

Redox and transport behaviors of Cu(I) ions in TMHA-Tf₂N ionic liquid solution

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Abstract

The redox and transport behavior of monovalent copper species in an ammonium imide-type ionic liquid, trimethyl-*n*-hexylammonium bis((trifluoromethyl)sulfonyl)amide (TMHA-Tf₂N) were examined with a micro-disc electrode to clarify its applicability to, for example, electroplating. It was found that the diffusion coefficient of Cu(I) ions in TMHA-Tf₂N containing 12 mmol dm⁻³ Cu(I) ions was 1.2×10^{-6} cm² s⁻¹ and the redox potential of Cu(I)/Cu was in the potential range 0.1–0.2 V vs. I^-/I_3^- at 50 °C. The diffusion coefficient was one order smaller than that of Cu(II) ions in aqueous solution due to the high viscosity of the ionic liquid. The diffusion coefficient of Cu(I) ion increased with rising temperature and was 1.0×10^{-5} cm² s⁻¹ at 112 °C, which was comparable to that of Cu(II) ions in aqueous CuSO₄ solutions at ambient temperature. This is accounted for by the drastic decrease in the viscosity of the ionic liquid solution with increasing temperature. The activation energy of diffusion was estimated to be 39 kJ mol⁻¹ in the ionic liquid solution.

1. Introduction

Room temperature ionic liquids are expected to act as new functional electrochemical media due to their unique physical and chemical properties. Since the discovery of the moisture-stable ionic liquid, 1-ethyl-3-methylimidazolium tetrafluoroborate in 1992 [1], a number of ionic liquids have been synthesized by combining alkylimidazolium cations and inorganic or organic fluoro-anions [2, 3]. One of the applications of ionic liquids is as electrolytic media for the electrodeposition of metals and alloys [4–12]. For example, a series of ionic liquids consisting of aliphatic quaternary ammonium cations and imide-type anions [13] have an electrochemical window larger than 5 V [14]; this suggests that ionic liquids of this type are potential media for the electrodeposition of less-noble metals, which cannot be electrodeposited from conventional aqueous media. We have also 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, i.e. TMHA-Tf₂N [15, 16]. In addition, ionic liquids can also be used as a solvent for electrodeposition processes at medium-low temperatures, i.e. 100–200 °C, that cannot

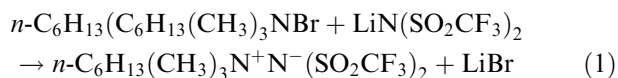
easily be attained with aqueous or volatile organic baths [17].

In the field of electrodeposition, it is important to understand the electrochemical properties, such as the redox potentials of various M^{n+}/M systems, and the transport properties, such as the diffusion coefficients of various metal ions active in electrodeposition. It is considered that the diffusion rate of metal ion in the ionic liquid, TMHA-Tf₂N, is relatively slow due to its higher viscosity [18] compared to water. In addition, the redox behavior of metal ions in an ionic liquid are expected to be different from those in aqueous solutions, due to the difference in the ionic valency and/or coordination environment. In the case of TMHA-Tf₂N solution, for example, we recently found that monovalent copper ions are stable, unlike in the case of common aqueous media. However, such diffusion data is still limited. In this work, the electrochemical features of the Cu(I)/Cu redox reaction and the mass transfer of Cu(I) ions were examined for a Cu(Tf₂N)–TMHA-Tf₂N ionic liquid solution by means of cyclic or linear sweep voltammetry using a micro-disk electrode. The redox potential of Cu(I)/Cu and the diffusion coefficient of Cu(I) ions were discussed based upon the experimental results obtained.

2. Experimental details

2.1. Ionic liquid

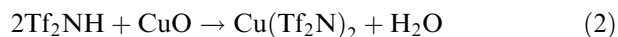
The ionic liquid, TMHA-Tf₂N, was prepared by the metathesis of trimethyl-*n*-hexylammonium bromide (TMHABr; Tokyo Kasei Kogyo Co., Ltd., 98%) with lithium bis((trifluoromethyl)sulfonyl)amide (LiTf₂N; Fluka, 99%) as follows:



The preparation procedures were described previously [15, 18]. The prepared TMHA-Tf₂N was dried *in vacuo* for more than 2 h at 120 °C in a flask connected to a liquid nitrogen trap, and its residual water was checked to be less than 50 ppm with the coulometric Karl-Fischer method [18]. The TMHA-Tf₂N dried was stored in a glove box filled with argon gas with a water content less than 5 ppm.

2.2. Copper salt

A divalent copper salt, Cu(Tf₂N)₂, was prepared using the acid-base reaction of copper(II) oxide, CuO, with bis((trifluoromethyl)sulfonyl)amine (TfN₂H; Fluka, 99%) as follows:



5.00 g (0.018 mol) of Tf₂NH was dissolved in 20 cm³ of deionized water to obtain an aqueous Tf₂NH solution. An excess amount of CuO was added to this solution and the resulting solution was stirred for 2 h at 70 °C to yield an aqueous solution of Cu(Tf₂N)₂ salt. After removing the unreacted CuO by filtration, the water was distilled off from the aqueous solution to yield a solid hydrated salt, Cu(Tf₂N)₂·*x*H₂O. The salt was dried by dehydration *in vacuo* for over 72 h at 120 °C and then transferred into the glove box for storage.

2.3. Preparation of electrolytic solution

In order to prepare a Cu(Tf₂N)₂-TMHA-Tf₂N ionic liquid solution, the divalent copper salt, Cu(Tf₂N)₂, was weighed and dissolved into the ionic liquid, TMHA-Tf₂N, in the glove box in such a way that the concentration of Cu(Tf₂N)₂ was 10 mM (M; mol dm⁻³). Then, the Cu(II) ions in the solutions were converted to Cu(I) ions by the following conproportionation reaction [15]:



Here, a metallic copper sheet was immersed in the 10 mM Cu(Tf₂N)₂-TMHA-Tf₂N solution. When immersed, the mass of the copper sheet decreased with

the time elapsed and, at the same time, the color of the original solution due to Cu(II) ions changed gradually from light green to paler, indicating the formation of color-less Cu(I) ions. Even after ample time, e.g. 72 h, had passed, the solution still had a pale green color, suggesting that a small amount of divalent Cu(II) ions remained in the solution. In other words, the Cu(II) ions in TMHA-Tf₂N are not completely converted to Cu(I) ions, even if a copper sheet is immersed in the Cu(II) solution for long period of time. Our recent study [15] revealed that the immersion of a copper sheet into 20 mM Cu(Tf₂N)₂-TMHA-Tf₂N for 72 h or longer yielded a solution containing 24 mM Cu(I) and 8 mM Cu(II) ions, indicating that 40% of the divalent copper ions that initially dissolved remained unchanged when equilibrium was reached. When electrolyzed, the resulting solution contained mixed Cu(I) and Cu(II) ions; however, the current efficiency for copper deposition was 97%, assuming that the reaction is one-electron, Cu(I) + e = Cu. This means that, even in the presence of Cu(II) ions, the electrodeposition takes place mainly from the Cu(I) state. Therefore, it should be reasonable to consider that the deposition current monitored with the micro-disk electrode, as described later, involves only information on the diffusion of Cu(I) ions.

Given that 40% of the Cu(II) ions remain unreacted with the copper sheet, the immersion of a copper sheet in the 10 mM Cu(Tf₂N)₂-TMHA-Tf₂N solution yields a solution containing 12 mM Cu(I) and 4 mM Cu(II) ions. We depict this solution as “12 mM Cu(Tf₂N)-TMHA-Tf₂N” for the sake of simplicity, and the electrolytic experiments were performed for this ionic liquid solution using a conventional three electrode set-up comprising a potentiostat driven by a function generator and connected to a coulometer. Cyclic and linear sweep voltammograms were measured by scanning the potential of the working electrode at 1 or 10 mV s⁻¹. The working electrode used was a micro-disk electrode, where a platinum wire 100 μm in diameter was cemented in a glass. One end of the electrode was polished with 0.06 μm alumina abrasives, and only a disk of platinum surrounded with insulating glass was exposed to the electrolyte. The reference electrode was an I⁻/I₃⁻ electrode; a platinum wire was immersed in a TMHA-Tf₂N solution containing 15 mM I₂ and 60 mM (*n*-C₃H₇)₄NI charged in a glass tube with a bottom of porous sintered-glass. The electrode potential of the redox pair of ferrocene/ferricinium in TMHA-Tf₂N media was reported to be +0.16 V vs. I⁻/I₃⁻ [15]. A glass vessel 20 cm³ in capacity was used as the cell. The solution was thermostatted at temperatures from 50 to 112 °C.

Aqueous solution containing 100 mM CuSO₄ was also examined for comparison. The reference electrode in this case was Ag/AgCl immersed in 3.33 M KCl, but the potential scale was recalculated for the standard hydrogen electrode (SHE).

3. Results and discussion

3.1. Optimization of potential scan rate

In the electrodeposition of metals the concentration of metal ions decreases in the vicinity of the cathode surface immediately after starting electrolysis, and a concentration boundary layer is developed on the surface of electrode. Both the thickness of the boundary layer and the concentration profile of metal ions within the layer reach those in a steady state after some time has elapsed, depending mainly on the viscosity of the electrolyte used. The ionic liquid, TMHA-Tf₂N, has a fairly high viscosity [18] as compared with aqueous solutions, and it was considered that it might take a long time to reach a steady state boundary layer condition. Therefore, instead of a macro electrode, a micro-disk electrode was employed to measure the cyclic and linear sweep voltammograms for Cu(Tf₂N)-TMHA-Tf₂N solution.

Figure 1 shows the cyclic voltammograms for the 12 mM Cu(Tf₂N)-TMHA-Tf₂N ionic liquid solution taken at 50 °C with scanning rates of 1 and 10 mV s⁻¹. At 10 mV s⁻¹, the cathodic current for copper deposition was observed from ca. 0.21 V vs. I⁻/I₃⁻ except for the first cycle. In the cathodic scan, the current increased rapidly with decreasing electrode potential, passed through a maximum value of -0.69 mA cm⁻² at ca. 0.04 V, and then stayed almost constant at -0.50 mA cm⁻² in the range -0.1 - -0.5 V. These trends were almost identical over four cycles. By integrating the current density, the amount of electric charge passed was evaluated as 4.5 to 4.7 × 10⁻⁶ C per cycle, corresponding to a deposited copper layer of 0.04 μm in thickness on the micro-disk electrode. Hence, the copper deposition has no significant effect on the geometry of the micro-disk electrode as long as the diameter is 100 μm. Conversely, the voltammogram at 1 mV s⁻¹ gave a different profile without a cathodic peak under the same potential range scanned. The voltammogram

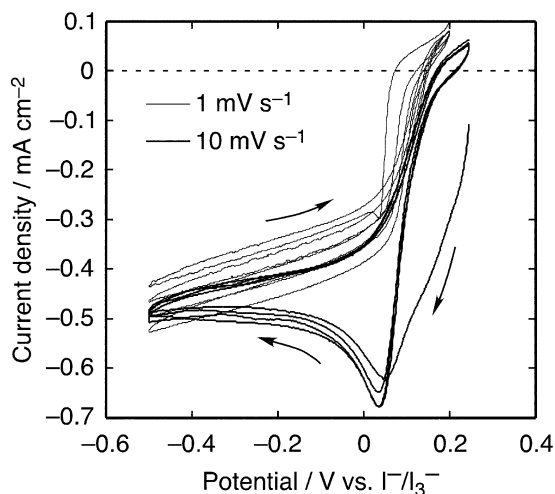


Fig. 1. Cyclic voltammograms for 12 mM Cu(Tf₂N)-TMHA-Tf₂N ionic liquid solution measured at 50 °C using micro-disk electrode (diameter 100 μm). Scanning rates were 1 and 10 mV s⁻¹.

in this case showed no loop and the resulting current-potential curves were almost identical in terms of potential sweeps in both directions. Furthermore, the current-potential curves were almost in agreement with those for the positive direction scan with a rate of 10 mV s⁻¹.

According to the results in the previous paragraph, it is clear that the current peak at ca. 0.04 V in the negative-going scan of 10 mV s⁻¹ is caused by a delay in the development of the concentration boundary layer at the electrode surface. In contrast the scanning rate of 1 mV s⁻¹ is sufficiently slow for the development of the boundary layer. Even at 10 mV s⁻¹, it is clear that the boundary layer was almost fully developed after switching the potential scan in the positive direction. Hence, the cyclic voltammogram obtained at 1 mV s⁻¹ can be regarded as a steady cathodic polarization curve for the 12 mM Cu(Tf₂N)-TMHA-Tf₂N solution at 50 °C. The amount of electric charge was evaluated to be 3.1–4.1 × 10⁻⁶ C per cycle at this scan rate, corresponding to a copper layer of 0.3–0.4 μm thickness. This thickness also has no significant effect on the geometry of the micro-disk electrode. If scanned at a lower rate, e.g. 0.1 mV s⁻¹, or if a much smaller micro-disk electrode is employed, then the copper layer becomes thicker, affecting the geometry of the electrode.

Judging from the voltammograms, the redox potential of Cu(I)/Cu locates in the potential range from 0.1 to 0.2 V at 50 °C. This is in accordance with the fact that a copper layer with a metallic luster was electrodeposited at 0.0 V on a Pt flag electrode [15].

3.2. Diffusion of Cu(II) ions in aqueous CuSO₄ solution

Using a micro-disk electrode, the diffusion coefficient of ionic species active on the electrode was calculated using the equation [19]:

$$I_L = 2nFcDa \quad (4)$$

where I_L is the diffusion limiting current (A) obtained from a steady state linear sweep voltammogram, n is the number of reacting electrons (-), F is the Faraday constant (96,485 C mol⁻¹), c is the concentration of ions (mol cm⁻³), D is the diffusion coefficient (cm² s⁻¹), and a is the electrode diameter (cm). To check the applicability of Equation (4) and the performance of the micro-disk electrode, the diffusion of Cu(II) ions in aqueous copper sulfate solution was examined before investigating the ionic liquid. Figure 2 shows the linear sweep cathodic voltammograms for 100 mM CuSO₄ aqueous solution at three different temperatures, i.e. 25, 40, and 55 °C, using a micro-disk electrode with 100 μm in diameter; the scanning rate was 1 mV s⁻¹. The onset potential of copper deposition was 0.21 V vs. SHE at each temperature and the currents increased with decreasing electrode potential. Then, the increment of current tapered off toward ca. 0.15 V and, at this potential, the electrodeposition of copper proceeded under cathodic

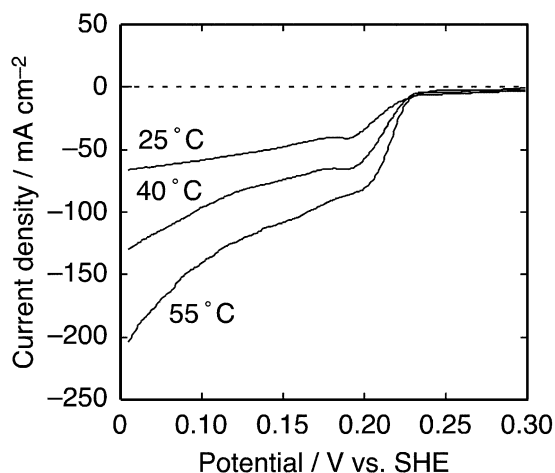


Fig. 2. Linear sweep voltammograms for 100 mM CuSO_4 aqueous solution measured at temperatures 25, 40, and 55 °C using micro-disk electrode (diameter 100 μm). Scanning rate was 1 mV s^{-1} .

diffusion limiting condition, where the rate of copper deposition is controlled by the mass transfer of Cu(II) ions through the concentration boundary layer. A further increase in cathodic current may well be attributed to the electrical migration of Cu(II) ions and/or the emergence of a rough surface due to the diffusion limiting copper deposition. According to Equation 4, the diffusion coefficient of Cu(II) ions at 25 °C was calculated to be $8.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ using the limiting current at 0.15 V. The value is in fairly good agreement with the reported value, i.e. $6.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ [20], measured with an optical method using a moiré image. Figure 3 depicts a set of diffusion coefficient data at three temperatures plotted in an Arrhenius fashion, which gives a single straight line. The activation energy of diffusion, Q , was calculated to be 20 kJ mol^{-1} from the following equation:

$$D = D_0 \exp(-Q/RT) \quad (5)$$

where D is the diffusion coefficient, D_0 is a constant, R is the gas constant and T is the absolute temperature. The

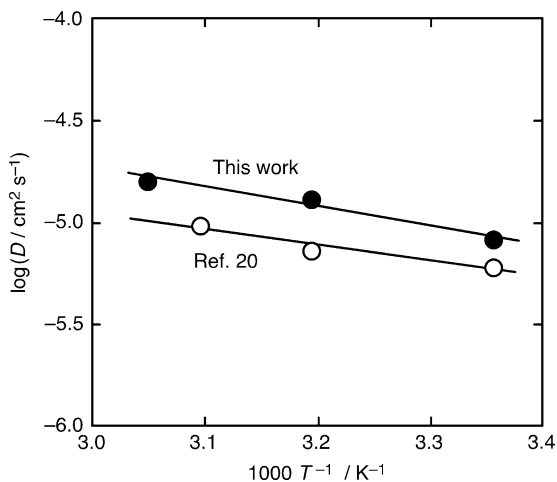


Fig. 3. Arrhenius plots of the diffusion coefficient of Cu(II) ions in 100 mM CuSO_4 aqueous solution.

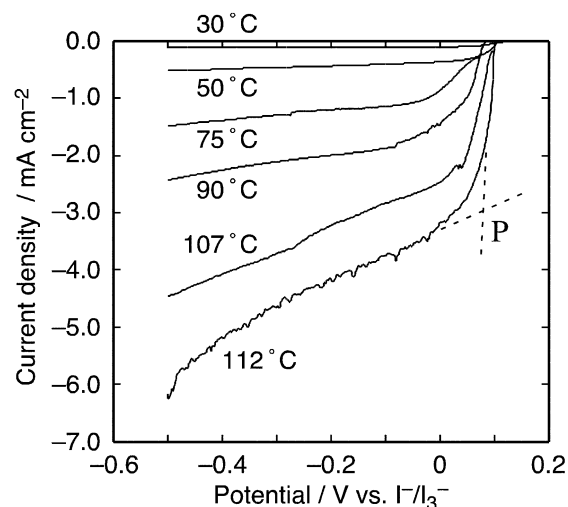


Fig. 4. Linear sweep voltammograms for 12 mM $\text{Cu(Tf}_2\text{N)-TMHA-Tf}_2\text{N}$ ionic liquid solution measured at six different temperatures from 30 to 112 °C using a micro-disk electrode (diameter 100 μm). Scanning rate was 1 mV s^{-1} .

value, 20 kJ mol^{-1} , is also in good agreement with that reported, i.e. 16 kJ mol^{-1} , within experimental uncertainty [20]. The results ensure that the micro-disk electrode employed works properly and that Equation 4 is applicable for the calculation of the diffusion coefficient.

3.3. Diffusion of Cu(I) ions in $\text{TMHA-Tf}_2\text{N}$ ionic liquid

Figure 4 shows the linear sweep voltammograms for the 12 mM $\text{Cu(Tf}_2\text{N)-TMHA-Tf}_2\text{N}$ ionic liquid solution using the same micro-disk electrode at 1 mV s^{-1} ; the data were collected at six different temperatures, ranging from 30 to 112 °C. The onset of the cathodic current was recognized at around 0.1 V vs. I^-/I_3^- at any temperature and the cathodic current increased with decreasing potential. Similarly to the case of the 100 mM CuSO_4 aqueous solution, the increase in current tapered off toward a potential of ca. -0.1 V, and the electrodeposition of copper showed a diffusion limiting current in the lower potential region, while an effect of electrical migration was also found. Drawing tangents to the current-potential curves from both the lower and higher potential sides, the value of the limiting current for copper electrodeposition without the effect of electrical migration was determined from the intercept, P , of the tangents, as indicated by dashed lines in Figure 4 for

Table 1. Diffusion coefficients D_{IL} and D_{aq} ($10^{-6} \text{ cm}^2 \text{ s}^{-1}$) of Cu(I) ions in 12 mM $\text{Cu(Tf}_2\text{N)-TMHA-Tf}_2\text{N}$ ionic liquid solution and of Cu(II) ions in 100 mM CuSO_4 aqueous solution, respectively

Diffusion coefficients	Temperature / °C								
	25	30	40	50	55	75	90	107	112
D_{aq}	8.2		13		16				
D_{IL}		0.3		1.2		3.5	5.7	7.8	10

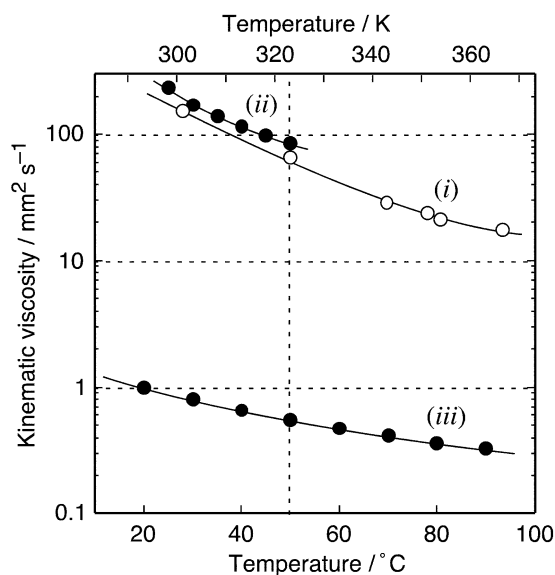


Fig. 5. Temperature dependence of kinematic viscosity of (i) pure TMHA-Tf₂N, (ii) 10 mM Cu(Tf₂N)₂-TMHA-Tf₂N ionic liquid solution, and (iii) pure H₂O.

112 °C. The diffusion coefficients were calculated from these limiting currents at each temperature using Equation 4. Table 1 summarizes the diffusion coefficient, D_{IL} , of Cu(I) ions in the 12 mM Cu(Tf₂N)-TMHA-Tf₂N ionic liquid solution together with those of Cu(II) ions, D_{aq} , in the 100 mM CuSO₄ aqueous solution at various temperatures. The D_{IL} values are one order smaller than D_{aq} when compared at a subequal temperature; for example, D_{IL} was $1.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at 50 °C, while D_{aq} was $1.6 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 55 °C. Figure 5 shows the temperature dependence of the kinematic viscosity of (i) pure ionic liquid TMHA-Tf₂N, (ii) 10 mM Cu(Tf₂N)₂-TMHA-Tf₂N ionic liquid solution (before the conversion of Cu(II) to Cu(I)), and (iii) pure water. The kinematic viscosity was measured with a vibration-type viscometer (VM-1G; CBC Materials Co., Ltd.) calibrated using a standard solution (NIPPON GREASE Co., Ltd.) with a kinematic viscosity of $20.11 \text{ mm}^2 \text{ s}^{-1}$ at 20 °C. The TMHA-Tf₂N itself has a high kinematic viscosity; as high as $65 \text{ mm}^2 \text{ s}^{-1}$ (50 °C), which is two orders of magnitude greater than that of pure water. The addition of 10 mM Cu(Tf₂N)₂ to TMHA-Tf₂N leads to a further increase in the viscosity as high as $86 \text{ mm}^2 \text{ s}^{-1}$ (50 °C). The smaller D_{IL} values compared to D_{aq} result from the higher viscosity, which inhibits the migration of copper ions. Seen from another standpoint, however, we can consider that the diffusion of Cu(I) in TMHA-Tf₂N is relatively fast compared to that of Cu(II) in water, since D_{IL} values are only one order smaller than D_{aq} , while the viscosities are two orders larger. Considering the Stokes-Einstein relationship where the solvodynamic radius of the diffusing copper entities is proportional to $(\eta D)^{-1}$ (η : viscosity), this might be due to the difference in the coordination environment of copper ions: Cu(II) ions in aqueous solution are tightly coordinated by six H₂O molecules, while Cu(I) ions in TMHA-Tf₂N only interact mildly with the large Tf₂N⁻ monovalent

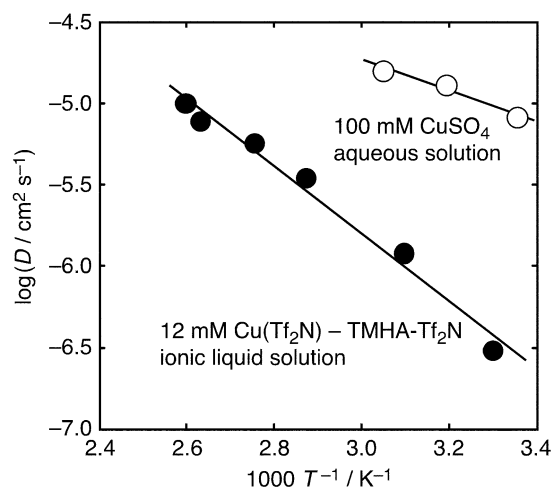


Fig. 6. Arrhenius plots of diffusion coefficients of Cu(I) ions in 12 mM Cu(Tf₂N)-TMHA-Tf₂N ionic liquid solution and of Cu(II) ions in 100 mM CuSO₄ aqueous solution.

anion(s). Recently, Abbott showed that the movement of ions in ionic liquids is controlled by the movement of the holes [21]. Given that the solvodynamic radius of Cu(I) ions in TMHA-Tf₂N is smaller than that of TMHA⁺ ions, the relatively fast diffusion of Cu(I) may be accounted for by the hole theory. In any case, such a slow ionic diffusion in TMHA-Tf₂N can become an obstacle when applying the liquid to electrochemical deposition technology. It should be noted, however, that the D_{IL} value rapidly increased with rising temperature, being $1.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 112 °C, which is almost the same as D_{aq} in aqueous solutions at ambient temperatures. Although ionic liquids are sometimes termed “room-temperature molten salts,” we should not adhere to the use of ionic liquids at room temperatures. We have recently been investigating the electrochemical alloying of a Cu-Sn layer at middle to low temperatures, 120–150 °C, using TMHA-Tf₂N as electrolyte [17]. At elevated temperatures, the advantages of ionic liquids, i.e. nonvolatility and nonflammability, can be exploited without the drawback regarding ion transport.

Figure 6 shows the Arrhenius plot of the diffusion coefficient of Cu(I) ions in 12 mM Cu(Tf₂N)-TMHA-Tf₂N solution. The diffusion coefficient of Cu(II) ions in the 100 mM CuSO₄ aqueous solution are also indicated for comparison. The activation energy of the diffusion of Cu(I) ions in TMHA-Tf₂N was estimated to be 39 kJ mol^{-1} , while that of Cu(II) ions in CuSO₄ aqueous solutions is 20 kJ mol^{-1} . It is clear that the kinematic viscosity of TMHA-Tf₂N decreased more rapidly with increasing temperature compared to that of H₂O. Owing to this, the activation energy of diffusion in TMHA-Tf₂N is larger.

4. Conclusion

A set of cyclic and linear sweep voltammograms were measured for the TMHA-Tf₂N ionic liquid containing

12 mM Cu(Tf₂N) to examine the redox behavior of Cu(I)/Cu and the mass transfer of Cu(I) ions using a micro-disk electrode. A scan rate of 1 mV s⁻¹ was found to be appropriate to obtain the steady state cathodic polarization curves under the experimental conditions. The Cu(I)/Cu redox formal potential was found to lie in the potential range 0.1–0.2 V vs. I⁻/I₃⁻ for the ionic liquid solution at 50 °C. The diffusion coefficient of Cu(I) ions in TMHA-Tf₂N was determined from the diffusion limiting current in the linear scanning voltammogram at temperatures from 30 to 112 °C. The diffusion coefficient at 50 °C was 1.2 × 10⁻⁶ cm² s⁻¹, which was one order of magnitude less than that of Cu(II) ions in aqueous CuSO₄ solution, due to the high viscosity of the ionic liquid. The diffusion coefficient of Cu(I) ions, however, increased with increase in temperature, reaching 1.0 × 10⁻⁵ cm² s⁻¹ at 112 °C. This is comparable to the value for Cu(II) ions in aqueous CuSO₄ solutions at ambient temperature. The activation energy of Cu(I) diffusion was 39 kJ mol⁻¹ in the ionic liquid and was about two times larger than that in aqueous media. This is accounted for by the temperature dependence of the kinematic viscosity of the ionic liquid, which decreases more rapidly with increasing temperature compared to the case of aqueous solution.

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