Cite this: Phys. Chem. Chem. Phys., 2011, 13, 13427-13432

Proton transport properties in an ionic liquid having a hydroxyl group

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Received 2nd May 2011, Accepted 2nd June 2011 DOI: 10.1039/c1cp21387c

An ionic liquid having a hydroxyl group, choline bis(trifluoromethylsulfonyl)amide $([N_{111(2OH)}][N(Tf)_2])$, was synthesized to investigate the effect of hydroxyl groups on the proton transport. 1,1,1-Trifluoro-*N*-(trifluoromethylsulfonyl)methanesulfoneamide $(HN(Tf)_2)$ as a proton source was mixed with the choline derivative at various molar ratios. Their thermal properties, viscosities, and ionic conductivities were investigated. $[N_{111(2OH)}][N(Tf)_2]$ showed a melting point at 27 °C, and its thermal stability was higher than 400 °C. The viscosity of $[N_{111(2OH)}][N(Tf)_2]/HN(Tf)_2$ mixtures increased as the acid molar fraction increased. The ionic conductivity of $[N_{111(2OH)}][N(Tf)_2]$ was 2.1×10^{-3} S cm⁻¹ at 25 °C; the ionic conductivity monotonously decreased as the acid molar fraction increased. There was a clear correlation between the ionic conductivity and the viscosity for the mixtures of the choline derivative and the acid. PFG-NMR measurements were carried out to investigate the diffusion behavior of protons. Although the acid and the hydroxyl group were indistinguishable by ¹H NMR, the self-diffusion coefficient of the ¹H of the hydroxyl group and the acid was larger than those of other ¹H nuclei. This difference suggests that a fast intermolecular proton transfer exists between the hydroxyl group and the acid.

Introduction

Polymer electrolyte fuel cells (PEFCs) have attracted significant attention because of their high power generation efficiencies and low pollution levels. Most of the PEFCs employ hydrated perfluoro-sulfonate ionomers, typically Nafion[®], and hydro-carbon ionomers as the polymer electrolyte membranes.^{1–3} Such materials impose water management and low temperature operation due to the use of water for the high proton conduction. Finding anhydrous highly proton-conducting polymer electrolytes has therefore become an important task for high temperature operations over 100 °C.^{4–6}

On the other hand, ionic liquids (ILs) are being considered as alternatives for conventional electrolyte materials. ILs offer unique properties such as low volatility, low flammability, and high ionic conductivity. Some ILs that show ionic conductivity values of over 10^{-2} S cm⁻¹ at room temperature have been reported.⁷ However, this value includes not only target ions such as protons but also other constituent ions. In order to achieve high proton conductivity in ILs, a variety of systems have been reported using Brønsted

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acid/base pairs,^{8–12} ILs having chemically active protons,^{13,14} and IL/acid mixtures.^{15–18} Recently, it was reported that hydroxyl groups were effective to transport protons in the IL matrix. Choline dihydrogen phosphate ([N_{111(2OH)}][dhp]) and 1-butyl-3-methylimidazolium dihydrogen phosphate ([C₄mim][dhp]) were synthesized as proton-conducting matrices. Although the ionic conductivity of [C₄mim][dhp] was 10^{-5} S cm⁻¹ at 90 °C, [N_{111(2OH)}][dhp] exhibited one order of magnitude higher conductivity than that of [C₄mim][dhp].¹⁹ It is thought that the ionic conductivity of [N_{111(2OH)}][dhp] arises from the transport of protons *via* phosphate anions and/or the hydroxyl groups of the choline cation.

In order to further study the proton transport properties in choline derivatives, we synthesized choline bis(trifluoromethylsulfonyl)amide ([N_{111(2OH)}][N(Tf)₂]) in this study, as shown in Fig. 1. Since N(Tf)₂-based ILs are generally hydrophobic and thermally stable up to 400 °C,^{20,21} [N_{111(2OH)}][N(Tf)₂] will be attractive for mid-temperature fuel cell applications. *N*,*N*,*N*-Trimethyl-*N*-propylammonium bis(trifluoromethylsulfonyl)amide ([N₁₁₁₃][N(Tf)₂]) that has a structure similar to that of the choline derivative except for the hydroxyl group was also used for comparison. We chose 1,1,1-trifluoro-*N*-(trifluoromethylsulfonyl)methanesulfoneamide (HN(Tf)₂) as an acid dopant to further improve the proton conductivity. The ILs were mixed with HN(Tf)₂ at various molar ratios, and thermal properties, ionic conductivities, and viscosities of their mixtures have been investigated.

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Fig. 1 Structures of [N_{111(2OH)}][N(Tf)₂], [N₁₁₁₃][N(Tf)₂], and HN(Tf)₂.

Experimental

Materials

Choline chloride (>98.0%) was purchased from Tokyo Chemical Industry Co., Ltd. Lithium bis(trifluoromethylsulfonyl)amide (LiN(Tf)₂) (>99.8%) and 1,1,1-trifluoro-*N*-(trifluoromethylsulfonyl)methanesulfoneamide (HN(Tf)₂) (>99.0%) were purchased from Morita Chemical Industries Co. Ltd. These materials were used without further purification. *N*,*N*,*N*-Trimethyl-*N*-propylammonium bis(trifluoromethylsulfonyl)amide ([N₁₁₁₃][N(Tf)₂]) was donated by Kanto Chemical Co., Inc. and was dried *in vacuo* at 80 °C for 24 h before use. The water content of each IL was less than 400 ppm as an average of three readings.

Synthesis of choline bis(trifluoromethylsulfonyl)amide ([N_{111(20H)}][N(Tf)₂])

[N111(20H)][N(Tf)2] was synthesized according to the procedure reported in the literature.²² Choline chloride (33.9 g, 0.243 mol) was dissolved in distilled water (25 ml), and an aqueous solution of slightly excess LiN(Tf)₂ (85.5 g, 0.298 mol) in 25 ml of water was added to the solution. The mixed solution was stirred at room temperature for several hours. The ionic liquid phase was washed several times with water until no precipitation was observed by means of the silver nitrate test. The ionic liquid was dried in vacuo at 120 °C overnight to provide $[N_{111(2OH)}][N(Tf)_2]$ as a colorless viscous liquid (yield = 78.6 g, 84%). [N_{111(2OH)}][N(Tf)₂] later solidified from a molten state. ¹H NMR (300 MHz, DMSO- d_6 , Me₄Si): δ 5.27 (t, 1H), 3.83 (m, 2H), 3.39 (m, 2H), 3.10 (s, 9H). MS (FAB): m/z 104.1 $[N_{111(20H)}]^+$; calcd. 104.1, m/z 280.0 $[N(Tf)_2]^-$; calcd 280.1. Anal. calcd for C₇H₁₄N₂O₅F₆S₂: C, 21.88; H, 3.67; N, 7.29%; found: C, 21.64; H, 3.55; N, 7.17%.

Thermal properties

Differential scanning calorimetry (DSC) was carried out with a Seiko Instruments differential scanning calorimeter DSC7020 under a nitrogen flow. DSC traces were recorded from -100 °C to 100 °C at a heating/cooling rate of 10 °C min⁻¹. Thermogravimetric analysis was conducted on a Seiko Instruments

TG-DTA200 at a heating rate of 10 $^{\circ}$ C min⁻¹ under a nitrogen flow.

Viscosity

Density measurements were conducted using an Anton Paar DMA 38 density meter. Viscosity measurements were conducted using an Anton Paar AMVn automated micro viscometer.

Ionic conductivity

Ionic conductivity measurements were carried out in a designed cell made from two platinum electrodes. Cell constants were calculated with 0.1 M KCl aqueous solution. Ionic conductivity was obtained by measuring the complex impedance of the cell between 5 Hz and 5 MHz using a Solartron 1260.

¹H NMR chemical shift

NMR measurements were conducted using a NMR spectrometer (JEOL GX-270) at 21 °C. ¹H chemical shifts were determined by using a double tube (SC-002, Shigemi Co. Ltd.; inner tube, 3 mm i.d., 4.1 mm o.d.; outer tube, 4.2 mm i.d., 4.965 mm o.d.) with the sample in the inner tube and DMSO- d_6 containing TMS as standard in the outer tube.

Self-diffusion coefficient

The diffusion coefficients of ILs were evaluated by a NMR spectrometer JEOL ECA-500 using a pulsed field gradient (PFG) method for ¹H nuclei. Within a pulse sequence of bipolar pulsed pairs-stimulated echo,²³ the pulse duration (δ) was set to 4 ms and the diffusion time (Δ) was 10 ms. The maximum amplitude of the pulsed field gradient (*G*) was 13.3 T m⁻¹. The diffusion coefficient, *D*, was estimated from signal reduction against the magnitude of *G*, using the following equation:

$$\ln(I/I_0) = -(\gamma G\delta)^2 (2/\pi)^2 4(\varDelta - \tau/2 - \delta/8)D$$
(1)

where I and I_0 correspond to the signal intensity at each G and no G, respectively, τ equals the sum of δ and gradient recovery on the two sides of the field gradient pulse (0.2 ms for this experiment), and γ is the gyromagnetic ratio.

Results and discussion

 $[N_{111(2OH)}][N(Tf)_2]$ is a white solid at room temperature and is water soluble up to about 0.2 mol 1^{-1} . This solubility was much higher than those of typical N(Tf)₂-based ILs. Such a tendency was also observed for a dabco-based IL having a tertiary amine, which can interact with water molecules.²⁴ This somewhat hydrophilic behaviour most likely results from the hydrogen bonding interaction between the hydroxyl group and the water molecule. Nockemann et al. reported that $[N_{111(20H)}][N(Tf)_2]$ formed one phase with water at temperatures above 72 °C.²² They also studied the temperature-dependent miscibility of [N_{111(2OH)}][N(Tf)₂] with water by means of ¹H NMR. The [N_{111(2OH)}][N(Tf)₂]/water mixtures showed the hydroxyl proton of the [N_{111(2OH)}] cation in the ¹H NMR spectrum at room temperature. The chemical shift of the hydroxyl proton completely disappeared at 100 °C, indicating that the protons undergo a fast exchange between the hydroxyl



Fig. 2 DSC traces of [N_{111(2OH)}][N(Tf)₂] and [N₁₁₁₃][N(Tf)₂].

proton of the $[N_{111(2OH)}]$ cation and water on the NMR time scale. This also suggested that a hydrogen bond was formed between the hydroxyl proton and water molecules. These results were consistent with our observations.

The melting points of [N_{111(2OH)}][N(Tf)₂] and [N₁₁₁₃][N(Tf)₂] were 27 °C and 17 °C, respectively, as shown in Fig. 2. Although the melting points of these ILs were almost the same, the enthalpy of fusion showed a big difference because [N_{111(20H)}][N(Tf)₂] also showed a solid-solid phase transition at -1 °C. Since the final entropy of fusion (ΔS_f) for [N_{111(2OH)}][N(Tf)₂] was 15.1 J K⁻¹ mol⁻¹, which conformed to the Timmermans criterion ($\Delta S_{\rm f}$ < 20 J K⁻¹ mol⁻¹) for molecular plastic crystals,²⁵ [N_{111(2OH)}][N(Tf)₂] can be categorized as a new ionic plastic crystal. Further details of the plastic crystalline behaviour of [N111(2OH)][N(Tf)2] will be reported elsewhere. These ILs were thermally stable up to 400 °C, which were identical to the behaviour of other N(Tf)₂-based ILs (data not shown).^{20,21} The thermal decomposition of [N_{111(2OH)}][N(Tf)₂] started at 404 °C. The thermal stability of ILs depends on the nucleophilicity of the component ions, especially the anions.²¹ The nucleophilicity of hydroxyl groups attached on the cations did not significantly affect the thermal stability of the IL.

A given amount of HN(Tf)₂ was mixed with [N_{111(2OH)}][N(Tf)₂] or [N₁₁₁₃][N(Tf)₂] in an argon filled glovebox to prepare a series of acid-doped systems. The mixtures were stirred at 50 °C for 2 hours. Thermal analysis of the IL/HN(Tf)₂ mixtures was also carried out by DSC measurements. The melting points of [N111(20H)][N(Tf)2]/HN(Tf)2 mixtures decreased with increasing the HN(Tf)₂ content. While the mixture with 33 mol% of the HN(Tf)₂ content ($[N_{111(2OH)}][N(Tf)_2]/HN(Tf)_2$ (33)) showed a glass transition temperature (T_g) at -63 °C and a melting point (T_m) at -7 °C, $[N_{111(2OH)}][N(Tf)_2]/HN(Tf)_2$ (50) and [N_{111(2OH)}][N(Tf)₂]/HN(Tf)₂ (67) mixtures showed a $T_{\rm g}$ only at -72 °C and -68 °C, respectively. The thermal properties of [N₁₁₁₃][N(Tf)₂]/H[N(Tf)₂] mixtures showed a similar tendency. The $T_{\rm m}$ values decreased with the H[N(Tf)₂] content and disappeared when the H[N(Tf)₂] content reached 33 mol%. $[N_{1113}][N(Tf)_2]/H[N(Tf)_2]$ (50) mixtures showed a T_g only at -85 °C, which was slightly lower than that of the [N_{111(20H)}][N(Tf)₂]/HN(Tf)₂ (50) mixtures. This result would be based on a hydrogen-bonding interaction between the hydroxyl groups of $[N_{111(2OH)}]$ cation and the acid molecules.



Fig. 3 Arrhenius plots of ionic conductivities for $[N_{111(2OH)}][N(Tf)_2]$ and $[N_{111(2OH)}][N(Tf)_2]/HN(Tf)_2$ mixtures.



Fig. 4 Arrhenius plots of ionic conductivities for $[N_{1113}][N(Tf)_2]$ and $[N_{1113}][N(Tf)_2]/HN(Tf)_2$ mixtures.

Fig. 3 and 4 show Arrhenius plots of the ionic conductivity for the ILs and the IL/HN(Tf)2 mixtures. The ionic conductivity of $[N_{111(2OH)}][N(Tf)_2]$ was 2.1 × 10⁻³ S cm⁻¹ at 25 °C, which was equal to those of N-(n-butyl)-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ([C₄mpyrr][N(Tf)₂]),²⁶ N,Ndiethyl-N-methyl-N-(n-propyl)-ammonium bis(trifluoromethylsulfonyl)amide ([N1223][N(Tf)2]), and N,N,N-triethyl-N-(2-methoxyethyl)ammonium bis(trifluoromethylsulfonyl)amide ([N222(102)]- $[N(Tf)_2]$;²⁷ and the ionic conductivity achieved $1.2 \times 10^{-2} \text{ S cm}^{-1}$ at 80 °C. The ionic conductivity of the [N_{111(2OH)}][N(Tf)₂]/ HN(Tf)₂ mixtures monotonously decreased with increasing the acid content. On the other hand, [N₁₁₁₃][N(Tf)₂] showed the ionic conductivity of 3.3×10^{-3} S cm⁻¹ at 25 °C, which was consistent with the value reported by Matsumoto et al.²⁸ Although [N₁₁₁₃][N(Tf)₂] showed higher ionic conductivity than those of $[N_{111(2OH)}][N(Tf)_2]$, the ionic conductivity of [N₁₁₁₃][N(Tf)₂]/HN(Tf)₂ mixtures also decreased by adding $HN(Tf)_2$ (Fig. 4). $[N_{111(2OH)}][N(Tf)_2]/HN(Tf)_2$ mixtures showed lower ionic conductivity than [N₁₁₁₃][N(Tf)₂] mixtures in all mixing ratios. This would result from the higher viscosity through the hydrogen-bonding interaction between the hydroxyl groups and the acid molecules.

Fig. 5 shows ionic conductivities at 25 °C (a) and viscosities at 30 °C (b) of the IL/HN(Tf)₂ mixtures as a function of the HN(Tf)₂ content. The viscosities of $[N_{111(2OH)}][N(Tf)_2]$ and



Fig. 5 Ionic conductivities at 25 °C (a) and viscosities at 30 °C (b) of $[N_{111(20H)}][N(Tf)_2]$ (closed square) and $[N_{1113}][N(Tf)_2]$ (closed circle) as a function of the acid content.

 $[N_{1113}][N(Tf)_2]$ were 94 mPa s and 61 mPa s at 30 °C, respectively. While $[N_{111(2OH)}][N(Tf)_2]$ showed higher viscosity than $[N_{1113}][N(Tf)_2]$, $[N_{111(2OH)}][N(Tf)_2]$ had lower conductivity than $[N_{1113}][N(Tf)_2]$.

Both mixtures showed almost the same tendency for the $HN(Tf)_2$ content dependence of the ionic conductivity. As mentioned above, the ionic conductivity gradually decreased with increasing the $HN(Tf)_2$ content. In contrast, the viscosities of the ILs/HN(Tf)₂ mixtures showed a totally different tendency. The viscosity of $[N_{111(2OH)}][N(Tf)_2]/HN(Tf)_2$ mixtures increased with increasing the HN(Tf)₂ content, whereas $[N_{1113}][N(Tf)_2]/HN(Tf)_2$ mixtures showed almost the same value regardless of the HN(Tf)₂ content. These results also suggest that there is a hydrogen-bonding interaction between the hydroxyl group of the $[N_{111(2OH)}]$ cation and the acid.

The ionic conductivity can be described by the following equation:

$$\sigma_i = n \, e \, \mu \tag{2}$$

where *n* is the number of carrier ions, *e* is the elementary charge quantity, and μ is the carrier ion mobility. In this equation, μ is affected by the viscosity of the electrolyte solution. The viscosity of $[N_{111(2OH)}][N(Tf)_2]/HN(Tf)_2$ mixtures reached 293 mPa s when the HN(Tf)₂ content was 67 mol%. $[N_{1113}][N(Tf)_2]/HN(Tf)_2$ mixtures showed almost the same viscosity of *ca*. 60 mPa s in all HN(Tf)₂ mixing ratios. Although the ionic conductivity of both systems decreased with the HN(Tf)₂ content, each decrement of the ionic conductivity would result from a different cause. While the increase in viscosity for $[N_{111(2OH)}][N(Tf)_2]$ mixtures induced the decrease in ionic conductivity, the viscosity of $[N_{1113}][N(Tf)_2]/$ HN(Tf)₂ mixtures did not change in the range of the acid content between 0 and 67 mol%. In the case of $[N_{1113}][N(Tf)_2]$, assuming the carrier ion mobility is the same, the number of carrier ions in the mixtures will decrease with increasing the HN(Tf)₂ content according to eqn (2). HN(Tf)₂ will exist as molecular HN(Tf)₂ in the mixture. Thus, the addition of HN(Tf)₂ cannot contribute to the ionic conduction.

¹H NMR measurements were carried out to gain more insight into the interaction between the ILs and HN(Tf)₂. Fig. 6 shows ¹H NMR spectra of $[N_{111(20H)}][N(Tf)_2]$ and [N_{111(2OH)}][N(Tf)₂]/HN(Tf)₂ mixtures obtained by using a double tube. The use of a double tube prevented mixing of a sample and a deuterium solvent. [N_{111(2OH)}][N(Tf)₂] showed four signals between 3 and 4.5 ppm. A sharp ¹H signal for the hydroxyl group of the [N_{111(2OH)}] cation was observed at 3.37 ppm. When the 10 mol% HN(Tf)₂ was added in the IL, a new ¹H signal appeared at 5.05 ppm, and the NMR spectrum still showed four signals. The ¹H signal at 5.05 ppm was assigned to the protons of the hydroxyl group and HN(Tf)₂. Since the proton exchange reaction between the HN(Tf)₂ and the hydroxyl group was too fast to separate those ¹H signals, the two species could not be distinguished by NMR. The ¹H signal at 3.37 ppm of the hydroxyl group shifted to 5.05 ppm. As the HN(Tf)₂ content in [N_{111(20H)}][N(Tf)₂]/HN(Tf)₂ mixtures increased, the ¹H chemical shifts of the hydroxyl group and the acid were further directed to a lower magnetic field. When the HN(Tf)₂ content was 80 mol%, the ¹H chemical shift reached 9.27 ppm without any shifts of other ¹H signals of the $[N_{111(2OH)}]$ cation observed at 3.12, 3.47, and 4.13. Such a shift should be based on the hydrogen-bonding interaction between the hydroxyl group and HN(Tf)₂. The hydroxyl group acted as a proton acceptor. Furthermore, the shift value



Fig. 6 ¹H NMR spectra of $[N_{111(2OH)}][N(Tf)_2]$ and $[N_{111(2OH)}][N(Tf)_2]/HN(Tf)_2$ mixtures obtained by using a double tube. Arrows indicate the ¹H signal for the hydroxyl group of $[N_{111(2OH)}]$ cation and the acid.



Fig. 7 ¹H NMR chemical shifts of $[N_{111(2OH)}][N(Tf)_2]/HN(Tf)_2$ (closed square) and $[N_{1113}][N(Tf)_2]/HN(Tf)_2$ (closed circle) mixtures as a function of the acid content.

appears to be dependent on the number of hydrogen-bonding species in the mixture.

Fig. 7 shows the ¹H NMR chemical shifts of $[N_{111(20H)}]$ - $[N(Tf)_2]/HN(Tf)_2$ mixtures and $[N_{1113}][N(Tf)_2]/HN(Tf)_2$ mixtures as a function of HN(Tf)₂ content. In the case of $[N_{1113}][N(Tf)_2]/HN(Tf)_2$ mixtures, the ¹H signal of the HN(Tf)₂ was observed at around 11.0 ppm in the range of the HN(Tf)₂ content from 10 to 50 mol% and shifted to a higher magnetic field in the HN(Tf)₂ excess compositions. These results indicate that the proton of HN(Tf)₂ molecules had less electron density in $[N_{1113}][N(Tf)_2]$ excess compositions. In spite of the weak interaction between the IL and HN(Tf)₂, the results of ¹H NMR chemical shifts indicated that the proton of HN(Tf)₂ had higher acidity than those of HN(Tf)₂ molecules in HN(Tf)₂ excess compositions. The dissociation state of the acid in the IL is still unclear.

To investigate proton transport properties in $[N_{111(2OH)}]$ - $[N(Tf)_2]/HN(Tf)_2$ mixtures, we measured the self-diffusion coefficients of each proton by means of the PFG-NMR method. This method is quite useful to discuss each component ion in ILs.^{8a,18b,29–31} Table 1 summarizes the self-diffusion coefficients of each proton for $[N_{111(2OH)}][N(Tf)_2]$ and $[N_{111(2OH)}][N(Tf)_2]/HN(Tf)_2$ (33) mixtures at 40 °C. The values for $[N_{111(2OH)}][N(Tf)_2]$ determined in this study were *ca*. 6.0×10^{-11} m² s⁻¹ at 40 °C and were in agreement with the values for other $[N(Tf)_2]$ -based ILs reported elsewhere.^{29–31} The self-diffusion coefficients of the protons of $[N_{111(2OH)}][N(Tf)_2]$ were larger than those of the mixtures. This difference confirmed that the decrease in ionic conductivity of $[N_{111(2OH)}][N(Tf)_2]/HN(Tf)_2$ mixtures was induced by the decrease in carrier ion mobility, μ , as mentioned above. Interestingly, the self-diffusion coefficient

Table 1 Self-diffusion coefficients for $[N_{111(2OH)}][N(Tf)_2]$ and $[N_{111(2OH)}][N(Tf)_2]/HN(Tf)_2$ mixtures at 40 $^\circ C$

| | $D_{(x)}^{a}/10^{-11} \text{ m}^2 \text{ s}^{-1}$ | | | |
|----------------------------------|---|--------------|--------------|--------------|
| Acid content/mol% | <i>(a)</i> | (b) | (<i>c</i>) | (<i>d</i>) |
| 0 | 5.9 | 6.4 | 5.9 | 6.2 |
| 33 | 3.8 | 3.8 | 3.8 | 4.2 |
| a D $_{\sim}$ denotes the s | self-diffusion | coefficients | of each | proton for |

 $[N_{111(2OH)}][N(Tf)_2]$ and $HN(Tf)_2$, as shown in Fig. 1.



Fig. 8 Arrhenius plots of self-diffusion coefficients of 1 H nuclei for $[N_{111(20H)}][HN(Tf_{2}]/HN(Tf_{2})]$ (33 mol%).

of the protons of the hydroxyl group and HN(Tf)₂ ($D_{(d)}$) was the largest in the mixtures. Since the ¹H signals of the hydroxyl group and HN(Tf)₂ cannot be distinguished by NMR, $D_{(d)}$ values seem to be an average self-diffusion coefficient of the two species. Fig. 8 shows the self-diffusion coefficients of each proton of [N_{111(2OH)}][N(Tf)₂]/HN(Tf)₂ (33) mixtures as a function of temperature. $D_{(d)}$ values were larger than the diffusion coefficients of other ¹H nuclei at all temperatures measured in this study. On the other hand, $D_{(a)}$, $D_{(b)}$, and $D_{(c)}$ showed identical values. These protons are not exchanged with any components but are transported as [N_{111(2OH)}] cations.^{8a} These results indicated the existence of a fast intermolecular proton transfer between the hydroxyl group and HN(Tf)₂. Therefore, the proton conduction would arise from the addition of HN(Tf)₂.

Conclusions

In order to study the effect of hydroxyl groups on the proton transport properties of ILs, we prepared [N_{111(20H)}][N(Tf)₂], [N₁₁₁₃][N(Tf)₂], and their HN(Tf)₂ mixtures. HN(Tf)₂ as a proton source was mixed with the ILs at various molar ratios. Although the mixtures were homogeneous liquids at all mixing ratios, the interaction between [N_{111(2OH)}][N(Tf)₂] and $HN(Tf)_2$ would be stronger than those of $[N_{1113}][N(Tf)_2]/acid$ mixtures due to the presence of the hydroxyl group. The decrease in ionic conductivity of [N_{111(2OH)}][N(Tf)₂]/HN(Tf)₂ mixtures arose from the increase in viscosity with increasing the HN(Tf)₂ content. There was a clear correlation between the ionic conductivity and the viscosity for [N_{111(2OH)}][N(Tf)₂]/ HN(Tf)2 mixtures. Such behaviour was not observed for [N₁₁₁₃][N(Tf)₂]/HN(Tf)₂ mixtures. For this reason, the protons of HN(Tf)₂ and the hydroxyl group of the $[N_{111(2OH)}]$ cation in [N_{111(2OH)}][N(Tf)₂]/HN(Tf)₂ mixtures were indistinguishable by ¹H NMR. The hydroxyl group acted as a proton acceptor. The self-diffusion coefficients of the protons of the hydroxyl group and the acid were larger than those of other protons in the mixtures. This difference suggested the existence of a fast intermolecular proton transfer between the hydroxyl groups and the HN(Tf)₂ molecules.

Hydroxyl groups would be a good candidate for realizing a fast proton transport in IL matrices. In order to achieve high

proton conductivity, it is necessary to construct proton transport networks among hydroxyl groups by optimizing the number of hydroxyl groups, alkyl chain lengths, *etc.* ILs having hydroxyl groups are attractive as anhydrous proton transport electrolytes with high operational temperatures.

Acknowledgements

This work was financially supported by the New Energy and Industrial Technology Development Organization (NEDO).

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