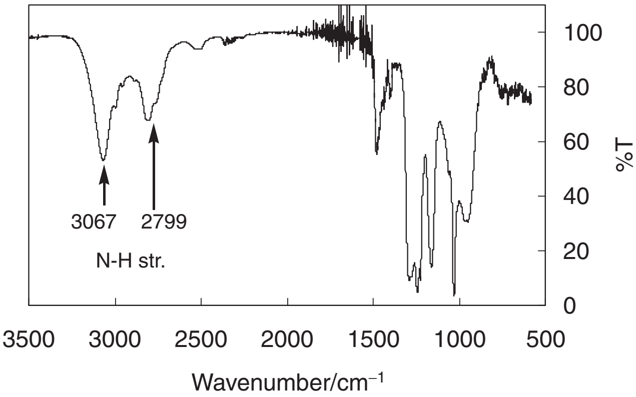

Figure 2. IR spectrum of neat [dema][TfOH] at ambient temperature.

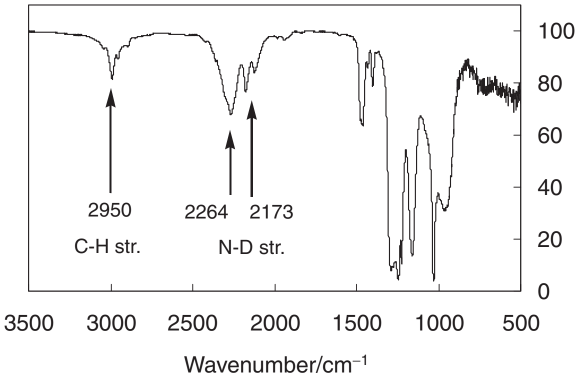

Figure 3. IR spectrum of neat deuterated [dema][TfOD] at ambient temperature.

is assumed to be bonded to nitrogen on an NMR time scale. Judging from the disappearance of $^3J_{\text{H–H}}$ couplings between neighboring methyl or methylene protons and the N–H proton at 120 °C, exchange seems to be too fast to be monitored by ^{1}H NMR. This is the first experimental report demonstrating clearly that an N–H proton in [dema][TfOH] is exchangeable in an alkylammonium ionic liquid. More rapid N–H proton exchange may contribute effectively to higher proton conductivity. It should be mentioned here that N–H protons present a broad singlet peak and no coupling is observed with neighboring methyl and methylene protons because of efficient fast relaxation by nitrogen (^{14}N) with a quadrupole magnetic moment. By raising probe temperature from 30 to 120 °C, the chemical shift of the N–H proton was observed to shift slightly toward higher field (7.30 ppm at 80 °C, 7.25 ppm at 150 °C). This experimental results may suggest the decrease of the population of hydrogen-bonded N–H protons coordinated to sulfonate anion in the cluster-like structure (vide infra, Figure 6). Further kinetic information regarding the N–H proton exchange may be investigated by IR spectral analyses.

IR Spectrum of [dema][TfOH]. As IR spectroscopy deals with larger transition energies than NMR, much faster dynamics of N–H proton exchange can be investigated by IR measurement. The IR spectrum of neat [dema][TfOH] in the form of liquid film is shown in Figure 2. At higher frequencies over 2700 cm^{-1}, we recognize two groups of peaks at around 3067 and 2799 cm^{-1}. Which peak is assigned to N–H stretching vibrational mode? It is rather difficult to assign N–H peaks of IL unambiguously because frequency numbers of the N–H peak in ammonium cations vary significantly depending on the structures (primary, secondary, or tertiary) ranging from 2600 and 3100 cm^{-1}.[10] In addition, the C–H stretching vibrations appear usually around 3100–2900 cm^{-1}. We have to carry out a specific experiment to distinguish N–H vibration from those of C–H in the IL spectrum. Our approach is to substitute N–H with N–D by reacting [dema][TfOH] with D_2O. In Figure 3, an IR spectrum of the deuterated [dema][TfOD] is shown. By comparing the deuterated [dema][TfOD] with [dema][TfOH], we find that the two signals located at 3067 and 2799 cm^{-1} in [dema][TfOH] disappear and two new signals appear at 2264 and 2173 cm^{-1} in [dema][TfOD]. This experimental result means that the two peaks located at 3067 and 2799 cm^{-1} can be assigned to N–H stretching vibrations. The C–H vibrational modes of alkyl side chains are found around 2950 cm^{-1} and their intensity is rather weak. Therefore, the C–H vibration signals are almost masked by strong N–H vibration in [dema][TfOH]. Polarized N–H bonds in [dema][TfOH] may reflect the stronger intensity of N–H vibrational modes than those of C–H. As we found two different vibrational modes for the N–H bond in [dema][TfOH], it is reasonable to think that [dema][TfOH] forms a cluster-like structure in the bulk-phase where two different N–H stretching modes exist.

Other characteristic bands associated with the N–H bond are located around 1150–1300 cm^{-1} in [dema][TfOH]. These rather strong bands originate from N–H out of plane bending deformation coupled with neighboring C–H bending and S–O stretching vibrations in triflate anion. Detailed study of the N–H stretching and N–H out of plane bending deformation vibrations provides useful information about the dynamic nature of N–H protons relevant to proton conductivity. A thorough assignment of the vibrational modes in the IR spectrum can be rationalized by normal mode vibrational analysis on the basis of the estimated bulk-phase structure calculated by MD simulation (vide infra).

MD (Molecular Dynamics) Simulated Bulk Phase Structure of [dema][TfOH]. As described above, [dema][TfOH] shows characteristic spectroscopic features inherent to proton-conductive IL. It may be certain that structural specificity of [dema][TfOH] must be reflected in these NMR and IR spectral features. Therefore, we have carried out MD simulation by using OPLS-AA force field[11] to evaluate the stable structure in the bulk phase. In order to ensure the validity of the OPLS force field for IL's composed of various alkylamines ($NR^1R^2R^3$) and trifluoromethanesulfonic acid [TfOH], the potential energy surface of [dema][TfOH] has been investigated by full geometry optimization calculations with HF/6-31+G* and B3LYP/6-31+G*. As it is necessary to find possible local minima structures existing at ambient temperature, exhaustive conformational search has been carried out on the diethylmethylammonium cation by using the MM3 force field[12] with possible dihedral angles driving and/or the stochastic search algorithm developed by Saunders.[13] For the obtained local minima structures of diethylmethylammonium cation with their relative steric energies (ΔE) from the global minimum structure ranging within 17 kJ mol^{-1} (4 kcal mol^{-1}), trifluoromethanesulfonate anion is coordinated randomly[14] to create many conceivable initial geometries of [dema][TfOH]. These initial geometries were optimized by the OPLS-AA force field and a search was made for possible existing conformations of [dema][TfOH]. Then calculated geometries were checked by HF/6-31+G* and B3LYP/6-31+G* ab initio calculations. The consistency of the OPLS-AA force field with the ab initio methods (HF/6-31+G* and B3LYP/6-31+G*) has been rigorously checked with regard to the geometries and conformational energies. In fact, default force field parameters in the program and augmented parameters for triflate anion determined by Lopes's group[15] are very trustworthy and could reproduce accurately the ab initio results. RMS (root-mean-square) errors for the structural parameters of [dema][TfOH] by comparing the geometries calculated with OPLS-AA force field with those of HF/6-31+G* are 0.013 Å (bond length), 1.88° (bond angle), and 2.70° (dihedral angle), respectively. The local electronic charges on each atom in [dema][TfOH] has been evaluated by CHelpG[16] from electrostatic potential calculated by Gaussian 03,[17] and each electronic charge thus obtained is used for MD simulations of [dema][TfOH]. The optimized structures of [dema][TfOH] with conformational populations at ambient temperature over 1% by HF/6-31+G* calculations are shown in Figure 4 with their relative conformational energies (ΔE: kJ mol^{-1}). The calculated optimized geometry and conformational energy by HF/6-31+G* for each conformer in Figure 4 were almost identical with those calculated by B3LYP/6-31+G*. The molecular mechanics (MM) calculation with the OPLS-AA force field reproduced correctly the optimized geometries and their energies evaluated by ab initio methods. As shown in Figure 4, the most stable conformation of [dema][TfOH] is with alkyl side chains in anti/anti conformation in the C–C–N$^+$–C–C atom sequence designated as **AA**. In Figure 4, **A** and **G** stand for anti and gauche conformation, and the + (plus) and − (minus) signs signify the direction of each dihedral angle. It should be noticed that all of the optimized stable conformations for diethylmethylammonium cation remain after forming IL [dema][TfOH]. Without any structural change of the diethylmethylammonium cation, trifluoromethanelsulfonate anion seems to be able to occupy the best location by balancing attractive electrostatic energy and repulsive van der Waals energy as it anion takes only one conformation. Therefore, relative conformational energy differences found in diethylmethylammonium cation are reflected in parallel to the relative conformational energies ΔE of [dema][TfOH]. The relative conformational energies for diethylmethylammonium cation (ΔE_{cation}) conformers are 0.0 (**AA**), 0.33 (**G−A**), 2.84 (**G+A**), 3.09 (**G+G−**), and 16.9 (**G+G+**) kJ mol^{-1}, respectively. On the basis of the optimized most stable conformation and electronic charge on each atom of [dema][TfOH], MD simulation has been carried out by using TINKER[18] with OPLS-AA force field. The MD simulations were carried out in the *NPT* ensemble where 216 cation–anion ion pairs are put in unit cell and *P* (pressure) is set to be 1 atom at three different temperatures ($T = 273$ K (0 °C), 303 K (30 °C), and 393 K (120 °C)) with a time step (Δt) 1 fs elapsing 800 ps (total simulation time) after the *NPT* ensemble reaches equilibrium with regard to energy and density. It took at least 800 ps for the energy and density of the system to converge. Integration was performed with a Verlet[19] method. To take into account the long-range Coulomb force appropriately, Ewald's[20] method was adopted. Temperature and pressure were controlled by using a method of Nosé[21] and Hoover.[22] Calculated density from the *NPT* ensemble MD simulation at 303 K for the equilibrium bulk phase structure of [dema][TfOH] was 1.28 g cm^{-3}, which shows good agreement with the experimental value (1.29 g cm^{-3}) indicating high reliability of this MD simulation. Radial distribution function plot was derived from the MD simulated structures at times ranging $t = 770$–800 ps after convergence of the energy and density. As a parameter for the horizontal axis in the radial distribution function plot to search for structural features, a distance (R_{CH_3}) between terminal methyl carbon atoms in the diethylmethylammonium cation was adopted. In Figure 5, radial distribution function plot at three different temperatures ($T = 0$, 30, and 120 °C) with regard to the distance between two terminal methyl carbons (R_{CH_3}) is shown. If alkyl side chains in [dema][TfOH] take **AA** conformation, averaged R_{CH_3} evaluated from equilibrium structure by MD simulation is around 5 Å. In the case that alkyl side chains take **AG** (**AG+** or **AG−**) conformation, averaged R_{CH_3} shortens to 4.5 Å. From the radial distribution plots when $T = 0$ °C (273 K) and 30 °C (303 K), the most dominant conformation is assumed to be **AA** because the highest radial distribution peak is located in the $R_{\text{CH}_3} = 5$ Å region, and **AG** conformation also exists to some extent. The stable structure of [dema][TfOH] in the bulk phase can be viewed as being mainly composed of **AA** conformation from these radial distribution plots. To the contrary at $T = 120$ °C (393 K), the biggest radial

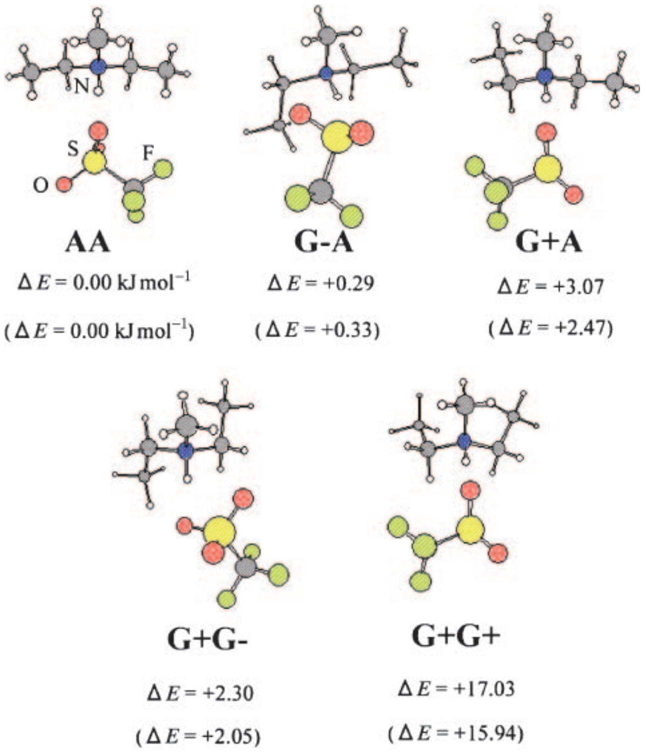

Figure 4. Stable conformations with their relative energies (ΔE: kJ mol^{-1}) obtained by exhaustive conformational search with HF/6-31+G* and OPLS-AA force field (in parentheses) calculations.

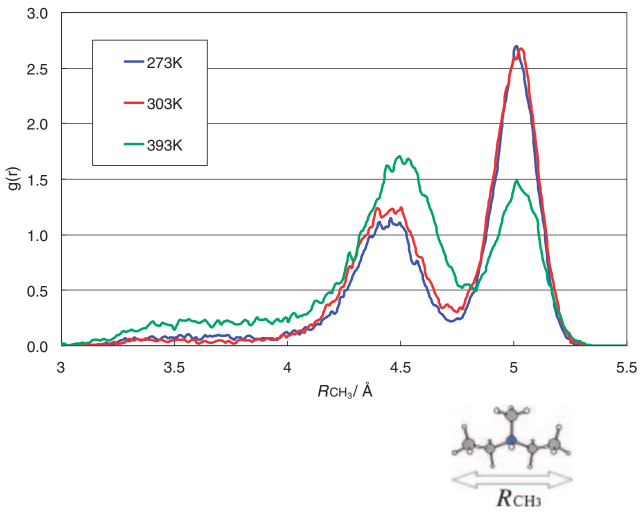

Figure 5. Radial distribution function plot against a distance between terminal methyl carbon atoms in the diethylmethylammonium cation (R_{CH_3}) at three different temperatures ($T = 273$, 303, and 393 K).

distribution peak is found at $R_{CH_3} = 4.5$ Å and a second big peak with almost the same peak height is located at $R_{CH_3} = 5$ Å indicating that hindered rotation along alkyl side chains takes place smoothly and conformational equilibrium changes occur. These calculated results are consistent with the ^{1}H NMR spectral changes observed by raising temperature from 30 to 120 °C as shown in Figure 1.

It is interesting to see the consistency between the MD simulated equilibrium structure of [dema][TfOH] in the bulk phase and experimental structures conceived from ^{1}H NMR and IR measurements. It is easy to clip a number of [dema][TfOH] molecules from the equilibrium structure in the unit cell after 800 ps MD simulation. A clipped ion pair structure composed of **AA** [demaH$^+$] cation conformer was just like one shown in Figure 4. The most plausible equilibrium structure may be one where alkyl side chain takes **AA** conformation considering the radial distribution plot shown in Figure 5. Therefore, a plausible equilibrium structure of the clipped [dema][TfOH] aggregate at 30 °C is represented in Figure 6. Configuration of the unisochronous methylene protons relative to N–H proton was investigated on this clipped structure. The dihedral angle (ω) of H–N–C–H$_{trans}$ and H–N–C–H$_{cis}$ atom sequences are ω(H–N–C–H$_{trans}$) = 179.2° and ω(H–N–C–H$_{trans}$) = 63.2°, respectively. These obtained dihedral angle values are consistent with the experimentally derived vicinal $^3J_{H\text{–}H}$ coupling constants between N–H proton and unisochronous methylene protons. Geometric parameters concerning the conductive N–H proton are shown in Figure 6. The N–H bond distance is 1.04 Å, and the distance between the N–H proton and its nearest neighboring oxygen atom in trifluoromethanesulfonate anion is 1.58 Å. Judging from an N–H bond distance estimated from the MD simulation of [dema][TfOH] at 30 °C, the conductive N–H proton is assumed to be bonded tightly to nitrogen. As conductive N–H protons are mobile, we should look for another appropriate theoretical method to monitor the N–H proton according to temperature change. At the present stage using classical molecular mechanics force fields such as MM3 and OPLS-AA, MD simulation cannot deal with bond breaking or bond formation properly. Therefore, a more simplified model that can handle mobile phenomena appropriately by using a quantum mechanical (QM) methods has been adopted on the basis of the MD simulated equilibrium structure.

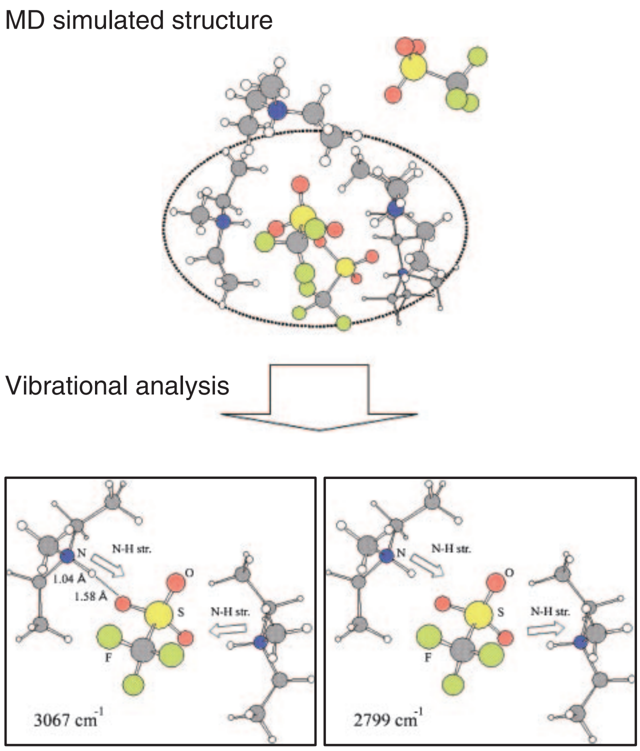

Figure 6. A clipped structure of [dema][TfOH] from the equilibrium MD simulations and the assignment of N–H stretching vibration.

For a clipped [dema][TfOH] structure evaluated from MD simulation, we can calculate NMR (chemical shifts) and IR (frequencies) spectra theoretically. Theoretically estimated NMR and/or IR spectra may be a criterion for assessing the validity of the MD simulation. By using a clipped [dema][TfOH] geometry as an input data for the ab initio calculation, ^{1}H NMR chemical shifts[23] (using GIAO) and normal vibrational analysis have been carried out by Gaussian 03. However, calculated ^{1}H NMR chemical shifts and IR spectral frequencies for a single ion pair were not consistent with the experimental spectra. Not only the absolute values of chemical shifts and frequencies, the relative order of signal positions on the NMR and IR spectra did not correspond to those obtained from experiments. This discrepancy between the experiments and theoretical calculations is supposed to come from ignoring inter/intra molecular interaction between ionic species composed of [dema][TfOH]. Perturbational ionic effects by neighboring IL molecules should be taken into account properly when we evaluate the NMR chemical shifts and vibrational frequencies. Therefore, we have introduced a simple model mimic to the bulk phase structure of [dema][TfOH] consisting of [demaH$^+$] cation–[TfO$^-$] anion–[demaH$^+$] cation for theoretical IR spectrum estimation. Geometry of the [demaH$^+$]–[TfO$^-$]–[demaH$^+$] unit was clipped from the MD simulated equilibrium structure. For the purpose of ^{1}H NMR calculations, another model consisting of [TfO$^-$]–[demaH$^+$]–[TfO$^-$] was adopted. Then, ^{1}H NMR chemical shifts and IR spectrum frequencies were estimated by using the geometry of the respective model stated above for IR and NMR spectra calculations. The optimized structures and their related geometric parameters in the models of [demaH$^+$]–[TfO$^-$]–[demaH$^+$] (IR spectrum evaluation) and [TfO$^-$]–[demaH$^+$]–[TfO$^-$] (^{1}H NMR spectrum evaluation) are shown in Supporting Information.

With regard to the IR spectrum, N–H stretching and its related out of plane bending vibrations could be evaluated well for the [demaH$^+$]–[TfO$^-$]–[demaH$^+$] model. Thus, two IR N–H stretching vibrational modes which were expected to be found at 3069 and 2799 cm^{-1} experimentally could be evaluated correctly at 3000 and 2963 cm^{-1}, respectively, when 6-31+G* calculation was applied with a scaling factor 0.90. The higher frequency peak at 3069 cm^{-1} could be assigned as concerted vibrations with two N–H bonds closely located vibrating antisymmetrically (antisymmetric mode), and the lower peak at 2799 cm^{-1} could be identified as symmetrically vibrating modes. Two different N–H vibrational modes may be expected to occur by dealing with cluster-like local structure (as shown in Figure 6) formed by firm ionic interactions of IL's. When we consider only one [dema][TfOH] ion pair for IR calculation, two N–H stretching vibrational peaks cannot be predicted to occur theoretically. Concerning the ^{1}H NMR spectrum, fair agreement of the chemical shifts between experiments and theoretical calculations was obtained by using a [TfO$^-$]–[demaH$^+$]–[TfO$^-$] model. Theoretically evaluated chemical shifts (δ) for the ^{1}H's shown in Table 1 (except for partially rotation hindered protons 2 and 3) were 6.63 (NH), 2.43 (proton 4), and 1.01 (proton 5) ppm, respectively. These spectral agreements between experiments and theoretical evaluation supports validity of the MD simulation of [dema][TfOH]. A point to be mentioned is characteristic features found in IR and NMR spectra of proton-conductive IL [dema][TfOH] originate in the bulk-phase structure where cluster-like local structure can be formed by ionic interactions among [demaH$^+$] and [TfO$^-$] ionic species. Experimental IR and ^{1}H NMR spectra cannot be reproduced by simple ab initio calculations on a single [dema][TfOH] ion pair.

Microscopic study with regard to the intra/intermolecular interaction between cationic and anionic species composed of [dema][TfOH] is possible by using the equilibrium bulk phase structure. Stabilization energy (ΔE_{IL}) after forming IL can be evaluated from eq 3.

$$\Delta E_{\mathrm{IL}} = E_{\mathrm{ion\ pair}} - (E_{\mathrm{cation}} + E_{\mathrm{anion}}) \tag{3}$$

The calculated stabilization energy (ΔE_{IL}) for [dema][TfOH] with HF/6-31+G* was -379 kJ mol^{-1} and has almost identical values found for IL molecules[24] composed of imidazolium, pyridinium, or quarternary alkylammonium cations and various anions such as $CF_3SO_3^-$ (trifluoromethanesulfonate), CF_3COO^-, BF_4^-, $(CF_3SO_2)_2N^-$, and PF_6^-. By varying the length of the alkyl side chains of ammonium cations, no remarkable variation of the ΔE_{IL} for [N$_{xyz}$][TfOH] IL's (Where, x, y, and z stand for the number of carbon composing alkyl side chain.) could be found, thus they have almost identical values around -376 kJ mol^{-1} in HF/6-31+G* level calculations. Interaction energies (ΔE_{IL}) found for IL molecules are smaller than those for inorganic ionic salts such as LiCl and NaCl, which show -460 and -543 kJ mol^{-1} respectively. This intermediate interaction energy for the IL may be an origin of specific structures and electrochemical properties. Ammonium N–H proton is a key chemical species to exert proton conductivity whose dynamic behavior has not be clarified as yet. From the ^{1}H NMR and IR experiments of [dema][TfOH], the lifetime of N–H proton showing proton conductivity ($\sigma = 43$ mS cm^{-1} at 150 °C) seems to range from 10^{-3} to 10^{-14} s at ambient temperature in this chemical environment. By raising temperature, enhancing mobility of N–H proton could be rationalized from ^{1}H NMR spectral changes as shown in Figure 1. More precise kinetic information of the N–H proton may be clarified from IR experiments at elevated temperature where two N–H stretching bands observed at ambient temperature are expected to merge by fast intermolecular exchange. We now set about this experiment to reveal a mechanism of proton conduction in the bulk phase of IL's.

Experimental

Preparation of the IL's. Proton-conductive IL [dema][TfOH] and related *tert*-alkylammonium trifluoromethanesulfonate [N$_{xyz}$]-[TfOH] were prepared by mixing amine and acid with strictly maintained equimolar ratio according to the method reported in electronic supplementary information of the previous paper.[7] All of the alkylamines and trifluoromethanesulfonic acid in this study were reagent grade and were used as received. Deuterated IL ([dema][TfOD]) was prepared by mixing [dema][TfOH] with D_2O in a 1:5 molar ratio at ambient temperature for one week. For complete deuteration, the obtained deuterated sample was evacuated to remove remaining H_2O and D_2O completely at 150 °C. Then, the deuteration process was repeated again for another week to accomplish complete deuteration.

Spectral Measurements. ^{1}H NMR spectra were recorded on a JEOL JNM-AL400 spectrometer with temperature controlling equipment. Neat IL samples were put into coaxial double sample tubes (Shigemi SC-002; inner diameter 3 mm, outer diameter 4.2 mm), and the chemical shift values were measured in reference to the external tetramethylsilane ($Si(CH_3)_4$) signal dissolved in 0.05 wt % DMSO-d_6 solution kept in the inner NMR tube. NMR probe temperature was controlled cautiously to rise in 5 °C intervals from 30 to 120 °C.

IR spectra of neat [dema][TfOH] and [dema][TfOD] samples as a liquid film put between CaF_2 window-plates were recorded on a Perkin-Elmer Spectrum 2000 at 30 °C under dry nitrogen atmosphere.

Theoretical Calculations. All theoretical calculations based on QM method (ab initio calculations) or MM method with MM3 and OPLS-AA force fields were carried out on Linux-OS PC's. Gaussian 03[17] installed on a Linux-OS PC with Xeon processor was used for ab initio calculations. The MD simulations were performed by the TINKER[18] program with OPLS-AA force field under the condition of *NPT* ensemble where 216 IL ion pairs were placed in the unit cell with a 1 fs time step (Δt) elapsing 800 ps after convergence of the density and the energy. Initial geometry for MD simulation was derived from the HF/6-31+G* optimized global minimum structure of [dema][TfOH], and electronic charges on each atom obtained by CHelpG schema were used for MD calculations.

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Supporting Information

The HF/6-31+G* optimized structures for the [demaH$^+$]–[TfO$^-$]–[demaH$^+$] model (IR spectrum simulation) and the [TfO$^-$]–[demaH$^+$]–[TfO$^-$] model (^{1}H NMR spectrum simulation) based on the clipped geometries from MD simulations shown in the Supporting Information which is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/bcsj/.

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