Water content and related physical properties of aliphatic quaternary ammonium imide-type ionic liquid containing metal ions

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Abstract

The ionic liquid, trimethyl-n-hexylammonium bis((trifluoromethyl)sulfonyl)amide (TMHA–Tf$_2$N), has a wide electrochemical window of more than 5 V and is considered to be hydrophobic because of two –CF$_3$ groups in its Tf$_2$N$^-$ anion. However, a small amount of water remains in the ionic liquid even after dehydration in vacuo, which causes some problems in metal electrodeposition when using the ionic liquid as a solvent. We measured the water content of the ionic liquids, TMHA–Tf$_2$N containing M(Tf$_2$N)$_n$ (M = H, Li, Mg, Ni, Cu, Zn, La, and Dy; n = 1, 2, or 3), as well as their kinematic viscosity and electrical conductivity in the temperature range of 25–130°C. Furthermore, differential scanning calorimetry was performed for these ionic liquids to find their glass transition temperature, crystallization temperature, and melting temperature. The water content of TMHA–Tf$_2$N containing M(Tf$_2$N)$_n$ salts decreased with an increase in temperature. At the same time, the kinematic viscosity decreased and the electrical conductivity increased. By measuring the optical absorption spectrum, it was found that the metal ions in TMHA–Tf$_2$N were hydrated. The addition of M(Tf$_2$N)$_n$ to TMHA–Tf$_2$N increased the water content at a constant temperature, which resulted in slight increases in the kinematic viscosity and decrease in the electrical conductivity. A Walden-like plot of the electrical conductivities against the kinematic viscosities, measured over various temperatures and water contents, gave a single straight line.

1. Introduction

Due to their unique physical and chemical properties, such as less volatility, nonflammability, low hygroscopicity, and availability at mild temperatures, room temperature ionic liquids containing fluoro-anions are expected to act as new electrochemical media, e.g. for batteries [1,2], capacitors [3–5], and electrochemical solar cells [6,7]. Since the discovery of the moisture stable ionic liquid, 1-ethyl-3-methylimidazolium tetrafluoroborate in 1992 [8], many ionic liquids have been synthesized by combining alkylimidazolium cations and inorganic or organic fluoro-anions. Recently, the number of reports on alkylimidazolium type ionic liquids combined with the highly stable bis((trifluoromethyl)sulfonyl)amide (or “imide”) anion (Tf$_2$N$^-$) [9–11] have been increasing.

On the other hand, a new series of ionic liquids have been prepared that consist of aliphatic quaternary ammonium cations and imide-type anions [12–14], and have an electrochemical window larger than 5 V [15]. Such a wide electrochemical window suggests that ammonium imide-type ionic liquids are potential media for the electrodeposition of less-noble metals that cannot be deposited from aqueous media. Therefore, we have been investigating the electrodeposition behavior of metals, e.g. Cu, Zn, Ni, and Mg, from one of the ammonium imide-type ionic liquids, trimethyl-n-hexylammonium bis((trifluoromethyl)sulfonyl) amide (TMHA–Tf$_2$N) [16,17], which is commonly considered to be hydrophobic due to two –CF$_3$ groups in the Tf$_2$N$^-$ anion. It was found, however, that some water (about 40 ppm) remained in this ionic liquid even after careful dehydration in vacuo for 2 h at 120°C using an oil-sealed rotary vacuum pump (ultimate pressure, 0.13 Pa).

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connected to a liquid nitrogen trap, and that this residual water affected the electrodeposits from the ionic liquid. Although such a slight “hygroscopicity” of hydrophobic ionic liquids has been well investigated for alkylimidazolium-type ionic liquids [18, 19], comprehensive data on the ammonium imide-type ionic liquids are not yet available. Additionally, little research on ionic liquids containing metal ions has been carried out.

Recently, we reported the water content of the ionic liquid TMHA–Tf2N with or without Mg2+ ions [20]; here, the water contents of the ionic liquid in the presence of other metal ions at 25 °C were also briefly presented. In the present study, we examined the temperature dependence of the water content of TMHA–Tf2N containing various metal ions, together with related physical and thermal properties, i.e. the kinematic viscosity, electrical conductivity, melting point, crystallization point, glass transition point, and the absorption spectrum of TMHA–Tf2N–M(Tf2N)n solution containing a small amount of water.

2. Experimental

The ionic liquid, TMHA–Tf2N, was prepared by the metathesis of trimethyl-n-hexylammonium bromide (TMHABr; Tokyo Kasei Kogyo Co., Ltd., 98%) with lithium bis((trifluoromethyl)sulfonyl)amide (LiTf2N; Fluka, 99%) as

\[ n-C_{6}H_{13}(CH_{3})_{3}NBr + LiN(SO_{2}CF_{3})_{2} \rightarrow n-C_{6}H_{13}(CH_{3})_{3}N^{+}N^{-}(SO_{2}CF_{3})_{2} + LiBr. \]  

(1)

The detailed procedure for this preparation was described in our previous paper [20] on water content and properties of TMHA–Tf2N. The resulting crude TMHA–Tf2N was then dried in vacuo for more than 2 h at 120 °C in a flask connected to a liquid nitrogen trap. The content of residual water was less than 50 ppm after drying, checked using a coulometric Karl–Fischer method (MKC-510 N; Kyoto Electronics Manufacturing Co., Ltd.). The TMHA–Tf2N prepared had a melting point of ~26 °C and was identified by elemental analysis at the Center for Organic Elemental Microanalysis of Kyoto University; the oxygen and sulfur contents could not be analyzed because TMHA–Tf2N contains fluorine. The dried TMHA–Tf2N was kept in an argon-filled glove box where the partial pressures of water vapor and oxygen gas were both less than 10⁻⁶ atm.

Metal salt, M(Tf2N)n, was prepared under ambient atmospheric conditions using the acid–base reaction of inorganic metal salts, e.g. metal oxide or carbonate with bis((trifluoromethyl)sulfonyl)amine (HTf2N; Fluka, 99%). The detailed reactions were described in our previous paper [20]. Five grams (0.018 mol) of HTf2N was dissolved in 20 cm³ of de-ionized water to obtain an aqueous HTf2N solution. An excess amount of the inorganic salts were added and suspended in the solution by stirring for 2 h at 70 °C, yielding an aqueous solution of M(Tf2N)n salt. After the elimination of unreacted inorganic salts by filtration, the water in the solution was distilled off to yield a solid hydrated salt M(Tf2N)n·xH2O. These salts were dried with dehydration in vacuo for over 72 h at 120 °C and then transferred into the glove box.

In order to prepare the TMHA–Tf2N–M(Tf2N)n solution, that is the ionic liquid TMHA–Tf2N containing M(Tf2N)n salt, the salt M(Tf2N)n was weighed in the glove box and dissolved into TMHA–Tf2N to yield a metal ion concentration of 1–500 mM (M; mol dm⁻³). About 5 cm³ of TMHA–Tf2N or TMHA–Tf2N–M(Tf2N)n solution in a cylindrical glass container (inner diameter 24 mm, height 55 mm) was allowed to stand in direct contact with the atmosphere outside the glove box. To keep the temperature of the ionic liquid constant, the glass container was placed in either (i) a double-walled glass heating jacket, through which warm water was circulated from a constant-temperature bath (25 < T < 60 °C), or (ii) a double-walled glass tube, the outer space of which was filled with ceramic fiber as a heat-insulating material, and placed on a hot plate with a thermo-regulator (60 < T < 130 °C). In each case, the ionic liquid was agitated with a magnetic stirring unit using a glass-coated spinbar. The temperature of the ionic liquid was measured with a thermocouple.

Fig. 1. Relationship between the saturated water content, W, and water vapor pressure, P, of the atmosphere: (a) pure ionic liquid TMHA–Tf2N measured at 55.6 °C, (b) TMHA–Tf2N containing 1 mM Al(Tf2N)n measured at 25.0 °C.
The water content of the ionic liquid was determined by the coulometric Karl–Fischer method. The performance of the Karl–Fischer titrator was checked using a standard solution (Riedel-de Haën) containing 100 ppm of water. The kinematic viscosity and electrical conductivity were measured using a vibration-type viscometer (VM-1G; CBC Materials Co., Ltd.) and a conventional conductivity measuring cell (CM-30G; DKK-TOA), respectively. The instruments were calibrated using a standard solution (NIPPON GREASE Co., Ltd.) with a kinematic viscosity of 20.11 mm² s⁻¹ at 20 °C and a 0.1 M KCl solution with an electrical conductivity of 1.28 S m⁻¹ at 25 °C. The melting point, crystallization point, and glass transition point were measured using differential scanning calorimetry (DSC-60; Shimadzu).

3. Results and discussion

When allowed to stand in an ambient atmosphere, dried pure TMHA–Tf₂N or TMHA–Tf₂N–M(Tf₂N)ₙ solution gradually absorbed water from the atmosphere, so the water content of the ionic liquid increased with time. After ample time had passed, however, the water content reached a constant value [20], which we termed a “saturated” water content in this report. Fig. 1 shows plots of the saturated water contents of (a) pure TMHA–Tf₂N at 55.6 °C and (b) TMHA–Tf₂N–1 mM Al(Tf₂N)₃ solution at 25.0 °C against various atmospheric water vapor pressures. A linear relationship between them, which passed through the origin, was obtained, suggesting that the dissolution of water molecules in the ionic liquid, TMHA–Tf₂N (with or without metal ions), obeys a rule similar to Henry’s law on the solubility of a gas in a liquid at a constant temperature.

Since the atmospheric water vapor pressure fluctuated during the experiment, the water content, \( W \), measured at the fluctuating water vapor pressure, \( P \), was converted to the water content, \( W_r \), at 1600 Pa of water vapor pressure, which corresponds to a relative humidity of 50% at 25 °C:

\[
W_r = 1600W \rho^{-1}. \tag{2}
\]

Fig. 2. Relationship between saturated water content, \( W_r \), and temperature of the ionic liquid TMHA–Tf₂N containing M(Tf₂N)ₙ (M = H, Li, Mg, Ni, Cu, Zn, La, and Dy; \( n = 1, 2, \) or 3) in contact with the atmosphere of a relative humidity of 50% at 25 °C, i.e., 1600 Pa of water vapor pressure.
Hereafter, the water content, $W_r$, will be used to discuss the effect of temperature on water content.

Fig. 2 shows the relationships between the water content $W_r$ and the temperature of pure TMHA–Tf$_2$N and various TMHA–Tf$_2$N–M(Tf$_2$N)$_n$ solutions, where M includes H, Li, Mg, Ni, Cu, Zn, La, and Dy. Even when containing each metal ion, the water content of TMHA–Tf$_2$N–M(Tf$_2$N)$_n$ solutions were larger than that of pure TMHA–Tf$_2$N, and the increment of water content increased with increasing metal ion content. However, the increment of water content decreased with rising temperature. For example, the water content of TMHA–Tf$_2$N–100 mM Ni(Tf$_2$N)$_2$ solution was 9970 ppm at 25°C while that of the TMHA–Tf$_2$N was 2430 ppm. In contrast, the water content of all TMHA–Tf$_2$N–M(Tf$_2$N)$_n$ solutions at 130°C were almost the same as that of pure TMHA–Tf$_2$N. It is thought that water molecules dissolve in the ionic liquid to aggregate or coordinate around metal ions. The addition of 100 mM Ni(Tf$_2$N)$_2$ to TMHA–Tf$_2$N increased the water content from 180 to 740 mM at 25°C. This increase of 560 mM in the water content corresponds to 5.6 molecules of water aggregate or coordinate around a single nickel ion, Ni$^{2+}$, in TMHA–Tf$_2$N. The number of aggregated or coordinated water molecules is in good agreement with that in aqueous solution, i.e. 6. Fig. 3(a) shows the absorption spectra of TMHA–Tf$_2$N containing (i) 1, (ii) 10, and (iii) 100 mM Ni(Tf$_2$N)$_2$ with saturated water measured at 25°C using pure TMHA–Tf$_2$N as a reference. Every spectrum exhibits the absorption peak of 393 nm, whose height increases with increasing Ni$^{2+}$ ion content. On the other hand, Fig. 3(b) shows the comparison of the spectra of TMHA–Tf$_2$N–100 mM Ni(Tf$_2$N)$_2$ solution (iii) with water saturation and (v) without water, with that of (iv) 100 mM NiSO$_4$ aqueous solution at 25°C; here, (ii) and (v) were measured with reference to a pure TMHA–Tf$_2$N while (iv) to a pure water. The absorption peak of 428 nm of dried TMHA–Tf$_2$N–Ni(Tf$_2$N)$_2$ solution shifted to 393 nm with saturating water, which is in agreement with that of NiSO$_4$ aqueous solution. It is considered that the water molecules in the TMHA–Tf$_2$N–Ni(Tf$_2$N)$_2$ solution coordinate around the Ni$^{2+}$ ions. For this reason, the saturated water content of TMHA–Tf$_2$N–M(Tf$_2$N)$_n$ solutions are larger than that of pure TMHA–Tf$_2$N solution. Using the absorbance at 393 nm, the concentration of Ni$^{2+}$ ions in TMHA–Tf$_2$N when saturated with water could be determined based upon the absorption index reported for Ni$^{2+}$ aqueous solution.

Fig. 4 shows the temperature dependences of the kinematic viscosity, $\nu$ for pure TMHA–Tf$_2$N and TMHA–Tf$_2$N–M(Tf$_2$N)$_n$ solutions saturated with water. Their temperature dependences of electrical conductivity, $\kappa$ are depicted in Fig. 5. The kinematic viscosity decreased and the electrical conductivity increased with rising temperature. The addition of M(Tf$_2$N)$_n$ increased the kinematic viscosity of TMHA–Tf$_2$N, and this increase became larger with an increase in the concentration of M(Tf$_2$N)$_n$. At 25°C, for example, the kinematic viscosity of pure TMHA–Tf$_2$N was 151 mm$^2$ s$^{-1}$, and the addition of Mg(Tf$_2$N)$_2$ at 10 and 100 mM increased this value to 212 and 255 mm$^2$ s$^{-1}$. At all temperatures, the electrical conductivity of TMHA–Tf$_2$N–M(Tf$_2$N)$_n$ solutions were lower than that of pure TMHA–Tf$_2$N. The addition of M(Tf$_2$N)$_n$ decreased the electrical conductivity of TMHA–Tf$_2$N, and this decrease became larger with an increase in the concentration of M(Tf$_2$N)$_n$. Table 1 summarizes the electrical conductivities and water contents of TMHA–Tf$_2$N–10 mM M(Tf$_2$N)$_n$ solutions at 40°C. The increase in metal ion valence decreases the electrical conductivity of TMHA–Tf$_2$N–M(Tf$_2$N)$_n$ solutions. In the case of pure TMHA–Tf$_2$N, the electrical conductivity increases with an increase in the water content [20], but the trend is not observed in TMHA–Tf$_2$N–M(Tf$_2$N)$_n$ solutions.

![Absorption spectra of ionic liquid TMHA–Tf$_2$N containing (i) 1, (ii) 10 and (iii) 100 mM Ni(Tf$_2$N)$_2$ saturated with water. (b) Absorption spectra of (iv) 100 mM NiSO$_4$ aqueous solution and (v) ionic liquid TMHA–Tf$_2$N containing 100 mM Ni(Tf$_2$N)$_2$ without water; the spectrum (iii) is also indicated.](image-url)
In Fig. 6, all the values of $k$ measured at various temperatures and water contents were plotted against the values of $n$ under the same conditions in log–log scale. The relationship between $\log n$ and $\log k$ gives a single straight line with a gradient of $-1$, indicating that a kind of Walden’s rule, expressed by Eq. (3), is applicable to both pure TMHA–Tf$_2$N and TMHA–Tf$_2$N–M(Tf$_2$N)$_n$ solutions with and without trace amounts of water:

$$\nu k = K \quad (K: \text{constant}).$$

This indicates that, even in the presence of water, the electrical conduction of this ionic liquid is attributed to the transfer of cations (TMHA$^+$ and M$^{n+}$) and/or anions (Tf$_2$N$^-$), and that the Stokes radius of these ions does not
Fig. 5. Temperature dependence of electrical conductivity of ionic liquid TMHA–Tf$_2$N containing $\text{M(Tf}_2\text{N)}_n$ ($\text{M} = \text{H}, \text{Li}, \text{Mg}, \text{Ni}, \text{Cu}, \text{Zn}, \text{La}, \text{and Dy}; \ n = 1, 2, \text{or} \ 3$) under the condition that the ionic liquid was allowed to stand in contact with the atmosphere.

Table 1
Electrical conductivity and saturated water content of ionic liquid TMHA–Tf$_2$N containing 10 mM $\text{M(Tf}_2\text{N)}_n$ ($\text{M} = \text{H}, \text{Li}, \text{Mg}, \text{Ni}, \text{Cu}, \text{Zn}, \text{La}, \text{and Dy}; \ n = 1, 2, \text{or} \ 3$)

| Metal ions | Non | $\text{H}^+$ | $\text{Li}^+$ | $\text{Mg}^{2+}$ | $\text{Ni}^{2+}$ | $\text{Cu}^{2+}$ | $\text{Zn}^{2+}$ | $\text{La}^{3+}$ | $\text{Dy}^{3+}$ |
|------------|-----|-------------|-------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Conductivity (S m$^{-1}$) | 0.242 | 0.252 | 0.230 | 0.211 | 0.215 | 0.210 | 0.227 | 0.206 | 0.207 |
| Water content (ppm) | 1360 | 2200 | 1440 | 3670 | 2030 | 2170 | 3270 | 1700 | 2830 |

Temperature of the liquid was 40 $^\circ$C.
change with the change in temperature and the presence of water. In general, Walden’s rule is applicable to the infinite-diluted solution, while the ion concentration of ionic liquid examined in this study is quite high at about 3 M. Such behavior of the ionic liquid is of interest and further studies are necessary to understand the electrical conduction mechanism of the ionic liquid, particularly, what kind of role the added metal ions play in the electrical conductivity.

Fig. 7 illustrates the DSC thermograms of pure TMHA–Tf$_2$N and TMHA–Tf$_2$N–Mg(Tf$_2$N)$_2$ solution measured with increasing temperature from −100 to 100 °C. The rate of temperature change employed was...
5 °C min⁻¹. In the case of pure TMHA–Tf₂N, the glass transition point Tₖ, the crystallization point Tₖc, and the melting point Tₘ were −77.7, −41.0, and 25.5 °C, respectively; the glassy state of TMHA–Tf₂N at −100 °C changed to a supercooled liquid at Tₖ, to crystalline solid at Tₖc, and to liquid at Tₘ. In contrast, in the case of TMHA–Tf₂N–100 mM Mg(Tf₂N)₂ solution, Tₖ, Tₖc and Tₘ were shifted to −74.5, −16.2, and 24.3 °C, respectively. In the case of TMHA–Tf₂N–500 mM Mg(Tf₂N)₂ solution, Tₖ and Tₘ were not observed. It is considered that the addition of metal ions causes the increase of ion–ion interactions as they have a smaller radius than TMHA⁺ cations or Tf₂N⁻ anions. The thermal properties of TMHA–Tf₂N–M(Tf₂N)ₙ solutions derived from the DSC traces are summarized in Table 2. In the case of TMHA–Tf₂N–M(Tf₂N)ₙ solutions, Tₖ and Tₖc increased with increasing metal ion concentration, while Tₘ decreased with increasing metal ions.

4. Conclusion

In this study, the saturated water contents of ionic liquid TMHA–Tf₂N containing M(Tf₂N)ₙ salts (M = H, Li, Mg, Ni, Zn, Al, La, and Dy; n = 1, 2, or 3), as well as their kinematic viscosities and electrical conductivities, were measured in the temperature range of 25 to 130 °C. It was found that the “hydrophobic” ionic liquids, TMHA–Tf₂N–M(Tf₂N)ₙ solutions, absorb water up to a few thousand ppm from the atmosphere. The saturated water contents depend on the kinds of M(Tf₂N)ₙ present in these solutions, and they increase with increasing salt concentration, and decrease with increasing temperature. The viscosity increased, while the conductivity decreased, with increasing M(Tf₂N)ₙ concentration and/or valence. Over the above temperature range, a rule similar to Walden’s law is applicable to the TMHA–Tf₂N–M(Tf₂N)ₙ solutions. The water molecules in TMHATf₂N–M(Tf₂N)ₙ solutions are coordinated around the metal ions. DSC thermograms revealed the glass transition temperature, Tₖ, crystallization temperature, Tₖc, and melting temperature, Tₘ of TMHA–Tf₂N–M(Tf₂N)ₙ solutions. Tₖ’s ranged from −65.1 to −78.9 °C, and Tₖc’s from −18.1 to −43.2 °C, depending on the metal salt dissolved. On the other hand, Tₘ’s were almost constant at 25 °C.

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References

[1] R.T. Carlin, H.C. De Long, J. Fuller, P.C. Trulove, J. Electrochem. Soc. 141 (1994) L73.
[2] S. Tobishima, Electrochemistry 70 (2002) 198.
[3] C. Nanjundiah, S.F. McDevitt, V.R. Koch, J. Electrochem. Soc. 144 (1997) 3392.
[4] A.B. McEwen, S.F. McDevitt, V.R. Koch, J. Electrochem. Soc. 144 (1997) L84.
[5] M. Ue, M. Takeda, T. Takahashi, M. Takehara, Electrochem. Solid-State Lett. 5 (2002) A119.
[6] N. Papageorgiou, Y. Athanassov, M. Armand, P. Bonhôte, H. Pettersson, A. Azam, M. Grätzel, J. Electrochem. Soc. 143 (1996) 3099.
[7] H. Matsumoto, T. Matsuda, Electrochemistry 70 (2002) 190.
[8] J.S. Wilkes, M.J. Zaworotko, J. Chem. Soc., Chem. Commun. (1992) 965.
[9] K. Hayashi, Y. Nemoto, K. Akuto, Y. Sakurai, J. Power Sources 146 (2005) 689.
[10] M. Egashira, S. Okada, J. Yamaki, Solid State Ion. 148 (2002) 457.
[11] P.C. Innis, J. Mazurkiewicz, T. Nguyen, G.G. Wallace, D. MacFarlane, Curr. Appl. Phys. 4 (2004) 389.
[12] J. Sun, M. Forsyth, D.R. MacFarlene, J. Phys. Chem. B 102 (1998) 8858.
[13] H. Matsumoto, M. Yanagida, K. Tanimoto, M. Nomura, Y. Kitagawa, Y. Miyazaki, Chem. Lett. (2000) 922.
[14] H. Matsumoto, H. Kageyama, Y. Miyazaki, Chem. Lett. (2001) 182.
[15] H. Matsumoto, Y. Miyazaki, H. Ishikawa, Japanese Patent Applications, (3 April 1997) 11-297 355 A.
[16] K. Murase, Y. Awakura, Trans. Mater. Res. Soc. Jpn. 29 (2004) 55.
[17] K. Murase, K. Nitta, T. Hirato, Y. Awakura, J. Appl. Electrochem. 31 (2001) 1089.
[18] K.R. Seddon, A. Stark, M. Torres, Pure Appl. Chem. 72 (2000) 2275.
[19] L. Cammarate, S.G. Kazarian, P.A. Salter, T. Welton, Phys. Chem. Chem. Phys. 3 (2001) 5192.
[20] T. Katase, T. Onishi, S. Imashuku, K. Murase, T. Hirato, Y. Awakura, Electrochemistry 73 (2005) 686.