We report here the temperature dependence of the water content, viscosity, and conductivity of ionic liquid, trimethyl-n-hexylammonium bis((trifluoro-methyl)sulfonyl)amide (TMHA-Tf$_2$N), which has a wide electrochemical window larger than 5 V. Although the ionic liquid is considered to be hydrophobic, since the Tf$_2$N$^-$ anions has two -CF$_3$ groups, a certain amount of water remained in the ionic liquid even after dehydration in vacuo. The content of the residual water in equilibrium with atmospheric moisture decreased with increasing temperature of the ionic liquid up to 150 °C. The increase in the water content resulted in a slight decrease in viscosity and an increase in conductivity. Since the influence of the residual water over these properties was, however, much smaller than that of the temperature, Walden's plot for the data over various temperatures and water contents gave a single straight line.

ROOM TEMPERATURE IONIC LIQUID

Room temperature ionic liquids (ILs) are expected to be new electrochemical media due to their unique physical properties, such as less-volatility, non-flammability, low hygroscopicity, and availability at mild temperatures. Therefore, various approaches have been made to gain a fundamental understanding of ILs and to put them in practical applications, such as batteries, capacitors, and electrochemical solar cells (1). Since the discovery of the moisture stable ionic liquid, 1-ethyl-3-methylimidazolium tetrafluoroborate in 1992 (2), many ILs have been reported by the combination of alkylimidazolium cations and inorganic and organic fluoroanions. Recently, the number of reports on the alkylimidazolium ILs combined with a highly stable bis((trifluoromethyl)sulfonyl)amide (or “imide”) anion (Tf$_2$N$^-$) have been increasing (3).

On the other hand, a new series of ILs, consisting of aliphatic quaternary ammonium cation and the imide type anion (4,5), were prepared and found to have a wide electrochemical window larger than 5 V (6). Such a wide electrochemical window suggests that the ammonium imide-type ILs will be a potential media for the electrodeposition of less-noble metals. Therefore, we have been investigating the electrodeposition behavior of metals, e.g. Cu, Zn, Ni, and Mg, from one of the ILs, trimethyl-n-hexylammonium bis((trifluoromethyl)sulfonyl)amide (TMHA-Tf$_2$N)(7,8). TMHA-Tf$_2$N IL is commonly considered to be hydrophobic due to the Tf$_2$N$^-$ anion which has two -CF$_3$ groups. It was found, however, that some amount of water remained in this IL even after careful dehy-
dration in vacuo and that the residual water affected the electrodeposits from the ionic liquid. Although such hygroscopicity of "hydrophobic" ILs has been well investigated for alkylimidazolium ILs (9,10), the data on the ammonium imide ILs are still lacking.

In the present study, we examined the temperature dependence of the content of the residual water and concomitant change in some physical properties of the ionic liquid TMHA-Tf$_2$N IL.

EXPERIMENTAL

Materials

**Synthesis of TMHA-Tf$_2$N.** The IL, TMHA-Tf$_2$N, was synthesized under ambient atmosphere by the metathetic reaction of trimethyl-n-hexylammonium bromide (TMHABr; Tokyo Kasei Kogyo Co., Ltd., 98%) with lithium bis((trifluoromethyl)sulfonyl)amide (LiTf$_2$N; Fluka, 99%) as:

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50.00 \text{g} (0.224 \text{ mol}) \text{ of TMHABr and 64.02 g} (0.224 \text{ mol}) \text{ of LiTf}_2\text{N were weighted and each was dissolved in 100 cm}^3 \text{ of deionized water. The two aqueous solutions were mixed and agitated with a magnetic stirring unit for 1 hr at 70 °C. According to the above reaction, TMHA-Tf}_2\text{N was formed and made a biphasic system with water containing Li}^+ \text{ and Br}^- \text{ ions. To extract the TMHA-Tf}_2\text{N completely from the aqueous phase, 100 cm}^3 \text{ of 1,2-dichloroethane (Nacalai Tesque, Inc., 99%) was added and stirred for 1 hr at room temperature. The IL phase (i.e. lower layer) was then separated using a separating funnel. The 1,2-dichloroethane solution of TMHA-Tf}_2\text{N was washed with 100 cm}^3 \text{ of deionized water three times in order to remove residual LiBr. The complete removal of Br}^- \text{ ion was ascertained by the addition of a AgNO}_3 \text{ aqueous solution to the washings; if Br}^- \text{ remains, an insoluble AgBr forms. The 1,2-dichloroethane was then distilled off using a rotating evaporator and the resulting crude TMHA-Tf}_2\text{N was dried in vacuo at 120 °C for 2 hrs with a liquid nitrogen trap. The synthesized TMHA-Tf}_2\text{N obtained has a melting point ~ 27 °C and was identified by elemental analysis at the Center for Organic Elemental Microanalysis of Kyoto University as C 31.02 % (31.13%), H 5.16 % (5.22%), N 6.57 % (6.60%), F 27.18% (26.86%), Br 0 % (0 %) (calculated values are in parentheses); the contents of oxygen and sulfur could not be analyzed because the TMHA-Tf}_2\text{N contains fluorine.}

**Absorption of water.** After the drying process, TMHA-Tf$_2$N with water content less than 100 ppm was allowed to stand in contact with the atmosphere. During the experiments, the temperature of the ionic liquid was controlled to be constant between 30 to 150 °C using a thermostat.

Measurements

The water content in the IL was determined by a coulometric Karl-Fischer method (MKC-510N; Kyoto Electronics Manufacturing Co., Ltd.). Viscosity and electric con-
ductivity were measured by a vibration-type viscometer (VM-1G; CBC Materials Co., Ltd.) and a conventional conductivity measuring cell (CM-30G; DKK-TOA), respectively.

RESULTS AND DISCUSSION

When allowed to stand in the ambient atmosphere, a dried TMHA-Tf$_2$N gradually absorbed water from the atmospheric air and the water content was increased with the elapse of time. After ample time has passed, however, the water content reached a constant value, which we call a "saturated" water content. Figure 1 shows the changes in the water content of the IL at 55.6 °C. The water vapor pressure of the atmosphere is also indicated in the figure. It is clear that the water content depended on the water vapor pressure of the atmosphere: At the first stage (0-7 hr), we kept the water vapor pressure at 1600 Pa and the water content was saturated at around 800 ppm. After that, the vapor pressure decreased to 1100 Pa (25 hr) and then increased gradually to 1300 Pa (35 hr). During the decrease in the vapor pressure, the water content also followed a downward curve.

![Figure 1. Changes in water content of TMHA-Tf$_2$N and water vapor pressure of the atmosphere.](image)

Figure 2 gives the relationship between the saturated water content and temperature. The water content decreased with rising temperature. The data was taken with both ascending and descending temperature in order to make sure that the system is in equilibrium. The water content at 30 °C was about 800 ppm, while that at 150 °C was decreased to below 200 ppm, indicating that the residual water in the ionic liquid can be removed only by heating without reducing the pressure. The water content 800 ppm corresponds to $5.9 \times 10^{-3}$ mol dm$^{-3}$ in molarity or $1.9 \times 10^{-2}$ in mole fraction. Although the value is quite low compared to, for example, 1-butyl-3-methylimidazolium imide (9) and hence the TMHA-Tf$_2$N is better termed as hydrophobic liquid, we should take care of the residual water if we use TMHA-Tf$_2$N for the electrodeposition of some active metals.
Figures 3 and 4 show the water content dependencies of kinematic viscosity ($\eta$) at two different temperatures and of conductivity ($\Lambda$) at three different temperatures, respectively. Irrespective of the water content, $\eta$ was significantly decreased and $\Lambda$ was increased with the rise of temperature. In addition, $\eta$ decreased and $\Lambda$ increased also with increasing water content. However, it was found that the influence of the water content on these parameters was found to be much smaller than that of the temperature. It is considered that the decrease of $\eta$ and increase of $\Lambda$ are based upon the ion-ion interaction becoming weak by the water molecule which exists between TMHA$^+$ cation and Tf$_2$N$^-$ anion.
Figure 4. Relationship between water content and molar conductivity at three temperatures.

In Figure 5, all the $\eta$ and $\Lambda$ pairs measured at various temperatures and water contents were plotted together. The relationship between $\log \eta$ and $\log \Lambda$ gives a single straight line with a gradient of $-1$, indicating that the Walden's rule (2) is applicable even if TMHA-Tf$_2$N contains a trace amount of water, unless the water content exceeds the saturated value at each temperature.

$$\eta \Lambda = K \quad (K: \text{constant})$$

Figure 5. Relationship between the viscosity and conductivity of TMHA-Tf$_2$N with or without containing water.
Table 1 summarizes the saturated water content together with \( \eta \) and \( \Lambda \) of the ionic liquid at two temperatures: 49 and 99 °C. The data were taken first at 49 °C (left column), then at 99 °C (middle) and again at 49 °C (right). After the heating and cooling cycle, the properties of the ionic liquid did not change, demonstrating that, when water and ionic liquid are mixing with each other, an irreversible chemical reaction does not occur.

Table 1. Saturated water content together with viscosity and conductivity of the ionic liquid at two temperatures.

| Properties                  | 49 °C | 99 °C | 49 °C |
|-----------------------------|-------|-------|-------|
| Water Content / ppm         | 457   | 151   | 446   |
| Molar Conductivity / S cm\(^{-2}\) mol\(^{-1}\) | 2.07  | 4.50  | 2.10  |
| Kinematic Viscosity / mm\(^{-2}\) s\(^{-1}\) | 62.3  | 13.2  | 62.4  |

CONCLUSIONS

In this study, we examined the water content of TMHA-Tf\(_2\)N IL and its effect of viscosity and conductivity. It was found that the “hydrophobic” TMHA-Tf\(_2\)N can absorb water from the atmospheric air, resulting in a decrease in viscosity and increase in conductivity. The absorption of water did not lead to any irreversible chemical reaction or decomposition of TMHA-Tf\(_2\)N. Over a wide range of temperature, Walden’s rule is applicable to TMHA-Tf\(_2\)N.

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