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Electrode Kinetics of the Redox Reaction of Tris(2,2′-bipyridine) nickel Complexes in an Ionic Liquid

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ABSTRACT

Electrode reaction of tris(2,2′-bipyridine)nickel complexes, $[Ni(bpy)_3]^{3+}$ and $[Ni(bpy)_3]^{2+}$, was investigated in an aprotic ionic liquid, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide (BMPTFSA) using AC impedance spectroscopy. The formal potential of $[Ni(bpy)_3]^{3+/2+}$ was 1.37 V vs. ferrocene/ferrocenium at 25 °C. The diffusion coefficients of $[Ni(bpy)_3]^{3+}$ and $[Ni(bpy)_3]^{2+}$ at 25 °C were 4.2 and 7.0×10^{-8} cm^2 s^{-1}, respectively, which are close to those of $[M(bpy)_3]^{3+}$ and $[M(bpy)_3]^{2+}$ (M = Ru and Fe) due to the similarity in the charge densities. The activation energies for the diffusion coefficients were close to that for the viscosity of the ionic liquid, indicating the viscosity is a major factor that determine the diffusion of the complexes. The rate constant of $[Ni(bpy)_3]^{3+/2+}$ was 8.3×10^{-6} cm s^{-1}, which is smaller by two orders of magnitude than those for $[Ru(bpy)_3]^{3+/2+}$ and $[Fe(bpy)_3]^{3+/2+}$, reflecting the slow electron transfer caused by participation of the anti-bonding molecular orbital in the redox reaction. The apparent activation energy for the rate constant of $[Ni(bpy)_3]^{3+/2+}$ is considered determined not only by the activation energy for the viscosity but also by the reorganization energy, of which the inner component is larger than those in $[Ru(bpy)_3]^{3+/2+}$ and $[Fe(bpy)_3]^{3+/2+}$.

1. Introduction

Aprotic ionic liquids have been expected to be promising electrolytes alternative to conventional organic electrolytes due to intrinsic ionic conductivity, negligible volatility and wide electrochemical potential window[1]. Ionic liquids can be liquid at low temperature since they are composed of the bulky ions, of which the electrostatic interaction is weak. On the other hand, bulkiness of the constituent ions often leads to high viscosity and slow dynamics, which are expected to affect electrode kinetics of electroactive species in ionic liquids. We have already studied the electrode reactions of tris(2,2′-bipyridine) complexes of some transition metals ($[M(bpy)_3]^{n+}$) in the ionic liquids consisting of bis(trifluoromethylsulfonyl)amide (TFSA$^-$)[2–4]. It has been found that the diffusion of the charged species is affected not only by the viscosity of the ionic liquids but also by the coulombic interaction of the diffusing species with the ions composing the ionic liquids. Although the redox reactions of the bpy complexes are classified into an outer-sphere electron transfer reaction, the rate constant has been found to depend strongly on the viscosity, which is mainly related to the frequency (or pre-exponential) factor of Arrhenius-type expression of the rate constant. According to Marcus theory, the rate constant is related to the reorganization energy, which is divided into inner and outer components[5]. The inner component of the reorganization energy is mainly related to the change of bond length between the center atom and the ligands. The outer component of the reorganization energy in polar solvents is given by dielectric interaction between the complex and the solvent molecules. In case of ionic liquids, however, the outer component of the reorganization energy is expected to be replaced with the coulombic and inter-molecular interactions between the complex and the ions composing the ionic liquids. On the other hand, the inner component is considered independent of the physical properties of reaction media. In the present study, the influence of the inner component of the reorganization energy on the electrode kinetics of the bpy complexes was investigated in an TFSA$^-$-based ionic liquid, BMPTFSA (BMP$^+$ = 1-butyl-1-methylpyrrolidinium).

The redox reactions of metal complexes are expected to be applicable for the redox flow batteries using aprotic ionic liquids[6–10]. Since the electrochemical potential window of aprotic ionic liquids is often wider than that of aqueous solution, it may be possible to realize the larger cell voltage, which leads to increase the energy density. The bpy complexes are promising electroactive species for redox flow batteries since they can take multiple valence states including the electron transfer to/from the bpy ligands. Although some bpy complexes are unstable in conventional organic solvents[11], there is a possibility that such bpy complexes are stabilized in the ionic liquid based on TFSA$^-$, of which the

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donor ability is much lower than those of conventional organic solvents[8]. In this study, the redox reaction between divalent and trivalent tris(bpy) nickel complexes was investigated in BMPTFSA.

2. Experimental

BMPBr was prepared by the reaction of 1-methylpyrrolidine (Tokyo Chemical Industry, 98%) with butyl bromide (Tokyo Chemical Industry, 98%) in acetonitrile (Junsei Chemical, 99.5%) at ambient temperature. Then, BMPBr was purified by recrystallization from its acetonitrile solution with ethyl acetate (Junsei Chemical, 99.5%) for three times and finally dried under vacuum at 120 °C for 24 hours[12]. BMPTFSA was prepared by the metathesis reaction between BMPBr and LiTFSA (Kanto Chemical, 99.9%) in deionized water, then extracted into dichloromethane (Junsei Chemical, 99.5%), separated by evaporation and finally dried under vacuum at 120 °C for 24 hours. The water content of BMPTFSA was found to be below 10 ppm by Karl Fischer titration (Metrohm, 831KF Coulometer). $Ni(TFSA)_2$ was prepared by reacting $NiCO_3 \cdot Ni(OH)_2 \cdot 4H_2O$ (Kanto Chemical) with HTFSA (Morita Chemical Industry, 99%) aqueous solution at 80 °C, filtered to separate unreacted starting materials and finally dried under vacuum at 160 °C for 24 hours[13]. $[Ni(bpy)_3]^{2+}$ was introduced by adding $Ni(TFSA)_2$ and bpy (Wako Pure Chemical Industries, 99.5%) at a molar ratio of 1 : 3 into BMPTFSA. All the hygroscopic reagents were stored and handled in an argon filled glove box with a continuous gas purification apparatus (Miwa MFG, DBO-1KP-K01). The concentrations of water and oxygen were kept below 800 ppb and 1 ppm, respectively.

Electrochemical measurements were conducted with an air-tight three-electrode cell using a potentio/galvanostat (Hokuto Denko, HABF-501). A platinum disk (3 mmϕ) was used as a working electrode. The active area of the platinum disk was mechanically polished and washed with deionized water before use. A platinum wire was used as a counter electrode. A silver wire immersed in EMITFSA (EMI^+ = 1-ethyl-3-methylimidazolium, Kanto Chemical) containing 0.1 M $AgCF_3SO_3$ (Aldrich, 99%) was used as a reference electrode. All the potentials in this paper were given against this reference electrode denoted as Ag/Ag(I). The potential of this reference electrode was +0.44 V vs. ferrocene (Fc)/ferrocenium (Fc^+) couple in BMPTFSA at 25 °C[9]. The temperatrure dependence of the potential of the reference electrode is 0.55 ± 0.02 mV K^{-1}[14]. Bulk electrolysis was conducted in order to prepare the ionic liquid containing both $[Ni(bpy)_3]^{2+}$ and $[Ni(bpy)_3]^{3+}$ at the same concentration. A two-compartment cell separated by a glass filter was used for the bulk electrolysis, in which carbon felt was used as the cathode and anode. AC impedance measurements were carried out with PARSTAT 2273 (Princeton Applied Research). The AC amplitude was ±10 mV rms. The frequency range was from 1 Hz to 10 kHz. The influence of the reference electrode on the impedance measurements was assumed to be negligible in this study. The viscosity of the ionic liquid was measured by a vibronic viscometer (Yamaichi Electric, VM-1G-L). The ultra-violet and visible (UV-VIS) absorption spectrum of the ionic liquid was taken by UV-VIS spectrometer (JASCO, V-530) with an air-tight quartz cell (light path length: 1 mm).

3. Results and Discussion

$Ni(TFSA)_2$ dissolved in BMPTFSA to give a pale green ionic liquid, indicating Ni^{2+} is octahedrally coordinated by six oxygen atoms of $TFSA^-$anions[13]. When bpy was added to the ionic liquid at the molar ratio of Ni^{2+}: bpy = 1: 3, the color of the ionic liquid turned to pale pink. The UV-VIS spectrum of the ionic liquid gave two absorption bands at 521 and 787 nm, which were close to those observed in the aqueous solution containing $[Ni(bpy)_3](ClO_4)_2$, 521 and 790 nm, respectively[15]. Thus, it was confirmed that $[Ni(bpy)_3]^{2+}$ was introduced in BMPTFSA. Fig. 1 shows the cyclic voltammogram of a platinum electrode in BMPTFSA containing 40 mM $[Ni(bpy)_3]^{2+}$. Two pairs of anodic and cathodic current peaks were observed around +1.0 (A1/C1) and–2.1 (A2/C2) V. It has been reported that $[Ni(bpy)_3]^{2+}$ can be oxidized to $[Ni(bpy)_3]^{3+}$ in liquid SO_2[16] and acetonitrile[15,17]. Thus, the redox current peaks observed at the positive potential region can be assigned to the following reaction.

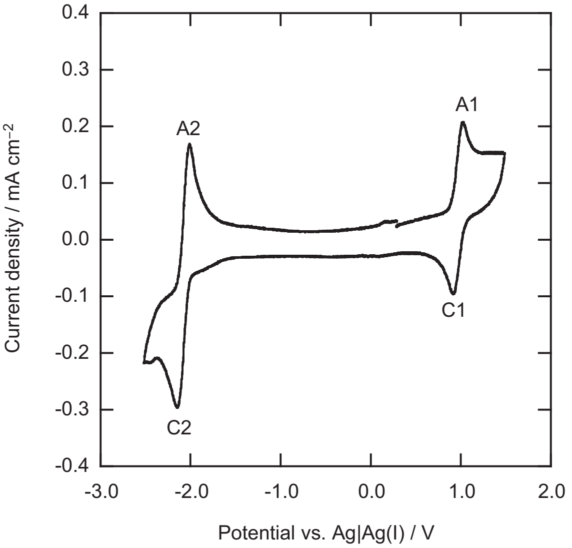

Fig. 1. Cyclic voltammogram of a Pt electrode in BMPTFSA containing 40 mM $[Ni(bpy)_3]^{2+}$ at 25 °C. Scan rate: 10 mV s^{-1}.

$$[Ni(bpy)_3]^{3+} + e^- \rightleftarrows [Ni(bpy)_3]^{2+} \quad (1)$$

The cathodic current peak at–2.1 V is considered corresponding to the two-electrode transfer reduction of $[Ni(bpy)_3]^{2+}$ to $Ni(bpy)_3$, which have been reported in acetonitrile [17,18] and propylene carbonate [6].

$$[Ni(bpy)_3]^{2+} + 2e^- \rightleftarrows Ni(bpy)_3 \quad (2)$$

In case of acetonitrile, further reduction of $Ni(bpy)_3$ and/or liberation of bpy from the complexes have been reported to occur[17,18], probably due to stronger donor ability of acetonitrile as compared with that of BMPTFSA[8]. On the other hand, $[Ni(bpy)_3]^{2+}$ is also reported to be reduced to $[Ni(bpy)_3]^+$ as is the case for $[M(bpy)_3]^{2+}$ (M = Fe and Ru)[19]. In this study, only the redox reaction between $[Ni(bpy)_3]^{3+}$ and $[Ni(bpy)_3]^{2+}$ was investigated in detail.

Fig. 2 shows the cyclic voltammograms of a platinum electrode in BMPTFSA containing 40 mM $[Ni(bpy)_3]^{2+}$ at various scan rates within the potential range including the redox reaction between $[Ni(bpy)_3]^{3+}$ and $[Ni(bpy)_3]^{2+}$. The anodic peak potential shifted to more positive side with an increase in the scan rate. In addition, the separation between the half peak potential and the peak potential at 10 mV s^{-1} was 83 mV, which was larger than the theoretical value for a one-electron transfer reversible reaction (56.5 mV) at 25 °C[20]. Thus, the electrode reaction can be regarded as quasi- or irreversible. Bulk electrolysis was conducted in order to prepare the ionic liquid containing both $[Ni(bpy)_3]^{3+}$ and $[Ni(bpy)_3]^{2+}$ at the same concentration. Fig. 3 shows the open circuit potential of a platinum electrode during the bulk electrolysis on the logarithm of the concentration ratio of $[Ni(bpy)_3]^{3+}$ to $[Ni(bpy)_3]^{2+}$. The concentration was calculated assuming the current efficiency to be 100%. The plots could be fitted to a straight line with a slope of 60 mV, which was consistent with the theoretical value for a one-electron