

Water in Hydrophobic Ionic Liquids Containing Metal Salts

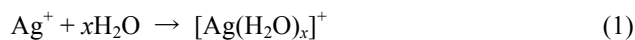
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The quaternary-ammonium ionic liquid, trimethyl-*n*-hexylammonium bis[(trifluoromethyl)sulfonyl] amide (TMHA-Tf₂N) is considered to be hydrophobic because of two -CF₃ groups in its Tf₂N⁻ anion. However, Murase reported that TMHA-Tf₂N itself can dissolve as much as 1% water by weight; moreover, TMHA-Tf₂N containing metal salt like Mg(Tf₂N)₂, dissolves more water than pure TMHA-Tf₂N [1]. It was also suggested that the metal ions in TMHA-Tf₂N were hydrated by measuring the optical absorption spectrum. The water around metal ion would change the solvation geometry of its ion and shift the redox potential, which probably affect how metals and alloys are electrochemically deposited in a “wet” ionic liquid bath. Therefore it is important to investigate the electrochemical effect of water in the metal-containing ionic liquid.

We measured the saturated water content (SWC) of TMHA-Tf₂N containing metal salts, M(Tf₂N)₂ (M = Zn, Mg, Ca, Sr, Cd, Ba). Figure 1 shows the relationship between hydrated water content and amount of added water for 50 mM Zn(Tf₂N)₂ / TMHA-Tf₂N. The water content monotonically increased until 25 mm³ water was added. When water was added more than 25 mm³, the solution underwent phase separation into an ionic liquid phase and a water phase, and the water content of the ionic liquid phase became steady. We regarded this water content as saturated. Here, we assume that the water content is the sum of SWC for pure TMHA-Tf₂N itself and metal salt Zn(Tf₂N)₂. Thus, by subtracting SWC for pure TMHA-Tf₂N, we obtained SWC for metal salt and coordination number of each metal ion as summarized in Table 1. The coordination number (CN) for M²⁺ = Ca²⁺, Sr²⁺ was 8.4 ~ 8.7, while CN for M²⁺ = Zn²⁺ and Mg²⁺ were a little large (CN = 10). We attributed the difference in CN to the ionic radius or Lewis acidity: the Lewis acidity of Zn²⁺ and Mg²⁺ was relatively stronger than that of Ca²⁺, Sr²⁺ and Cd²⁺. Additionally, the CN for Ba²⁺ was 1.7, much smaller than the others. It is possible that in the case of Ba²⁺ not only water molecules but also Tf₂N⁻ anions coordinate around the metal ions.

The open circuit potential (OCP) was measured between two Ag electrodes, the one in 20 mM Ag(Tf₂N) / TMHA-Tf₂N as reference electrode (RE) and the other in water-added one as working electrode (WE). The cell was schematically illustrated in Fig. 2. To avoid evaporation of water, the electrochemical cell was tightly capped with O-ring. All experiments were carried out in an N₂-filled glove box (H₂O, O₂ < 1 ppm). We plotted the results of OCP measurement against water content in Fig. 3. As water content increased, monotonic negative shift was observed, reaching -34.2 mV when the water content was saturated (12900 ppm). We estimated complex formation constant ($K_{cf} = \exp \{-F(E_{WE} - E_{RE})/RT\}$) of reaction (1):



As a result, K_{cf} was not so large (3.61), suggesting that water molecules weakly coordinate around Ag⁺ ions instead of Tf₂N⁻.

[1] K. Murase, T. Katase, S. Imashuku, T. Hirato and Y. Awakura, *Sci. Tech. Adv. Mater.*, 7, 502 (2006).

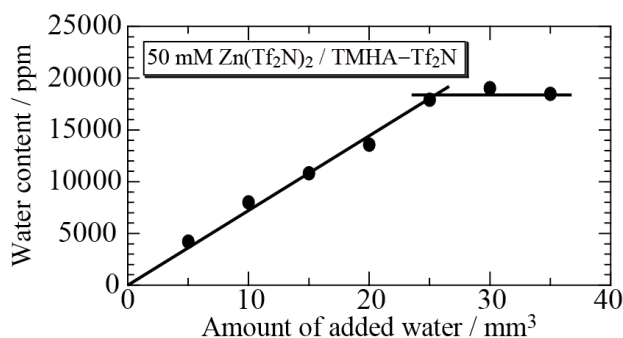


Figure 1. Relationship between amount of added water and water content in 1 cm³ 50 mM Zn(Tf₂N)₂ / TMHA-Tf₂N at room temperature. Lines are guide to the eyes.

Table 1. Saturated water content of 50 mM M(Tf₂N)₂ / TMHA-Tf₂N (M = Zn, Mg, Ca, Sr, Cd, Ba) and the estimated coordination number (CN).

Salt	Saturated water content / ppm	CN
Zn(Tf ₂ N) ₂	18,500	10
Mg(Tf ₂ N) ₂	18,000	10
Ca(Tf ₂ N) ₂	17,600	8.7
Sr(Tf ₂ N) ₂	17,400	8.4
Cd(Tf ₂ N) ₂	16,000	6.3
Ba(Tf ₂ N) ₂	12,900	1.7

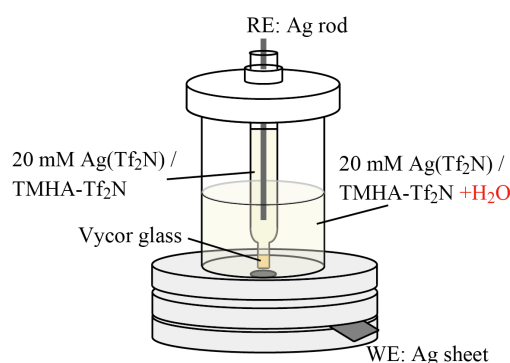


Figure 2. Schematic illustration of the electrochemical cell.

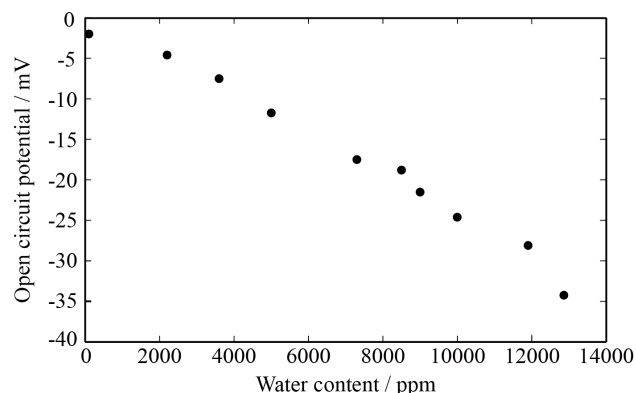


Figure 3. Open circuit potential against water content measured for 20 mM Ag(Tf₂N) / TMHA-Tf₂N.