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Electrochemical Oxidation of Ruthenium and Iron Complexes at Rotating Disk Electrode in Acetonitrile Solution

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The diffusion coefficient and the apparent rate of charge-transfer have been determined for various ruthenium and iron complexes in an acetonitrile solution by using a rotating disk electrode (RDE) method. The diffusion coefficients of $[Ru(bpy)_3]^{2+}$, $[Ru(acac)_3]$, and $[Fe(bpy)_3]^{2+}$ (bpy: 2,2′-bipyridine, acac: acetylacetone), being similar to each other, were about 2×10^{-10} m^2 s^{-1} in acetonitrile containing 0.1 mol dm^{-3} $(C_2H_5)_4NBF_4$. The apparent rate of electrochemical oxidation increased in the order $[Ru(bpy)_3]^{2+}<[Ru(acac)_3]<[Fe(bpy)_3]^{2+}$. The order of the rates was reciprocal to the order of their oxidation potentials in the same electrolyte.

The electrochemistry of transition-metal complexes with organic ligands has been widely investigated by many workers.[1] Some complexes such as Fe, Co, Ru, and Os with 2,2′-bipyridine (bpy), ethylenediamine (en), and 1,10-phenanthroline (phen) as ligands are oxidized and reduced reversibly. The multi-step valence changes of these complexes can be utilized in a rechargeable battery system.[2] The authors have proposed new-type redox batteries consisting of Ru complexes as active materials and organic electrolyte solutions.[3,4] It has been found that the performances of such redox batteries are greatly influenced by the electrochemical reversibility, i.e. the rates of charge-transfer and the diffusion of the electroactive species. The heterogeneous rate constants of Ru complexes have been determined at Pt or a dropping mercury electrode (DME) in aqueous and nonaqueous solutions by some workers.[5,6] However, to our knowledge, the diffusion coefficients and rate constants at the carbon electrode in organic media have not been reported. This paper presents the diffusion coefficients and the heterogeneous charge-transfer rates of some Ru and Fe complexes in an acetonitrile solution. These parameters have been determined by using a rotating disk electrode (RDE) method which would be useful to estimate the parameters simultaneously.

Experimental

The metal complexes used here were tris(2,2′-bipyridine)ruthenium(II) tetrafluoroborate, $[Ru(bpy)_3](BF_4)_2$, tris(acetylacetonato)ruthenium(III), $[Ru(acac)_3]$, and tris(2,2′-bipyridine)iron(II) tetrafluoroborate, $[Fe(bpy)_3](BF_4)_2$. These were prepared and purified by methods described in the literature.[7-9] The solvent acetonitrile (CH_3CN) was dehydrated and purified by the usual distillation method.[10] The supporting electrolyte was tetraethylammonium tetrafluoroborate (Et_4NBF_4). The concentration of the supporting electrolyte was 0.1 mol dm^{-3} throughout the experiments. The solution contained 0.5×10^{-3}—2.0×10^{-3} mol dm^{-3} of the metal complex.

A one-compartment glass cell (ca. 200 cm^3 volume) was used for the electrochemical measurements. The working electrode was a Pt ring-glassy carbon (GC) disk electrode, whose surface areas were 0.24 and 0.22 cm^2, respectively. Before use, the working electrode was mechanically polished with fine powder of alumina, throughly washed with distilled water and with acetone in a ultrasonic cleaner, and finally rinsed with a test solution. A Pt wire was used as the counterelectrode. The reference electrode was an SCE, which was connected to the working electrode through a salt bridge and a Luggin capillary filled with the test solution. Thus, the electrode potential in this paper is indicated with respect to the SCE. Dry N_2 was introduced into the electrolytic solution for about 30 min before a measurement in order to purge any O_2 dissolved in the electrolyte: then the top of the cell was filled with dry N_2 throughout the measurements.

The current-potential relations were measured by using cyclic voltammetry and an RDE method. The rate of the potential sweep during voltammetry measurements was usually 0.1 or 0.3 V s^{-1}. The potential of the ring-disk electrode and the rotation rate of the electrode were controlled by a dual-potentio/galvanostat (Nikko Keisoku DPGS-1) and a rotation controller unit (Nikko Keisoku RRDE-1, SC-1), respectively. The rotation rate, N, of the electrode was varied from 0 to 4500 rpm (rotation per minute). In some experiments the error in the electrode potential due to uncompensated solution resistance was estimated by a current-interrupting technique: it was negligibly small in most cases. These electrochemical experiments were carried out at room temperature (17—21 °C). The viscosity of the electrolytic solution was measured by a modified Ostwald viscometer in a water bath thermostatted at 20 °C.

Results and Discussion

The cyclic voltammograms for $[Ru(bpy)_3](BF_4)_2$, $[Fe(bpy)_3](BF_4)_2$ and $[Ru(acac)_3]$ at the stationary GC-disk electrode (N=0 rpm) are shown in Fig. 1. The shapes of the voltammograms are quite consistent with those shown in previous work.[11-14] The peak couples are attributable to simple one-electron transfer reactions of the complexes. The potential difference (ΔE_p) of each redox couple apparently showed that the reaction proceeds almost reversibly (ΔE_p=59—62 mV).

Figure 2 shows the voltammograms for $[Ru(bpy)_3](BF_4)_2$ at a rotating ring-disk electrode (RRDE). The increase in the disk current at 1.2 V or above is based on the oxidation of Ru(II) to Ru(III), and the ring current corresponds to the reverse reaction. The col-

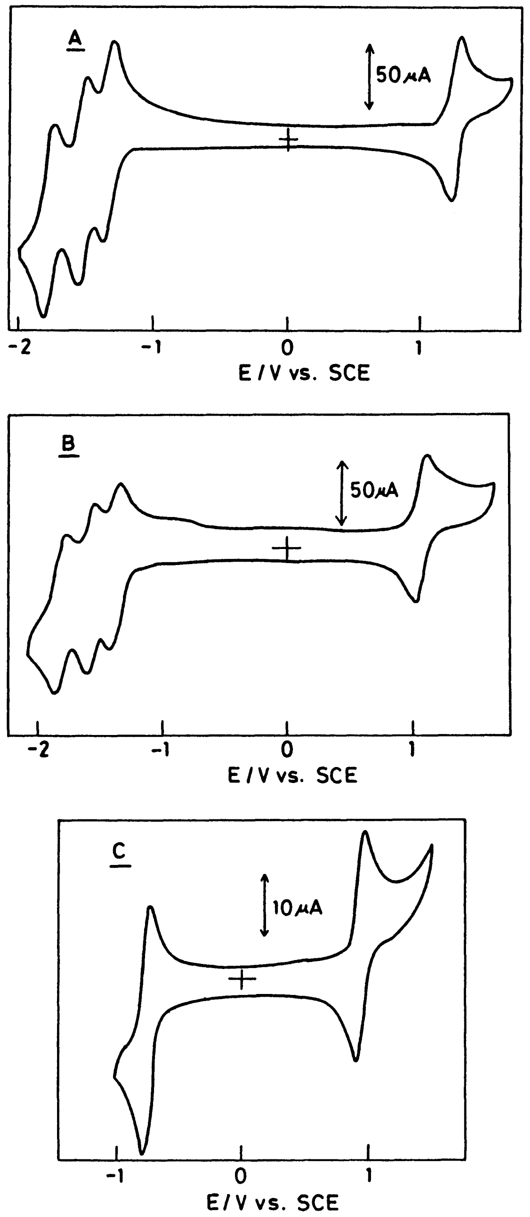

Fig. 1. Cyclic voltammograms for $[Ru(bpy)_3](BF_4)_2$, $[Fe(bpy)_3](BF_4)_2$, and $[Ru(acac)_3]$ at a stationary GC disk electrode in 0.1 mol dm^{-3} Et_4NBF_4/CH_3CN. Surface area of the disk electrode; 0.096 cm^2. Sweep rate; 0.3 V s^{-1}. (A): $[Ru(bpy)_3](BF_4)_2$ (2.0×10^{-3} mol dm^{-3}), (B): $[Fe(bpy)_3](BF_4)_2$ (2.0×10^{-3} mol dm^{-3}), (C): $[Ru(acac)_3]$ (8.0×10^{-4} mol dm^{-3}).

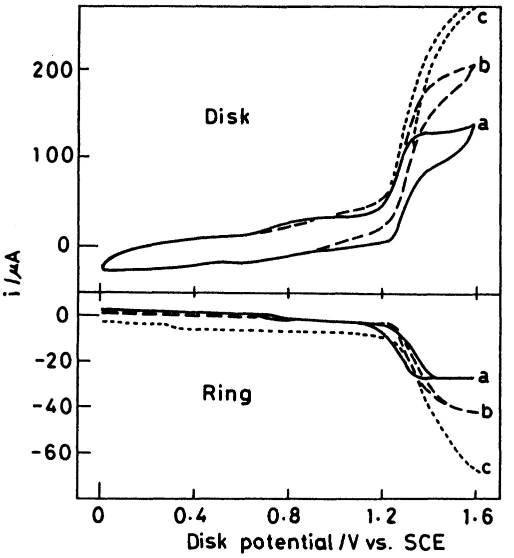

Fig. 2. Voltammograms for $[Ru(bpy)_3](BF_4)_2$ at RRDE in 0.1 mol dm^{-3} Et_4NBF_4/CH_3CN. Surface area of the electrode; 0.22 cm^2 (GC disk) and 0.24 cm^2 (Pt ring). Sweep rate of the disk potential; 0.1 V s^{-1}. Ring potential; 0.3 V vs. SCE. Rate of the electrode rotation (rpm); a: 300, b: 1000, c: 3000.

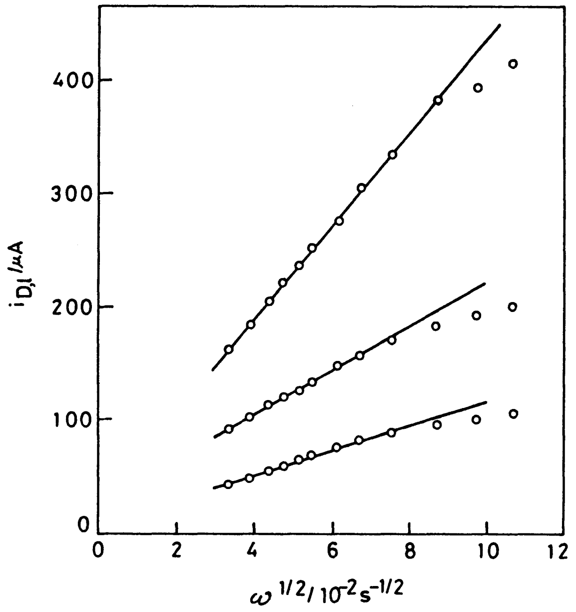

Fig. 3. Typical $i_{D,l}$ vs $\omega^{1/2}$ plots for the anodic oxidation of $[Ru(bpy)_3]^{2+}$. Concentration of the complex (10^{-3} mol dm^{-3}); a: 0.5, b: 1.0, c: 2.0.

lection efficiency obtained experimentally was in good agreement with that calculated from the electrode geometry: this also suggested the reaction is reversible. The steady-state limiting current at the disk electrode, $i_{D,l}$, depended on the rotation rate of the electrode: that is, it yielded the Levich equation:

$$i_{D,l} = 0.62\pi r^2 nFD^{3/2}\nu^{-1/6}\omega^{1/2} c, \tag{1}$$

where r, n, F, D, ν, ω, and c are the radius of the disk electrode, number of transferred electron (here, $n=1$), Faraday constant, diffusion coefficient of the complex ion, kinematic viscosity of the solution, rate of the electrode rotation ($\omega=120\ \pi N$, where N is rotation per minute), and concentration of the complex, respectively. Figure 3 shows a typical $i_{D,l}$ vs. $\omega^{1/2}$ plot. The diffusion coefficient, D, was determined from the slope of the plot. Table 1 summarizes the D's of $[Ru(bpy)_3]^{2+}$, $[Fe(bpy)_3]^{2+}$, and $[Ru(acac)_3]$ in Et_4NBF_4/CH_3CN. In the present electrolyte system, D was dependent neither on the central metal cation nor on the ligand of the complex. That is, there is little difference in the size of the diffusing species among the three complexes, in spite of some differences in the

Table 1. Diffusion Coefficient (D) of the Complex Ion Determined at an RDE in 0.1 mol dm^{-3} Et_4NBF_4/CH_3CN at 20 °C

Concn of complex/ 10^{-3} mol dm^{-3}	$D/10^{-10}$ m^2 s^{-1}		
	$[Ru(bpy)_3]^{2+}$	$[Re(bpy)_3]^{2+}$	$[Ru(acac)_3]$
0.5	2.4	2.4	2.3
1.0	1.8	2.3	2.3
2.0	2.1	2.1	2.1

ionic radius of the metal and in the size of the ligand. This is probably due to some compensation effects of the solvent, though details have not yet been made clear.[13]

As shown in Fig. 3, plots of $i_{D,l}$ vs. $\omega^{1/2}$ slightly deviate from a straight line that intersects the origin. This suggests that some kinetic step is involved in the electron transfer reaction.[15] The inconsistency of the results obtained at the RDE with those from cyclic voltammetry may be attributed to a difference in the experimental conditions. That is, the reaction rates observed under the steady-state condition of the RDE method might be somewhat different from those of cyclic voltammetry. If the disk current is considered to be formally expressed by Eq. 2, which is applicable to a totally irreversible reaction,

$$1/i_D = 1/i_{D,k} + 1/i_{D,l}, \qquad (2)$$

where $i_{D,k}$ represents the current in the absence of mass transfer effects, the intercepts of the $1/i_D$ vs. $\omega^{-1/2}$ plots will give the disk current at $\omega \to \infty$, i_D^∞ $(=i_{D,k})$. Figure 4 is an example of the $1/i_D$ vs. $\omega^{-1/2}$ plots, where the intercept of each line indicates $1/i_D^\infty$ at a given potential. The plots of log (i_D^∞) against the disk potential gave Tafel relations, which are shown in Figs. 5, 6, and 7. The Tafel slope, b, was about 0.2 V/decade for each anodic line. Thus, the apparent exchange current, $i_{0,app}$, is obtained by extrapolation of anodic log (i_D^∞)—E_D curve to the reversible potential, E_r, which had previously determined by the cyclic voltammogram at the stationary electrode. The resulting $i_{0,app}$'s are summarized in Table 2. If one tentatively estimates the heterogeneous rate constant, k, from Eq. 3,

$$i_0 = nFkc \qquad (3)$$

k will be 3.4×10^{-5} m s^{-1} for the $[Ru(bpy)_3]^{2+}$ system. This value is rather small compared with those deter-

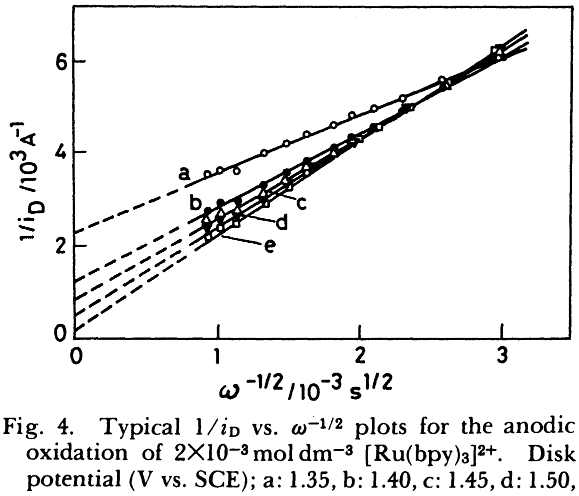

Fig. 4. Typical $1/i_D$ vs. $\omega^{-1/2}$ plots for the anodic oxidation of 2×10^{-3} mol dm^{-3} $[Ru(bpy)_3]^{2+}$. Disk potential (V vs. SCE); a: 1.35, b: 1.40, c: 1.45, d: 1.50, e: 1.60.

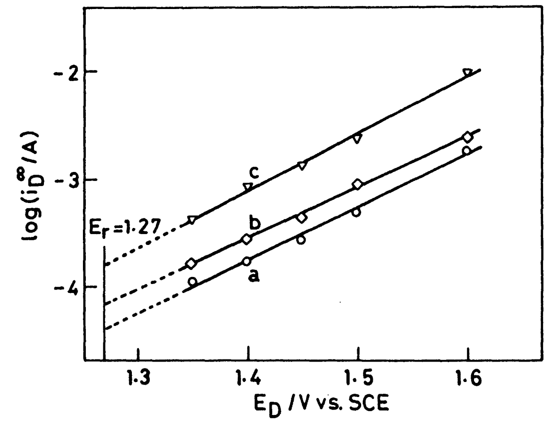

Fig. 5. Plots of log(i_D^∞) against disk potential (Tafel plots) for the anodic oxidation of $[Ru(bpy)_3]^{2+}$. Concentration of the complex (10^{-3} mol dm^{-3}); a: 0.5, b: 1.0, c: 2.0.

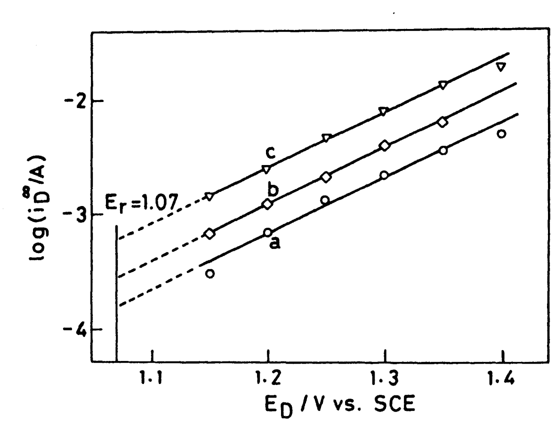

Fig. 6. Plots of log(i_D^∞) against disk potential (Tafel plots) for the anodic oxidation of $[Fe(bpy)_3]^{2+}$. Concentration of the complex (10^{-3} mol dm^{-3}); a: 0.5, b: 1.0, c: 2.0.

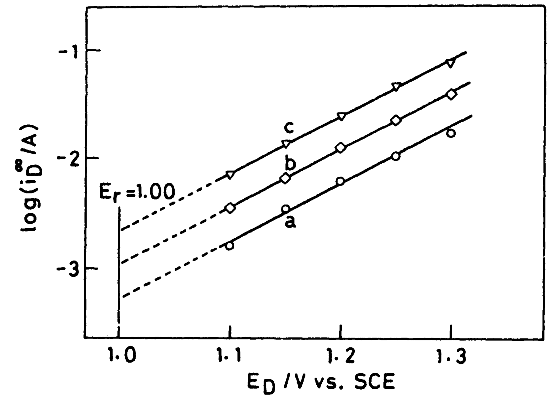

Fig. 7. Plots of log(i_D^∞) against disk potential (Tafel plots) for the anodic oxidation of $[Ru(acac)_3]$. Concentration of the complex (10^{-3} mol dm^{-3}); a: 0.5, b: 1.0, c: 2.0.

Table 2. Apparent Exchange Current ($i_{0,\,\mathrm{app}}$) for the Anodic Oxidation of the Complex in 0.1 mol dm^{-3} Et_4NBF_4/CH_3CN at 20 °C

Concn of complex/ 10^{-3} mol dm^{-3}	$i_{0,\,\mathrm{app}}/10^{-3}$ A cm^{-2}		
	$[Ru(bpy)_3]^{2+}$	$[Fe(bpy)_3]^{2+}$	$[Ru(acac)_3]$
0.5	0.16	0.68	2.2
1.0	0.33	1.3	4.5
2.0	0.64	2.7	9.1

mined previously in similar nonaqueous systems, but by different methods.[7,16] A possible reason for this is that the apparent i_0 obtained in this work is essentially based on the deviation of the rate equation from that for a totally reversible reaction.[15] Thus, the apparent rate, $i_{0,\mathrm{app}}$, might involve a somewhat different meaning from the heterogeneous rate constant that were previously determined by cyclic voltammetry. However, a discussion of $i_{0,\mathrm{app}}$ obtained under a steady-state condition will also be meaningful from the standpoint of any application of the redox system to a practical battery.[3,4]

The rate varies significantly with both the central metal cation and the ligand, in contrast to little variation of the diffusion constant among the complexes. The order of the rates,

$$[Ru(bpy)_3]^{2+} < [Fe(bpy)_3]^{2+} < [Ru(acac)_3],$$

was in agreement with the reciprocal order of the redox (reversible) potentials,

$$[Ru(bpy)_3]^{2+/3+}\ (1.27\ \mathrm{V}) > [Fe(bpy)_3]^{2+/3+}\ (1.07\ \mathrm{V}) > [Ru(acac)_3]^{0/+}\ (1.00\ \mathrm{V}),$$

The reason for this result has not yet been made clear. The relation between the redox potential and the electronic structure of the complex among the series of analogs has been widely investigated by means of cyclic voltammetry and polarography.[13,14,17—20] However, only a few studies have been carried out concerning the correlation between the charge-transfer rate and the structure of the complex.[5] This is probably due to the insufficiency of reliable data concerning the rate constant. Our present interest is how the rates of charge transfer and diffusion of the complexes influence the charge-discharge performance of the redox batteries with this type of complex. Some experiments are now in progress and the results will be reported in the near future.

Summary

The diffusion coefficients and the electron-transfer rates of some Ru and Fe complexes have been measured at a rotating disk electrode. The results are summarized as follows:

1. The cyclic voltammetry shows that the heterogeneous redox reactions of $[Ru(bpy)_3]^{2+}$, $[Fe(bpy)_3]^{2+}$, and $[Ru(acac)_3]$ proceed reversibly in an acetonitrile-based electrolyte.
2. The diffusion rate was almost constant among the complexes examined, while the current based on the electron transfer varied according to the structure of the complex.
3. The rate of electron transfer tended to increase with the decrease in the redox potential.

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