

Effects of the Charge Density of the Anions of Ionic Liquids on the Electrode Kinetics of Ruthenium 2,2'-Bipyridine Complexes

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The electrode reaction of ruthenium 2,2'-bipyridine complexes has been investigated in 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF₄) ionic liquid. The diffusion of the ruthenium complexes in EMIBF₄ was slower than that we have reported in EMITFSA (TFSA⁻ = bis(trifluoromethylsulfonyl)amide), of which the viscosity (36 mPa s) is close to that of EMIBF₄ (37 mPa s). The rate constant of the ruthenium redox couple in EMIBF₄ was also smaller than that in EMITFSA. It was suggested that the difference in these kinetic parameters in EMIBF₄ and EMITFSA is ascribed to the coulombic interaction between the positively charged species and the anions of ionic liquids.

Introduction

Electrode reactions of iron and ruthenium 2,2'-bipyridine (bpy) complexes have been investigated in some amide-type ionic liquids (1,2). The diffusion coefficients of [Fe(bpy)₃]²⁺ and [Fe(bpy)₃]³⁺ are close to those of [Ru(bpy)₃]²⁺ and [Ru(bpy)₃]³⁺ in the same ionic liquid, suggesting the diffusion of these species is primarily affected by the viscosity of the ionic liquid, as predicted by Stokes-Einstein equation (3). However, the diffusion coefficient of [M(bpy)₃]²⁺ (M = Fe or Ru) is larger than that of [M(bpy)₃]³⁺, indicating the diffusion of a charged species is also influenced by the coulombic interaction between the diffusing species and the ions of ionic liquid. In case of [Ru(bpy)₃]^{3+/2+} couple, the ratio of the diffusion coefficient of [Ru(bpy)₃]³⁺ to that of [Ru(bpy)₃]²⁺ was found to depend on the charge density of the anion of ionic liquids (2). Thus, the coulombic interaction is considered one of the major factor in the diffusion of the charged species in addition to the viscosity (4).

On the other hand, the rate constant of [Ru(bpy)₃]^{3+/2+} couple is also dependent on the viscosity of ionic liquids, as reported for ferrocenium (Fc⁺)/ferrocene (Fc) couple (2,5). The dependence of the rate constants for outer-sphere electron transfer reactions on the viscosity is often explained by the solvent dynamics, which mainly affects the frequency (or pre-exponential) factor in Arrhenius equation. Although the apparent activation energy for the rate constants of Fc⁺/Fc or [Fe(bpy)₃]^{3+/2+} couple is close to that for the viscosity of the ionic liquid, the activation energy for the rate constant of [Ru(bpy)₃]^{3+/2+} couple was obviously larger than that for the viscosity (2), indicating the reorganization energy appearing in Marcus theory contributes to the apparent activation energy. In the present study, the electrode reaction of [Ru(bpy)₃]^{3+/2+} couple was investigated in 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF₄) ionic liquid in order to elucidate the

influence of the charge density of anion on such kinetic parameters, as diffusion coefficient and rate constant, at various temperatures.

Experimental

EMIBF₄ was purchased from Kanto Chemical and used as supplied. The water content of EMIBF₄ was confirmed to be below 10 ppm by Karl Fischer titration (Metrohm, 831 KF). EMITFSA was prepared by interacting EMICl (Kanto Chemical) with LiTFSA (Kanto Chemical), followed by extraction into dichloromethane, separated by evaporation, and finally dried under vacuum (2). [Ru(bpy)₃](BF₄)₂ was prepared by the reaction between [Ru(bpy)₃]Cl₂·6H₂O (Aldrich, 99.5%) and NaBF₄ (Wako Pure Chemical Industries, 98%) in deionized water and dried under vacuum at 120 °C. Platinum was used as a working and counter electrode. Silver wire immersed in 0.1 M AgCF₃SO₃ (Aldrich, 99%) / EMITFSA was used as a reference electrode. The potential of this reference electrode was 0.46 V vs. Fc/Fc⁺ in EMIBF₄. The viscosity of ionic liquid was measured by a vibronic viscometer (Yamaichi Electric, VM-1G-L). All the electrochemical measurements were conducted with the aid of potentiogalvanostats, HABF-501 (Hokuto denko) and PARSTAT 2263 or 2273 using an air-tight electrochemical cell assembled in a glove box filled with dry argon (Miwa MFG, DBO-1KP-K01 and DBO-1K-SH).

Results and Discussion

Figure 1 shows the cyclic voltammograms of a Pt electrode in EMIBF₄ containing 40 mM [Ru(bpy)₃](BF₄)₂ at 25 °C at various scan rates. The anodic current peak around 0.5 V was assigned to the oxidation from [Ru(bpy)₃]²⁺ to [Ru(bpy)₃]³⁺. The cathodic current peak around 0.3 V was ascribed to the reduction of [Ru(bpy)₃]³⁺, which formed during the preceding anodic potential sweep. The anodic peak potential shifted slightly to the more positive side with an increase in the scan rate, probably reflecting the ohmic drop due to low conductivity of the ionic liquid. There was a linear dependence of the anodic peak current density on the square root of scan rate, as shown in Fig. 2. The difference between the peak and the half peak potential at 10 mV s⁻¹ was 60 mV, which is consistent with the theoretical value for reversible one-electron transfer electrode reaction. Thus, the redox reaction of [Ru(bpy)₃]^{3+/2+} couple in EMIBF₄ can be regarded as electrochemically reversible in the time scale of the cyclic voltammograms.

Potentiostatic bulk electrolysis of EMIBF₄ containing [Ru(bpy)₃]²⁺ was conducted in order to prepare the ionic liquid containing both [Ru(bpy)₃]²⁺ and [Ru(bpy)₃]³⁺ using a two-compartment cell, in which the counter electrode was separated from the ionic liquid containing the ruthenium species with a glass filter. The open circuit potentials of a Pt electrode immersed in the ionic liquid were plotted against the various logarithmic concentration ratio of [Ru(bpy)₃]³⁺ to [Ru(bpy)₃]²⁺, as shown in Fig. 3, assuming the current efficiency for oxidation of [Ru(bpy)₃]²⁺ to [Ru(bpy)₃]³⁺ to be 100%. The slope of plots was 59 mV decade⁻¹, which was consistent with the theoretical value for a one-electron transfer reaction at 25 °C. The formal potential was found to be 0.39 V vs. Ag/Ag(I), which was corresponding to 0.85 V vs. Fc/Fc⁺. The formal potential in EMIBF₄ was more negative than that in EMITFSA, 0.91 V vs. Fc/Fc⁺ (2), suggesting the

coulombic interaction of the cationic ruthenium species with $[\text{BF}_4]^-$ is stronger than that with TFSA^- .

Table I. Formal potential (E°) and diffusion coefficients of $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{bpy})_3]^{3+}$ (D_{2+} and D_{3+}) in EMIBF₄, EMITFSA, and acetonitrile. The ratio of D_{3+} to D_{2+} , viscosity (η), and the activation energy (E_a) for D_{2+} , D_{3+} , and η , are also listed.

	E° V vs. Fc/Fc ⁺	$10^8 D_{2+}$ $\text{cm}^2 \text{mol}^{-1}$	$E_a(D_{2+})$ kJ mol^{-1}	$10^8 D_{3+}$ $\text{cm}^2 \text{mol}^{-1}$	$E_a(D_{3+})$ kJ mol^{-1}	D_{3+}/D_{2+} -	η mPa s	$E_a(\eta)$ kJ mol^{-1}	Ref
EMIBF ₄	0.85	7.8 ± 0.1	23	3.3 ± 0.1	25	0.42	37	30	This study
EMITFSA	0.91	15 ± 1	25	9.5 ± 0.3	25	0.65	36	26	2
Acetonitrile	0.89	970							6

Diffusion coefficients of $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{bpy})_3]^{3+}$ were examined in EMIBF₄ containing both 20 mM $[\text{Ru}(\text{bpy})_3]^{2+}$ and 20 mM $[\text{Ru}(\text{bpy})_3]^{3+}$ at various temperatures. Figure 4 shows the chronoamperograms of a Pt electrode in the ionic liquid at 25 °C. The electrode potential was stepped to ± 0.1 , 0.2 and 0.3 V from the reversible potential. Since the current decay at ± 0.2 V was identical to that at ± 0.3 V, the step potentials were fixed at ± 0.3 V from the reversible potential. Cottrell plots were constructed based on the chronoamperograms, as shown in Fig. 5. The plots at each temperature were proportional to the inverse of square root of time. The calculated diffusion coefficients at 25 °C were listed in Table I, together with those in EMITFSA (2) and acetonitrile (6). The diffusion coefficients of $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{bpy})_3]^{3+}$ at 25 °C were $(7.8 \pm 0.1) \times 10^{-8}$ and $(3.3 \pm 0.1) \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, respectively. The viscosity of EMIBF₄ containing both 20 mM $[\text{Ru}(\text{bpy})_3]^{2+}$ and 20 mM $[\text{Ru}(\text{bpy})_3]^{3+}$ at 25 °C was 37 mPa s, which was close to that of EMITFSA containing both 20 mM $[\text{Ru}(\text{bpy})_3]^{2+}$ and 20 mM $[\text{Ru}(\text{bpy})_3]^{3+}$, 36 mPa s (2). However, the diffusion coefficient of $[\text{Ru}(\text{bpy})_3]^{2+}$ in EMITFSA was $(1.5 \pm 0.1) \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, which is larger than that in EMIBF₄, indicating the diffusion in these ionic liquids can not be explained by Stokes-Einstein relation, in which coulombic retarding force is not taken into account in addition to viscous retarding force (4). The diffusion coefficients in EMIBF₄ are considered smaller than those in EMITFSA probably because the charge density of $[\text{BF}_4]^-$ is higher than that of TFSA^- . The ratio of the diffusion coefficient of $[\text{Ru}(\text{bpy})_3]^{3+}$ to that of $[\text{Ru}(\text{bpy})_3]^{2+}$ can be regarded as an index for the coulombic interaction between the cationic diffusing species and the anion of ionic liquid. The ratio is expected to get smaller when the coulombic interaction gets stronger. The ratio in EMIBF₄ is 0.42, while that in EMITFSA is 0.65, indicating the diffusion of the cationic species in EMIBF₄ is slower in EMITFSA even if the viscosity is close to each other. Arrhenius plots of the diffusion coefficients calculated from the slopes are shown in Fig. 6. The activation energies for the diffusion coefficients of $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{bpy})_3]^{3+}$ were calculated to be 23 and 25 kJ mol^{-1} , respectively, which were close to that for the viscosity of ionic liquid, 30 kJ mol^{-1} , indicating the viscosity is still a major factor that affects the diffusion in the ionic liquid.

Figure 7 shows the Nyquist plots for the electrochemical impedance of a Pt electrode in EMIBF₄ containing both 20 mM $[\text{Ru}(\text{bpy})_3]^{2+}$ and 20 mM $[\text{Ru}(\text{bpy})_3]^{3+}$ at the reversible potential. The plots were analyzed according to an equivalent circuit shown in the inset of Fig. 7. The rate constant was calculated from the charge transfer resistance (R_{ct}), as listed in Table II together with some reference information. The rate constant at 25 °C in EMIBF₄ was $(6.7 \pm 0.2) \times 10^{-5} \text{ cm s}^{-1}$, which was smaller than that in EMITFSA, $(2.7 \pm 0.1) \times 10^{-3} \text{ cm s}^{-1}$. Figure 8 shows Arrhenius plots for the rate constants. The

activation energy for the rate constant was calculated to be 46 kJ mol⁻¹, which is larger than that in EMITFSA, 37 kJ mol⁻¹.

TABLE II. Rate constant (k°) of [Ru(bpy)₃]^{3+/2+} couple in EMIBF₄ and EMITFSA at 25 °C. The viscosity (η) and the activation energies (E_a) for the rate constant and viscosity are also given.

Ionic liquid	k° cm s ⁻¹	η mPa s	E_a for k° kJ mol ⁻¹	E_a for η kJ mol ⁻¹	Ref.
EMIBF ₄	$(6.7 \pm 0.2) \times 10^{-5}$	37	46	30	This study
EMITFSA	$(2.7 \pm 0.1) \times 10^{-3}$	36	37	26	2

The rate constant of an outer-sphere electron transfer reaction, k , can be represented by the following equation based on Marcus theory (7).

$$k = K_p \nu_n \kappa_{el} \exp\left(-\frac{\Delta^\ddagger G}{RT}\right) \quad [1]$$

where K_p is a precursor equilibrium constant, ν_n is the nuclear frequency factor, κ_{el} is the electronic transmission coefficient, and $\Delta^\ddagger G$ is the activation Gibbs energy. $\Delta^\ddagger G$ can be given by the following relation.

$$\Delta^\ddagger G = \frac{\lambda}{4} \left(1 + \frac{F(E - E^\circ)}{\lambda}\right)^2 \quad [2]$$

where λ is the reorganization energy, E is the electrode potential, and E° is the standard electrode potential. Thus, $\Delta^\ddagger G$ is equal to $\lambda/4$ at $E = E^\circ$. λ is divided into two components. One is the inner reorganization energy, which corresponds to the energy required for changing the chemical bonds in a complex. The other is the outer reorganization energy, which is related to the interaction between the complex and the species surrounding the complex. Since ν_n is known to approximately inversely proportional to the viscosity, there must be the contribution of the activation energy for the viscosity in the apparent activation energy for the rate constant. We have reported the activation energy for the rate constant of [Fe(bpy)₃]^{3+/2+} couple in BMPTFSA is close to that for the viscosity of ionic liquid (1), indicating the contribution of reorganization energy to the activation energy is small. In case of [Ru(bpy)₃]^{3+/2+} couple in BMPTFSA, however, the activation energy for the rate constant is larger than that for the viscosity, suggesting the inner reorganization energy contributes to the activation energy of the rate constant (2). The large activation energy for the rate constant of [Ru(bpy)₃]^{3+/2+} couple in EMIBF₄ as compared with that in EMITFSA implies the contribution of the outer reorganization energy due to the strong coulombic interaction between the ruthenium species and [BF₄]⁻.

Conclusions

Coulombic interaction between a redox couple and an ionic liquid has been found to affect not only the diffusion of species but also the rate constant of redox reaction. Although the viscosity of EMIBF₄ is very close to that of EMITFSA, the diffusion of ruthenium-bipyridine complexes in EMIBF₄ was slower than that in EMITFSA,

indicating the coulombic retarding force for the positively charged species in EMIBF₄ is stronger than that in EMITFSA. The rate constant for [Ru(bpy)₃]^{3+/2+} couple in EMIBF₄ was smaller than that in EMITFSA, suggesting the outer reorganization energy for the positively charged species is sensitive to the charge density of the anion of ionic liquid.

Acknowledgements

Part of this study was financially supported by MEXT-Supported Program for the Strategic Research Foundation at Private Universities, 2012-2016.

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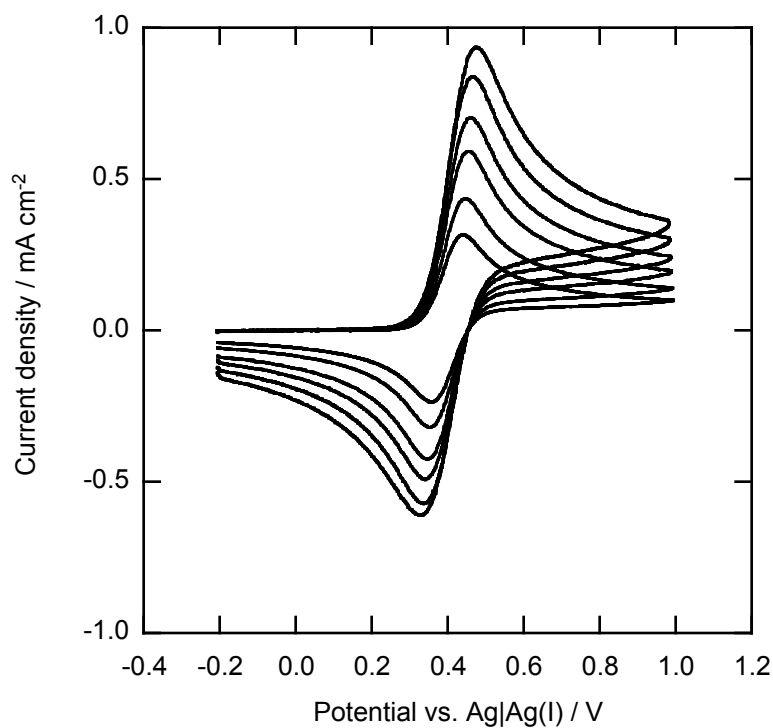


Figure 1. Cyclic voltammograms of a Pt electrode in EMIBF₄ containing 40 mM [Ru(bpy)₃](BF₄)₂ at 25 °C. Scan rates : 10, 20, 40, 60, 80, and 100 mV s⁻¹.

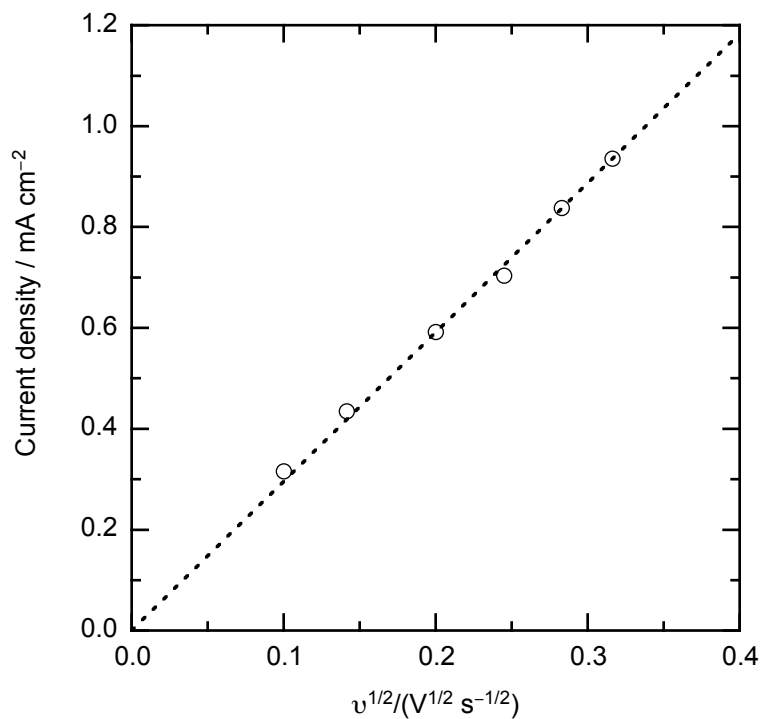


Figure 2. Dependence of the peak current density and the square root of scan rate for the cyclic voltammograms of a Pt electrode in EMIBF₄ containing 40 mM [Ru(bpy)₃](BF₄)₂ at 25 °C.

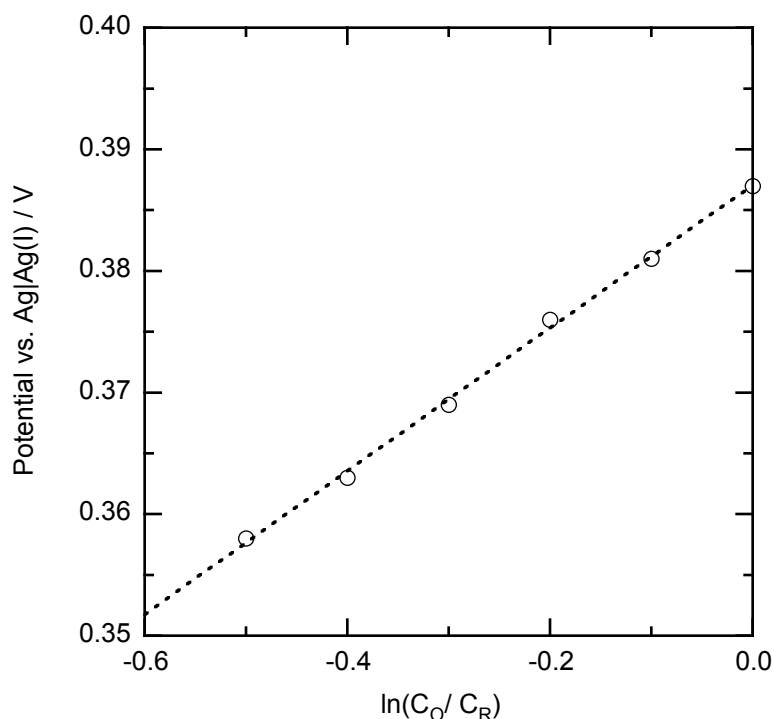


Figure 3. Open circuit potentials of a Pt electrode during the intermittent potentiostatic anodic oxidation from $[\text{Ru}(\text{bpy})_3]^{2+}$ to $[\text{Ru}(\text{bpy})_3]^{3+}$ in EMIBF₄ at 25 °C. The total concentration of $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{bpy})_3]^{3+}$ was 40 mM.

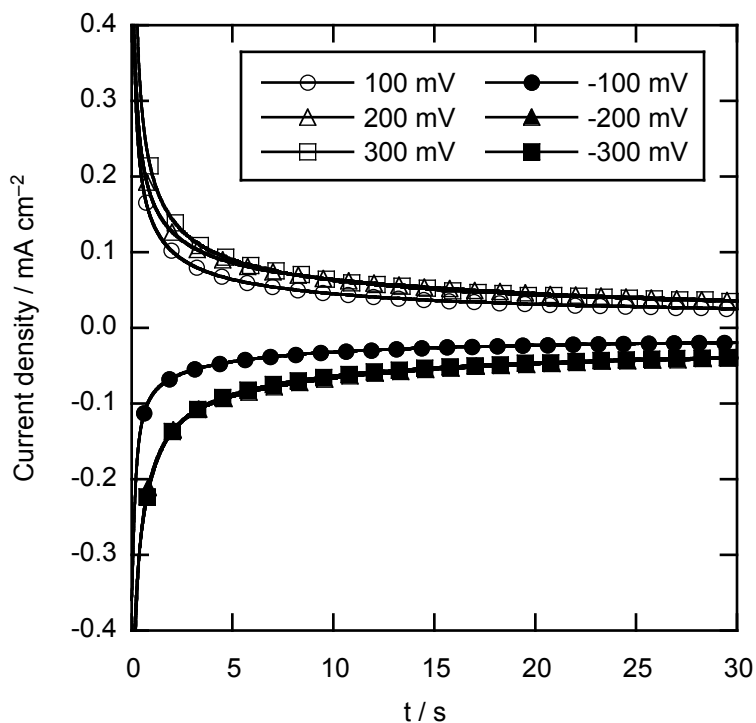


Figure 4. Chronoamperograms of a Pt electrode in EMIBF₄ containing both 20 mM $[\text{Ru}(\text{bpy})_3]^{2+}$ and 20 mM $[\text{Ru}(\text{bpy})_3]^{3+}$ at 25 °C. The step potentials were shown as the difference from the reversible potential.

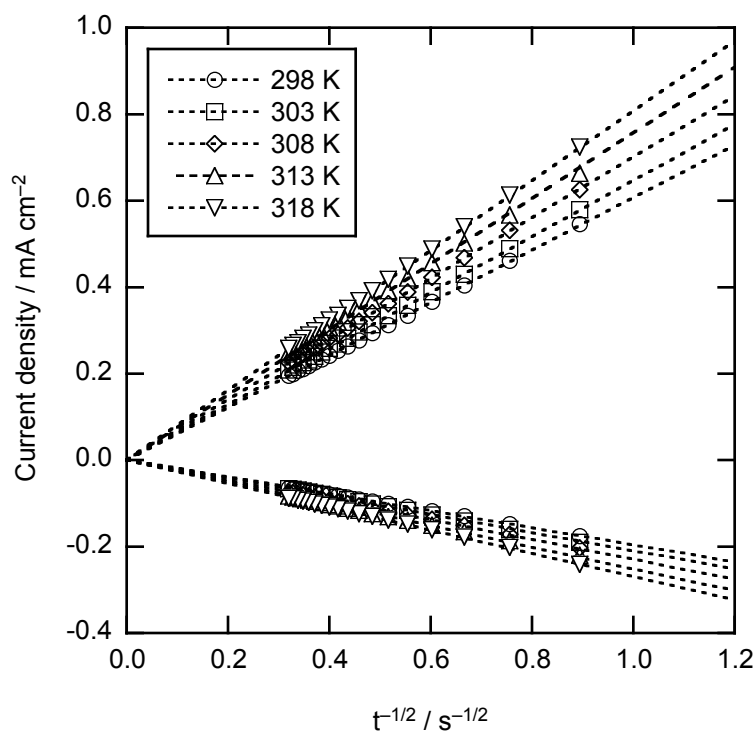


Figure 5. Cottrell plots for the chronoamperograms of a Pt electrode in EMIBF₄ containing both 20 mM [Ru(bpy)₃]²⁺ and 20 mM [Ru(bpy)₃]³⁺ at 25-45 °C. The step potential was ±300 mV from the reversible potential.

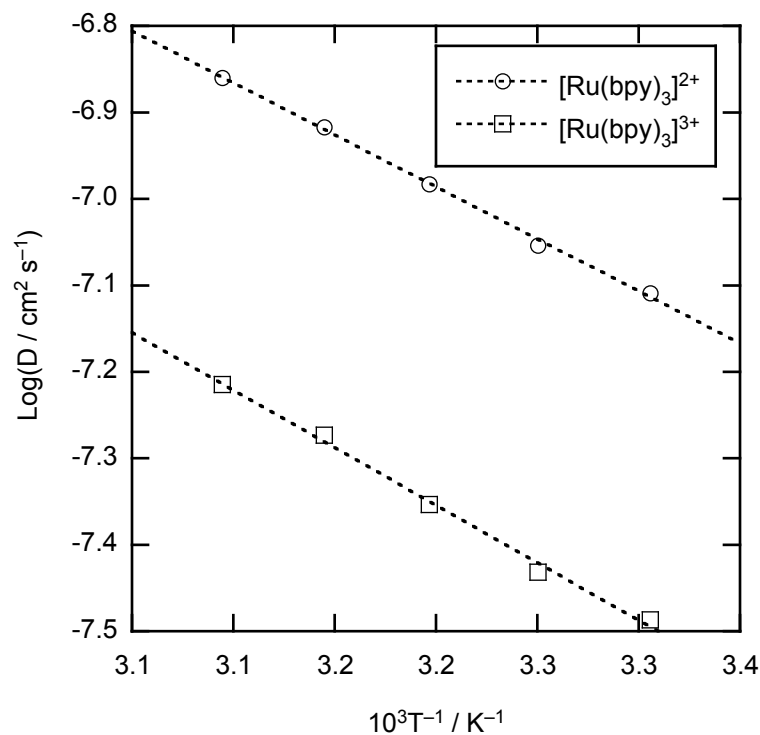


Figure 6. Arrhenius plots for the diffusion coefficients of [Ru(bpy)₃]²⁺ and [Ru(bpy)₃]³⁺ in EMIBF₄ containing both 20 mM [Ru(bpy)₃]²⁺ and 20 mM [Ru(bpy)₃]³⁺.

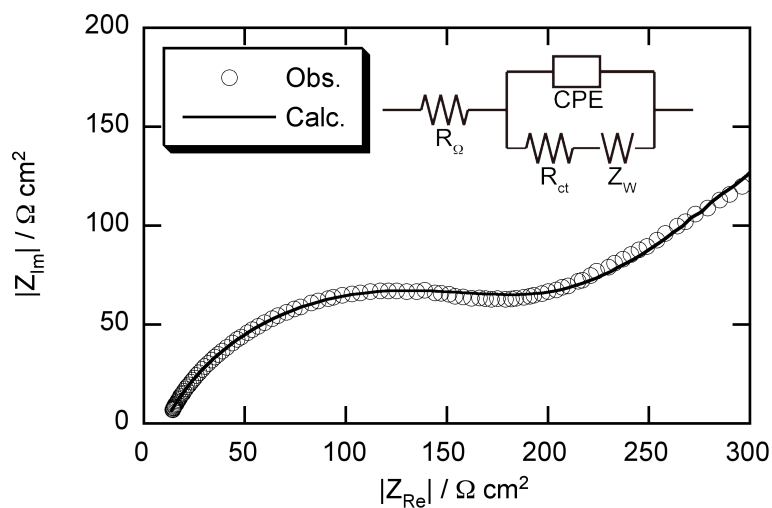


Figure 7. Nyquist plots of a Pt electrode in EMIBF₄ containing both 20 mM [Ru(bpy)₃]²⁺ and 20 mM [Ru(bpy)₃]³⁺ at 25 °C.

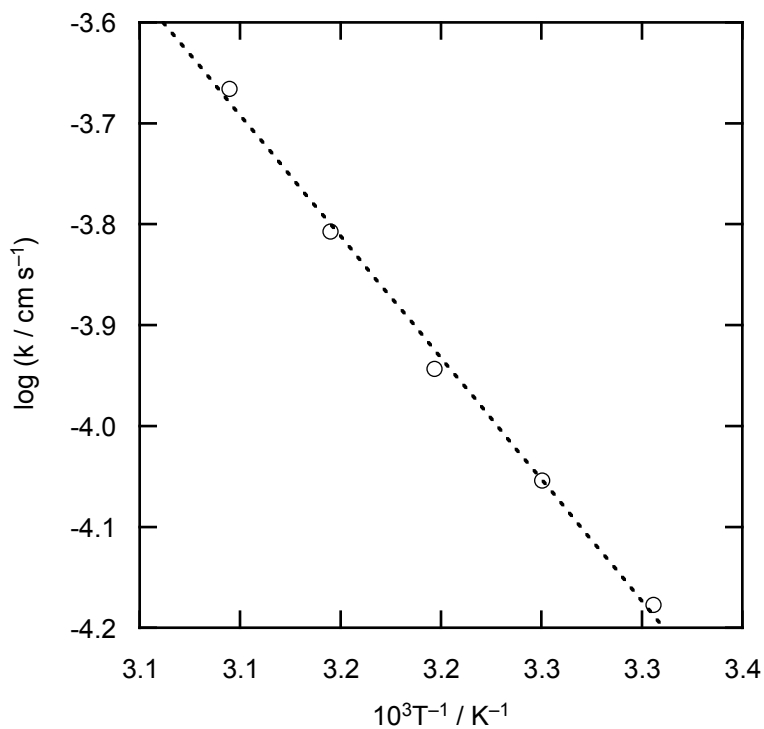


Figure 8. Arrhenius plots for the rate constants of a Pt electrode in EMIBF₄ containing both 20 mM [Ru(bpy)₃]²⁺ and 20 mM [Ru(bpy)₃]³⁺.