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Student Support Program for travel funds to make this work possible. This research was carried out at Brookhaven National Laboratory under contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical

Sciences, Office of Basic Energy Sciences. We also thank J. K. Newman and P. F. Fernandez for assistance with the experiments. This work was performed while one of us (E.A.W.) was on sabbatical leave from the University of New Mexico.

Charge-Transport Rates in Nafion Coatings on Electrodes. Surprisingly Disparate Diffusion Coefficients for a Single Molecule Containing Two Electroactive Centers

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The diffusion coefficient of the heterobinuclear complex $(\text{NH}_3)_5\text{RuC}_5\text{H}_4\text{NCH}_2\text{NHC(=O)-CpFeCp} \equiv \text{RuLFe}$ (Cp = cyclopentadienide or substituted cyclopentadienide) within Nafion coatings was measured chronocoulometrically in all three of its possible redox states ($\text{Ru}^{\text{II}}\text{LFe}^{\text{II}}$, $\text{Ru}^{\text{III}}\text{LFe}^{\text{II}}$, $\text{Ru}^{\text{III}}\text{LFe}^{\text{III}}$). The three oxidation states exhibited large differences in their diffusional rates. Possible origins of the differences and their concentration dependences are considered including intermolecular electron self-exchange, single-file diffusion, and electrostatic cross-linking. Both enhancement and depression of charge-transport rates produced by intermolecular electron-transfer cross-reactions between the fully oxidized and fully reduced complex were observed and compared with those calculated on the basis of a simple model. Reasonable agreement was obtained.

The rates of charge propagation through redox polymer coatings on electrode surfaces have been the subject of numerous recent investigations.¹⁻¹¹ Some of these studies have attempted to identify the elementary steps responsible for charge transport while others have focused on the possible use of redox polymer coatings in electrocatalysis,¹² inhibition of the photocorrosion of semiconductor electrodes,¹³ and electrochromic devices¹⁴ as well as other applications.¹⁵ Where the electroactive reactants incorporated in coatings are not part of the polymeric structure or permanently attached to functional groups present in the coatings, their diffusion within the polymeric matrix can include contributions from both molecular motion and electron exchange between adjacent pairs of the oxidized and reduced reactant.^{2a,b,d-f,3a,b,4a,b,5,8} A particularly clear example of the important contribution that electron exchange can make to diffusional rates measured for redox couples in polymeric coatings was provided by the $\text{Co}(\text{bpy})_3^{2+}$ complex (bpy = 2,2'-bipyridine) which exhibited a much larger diffusion coefficient when its concentration gradient was established at the electrode surface by reducing it to $\text{Co}(\text{bpy})_3^+$ than when the gradient arose from its oxidation to $\text{Co}(\text{bpy})_3^{3+}$.^{2b} We wondered what to expect from a molecule containing two separate electroactive redox groups with differing rates of electron self-exchange. It seemed possible that one might be able to observe molecular motion and electron exchange controlled diffusion in the same molecule depending upon which redox group was employed in an electrochemical measurement of diffusional rates. With this in mind we synthesized a molecule bearing two separate reversible redox groups and measured diffusion coefficients for all three of its possible redox states ($\text{Ox}_1\text{-Ox}_2$; $\text{Ox}_1\text{-Red}_2$; $\text{Red}_1\text{-Red}_2$). Large differences in diffusional rates among the various oxidation states were obtained and compared with those to be expected in cases where intermolecular electron self-exchange contributes significantly to the diffusional rates. In addition, the enhancement of the measured diffusion currents by means of intermolecular electron cross-exchange¹⁶ was detected and its magnitude compared with that calculated on the basis of a simple model.

Experimental Section

Materials. $[\text{Ru}(\text{NH}_3)_5\text{py}](\text{ClO}_4)_3$ (py = pyridine)¹⁷ and $[\text{Ru}(\text{NH}_3)_5\text{OH}_2](\text{PF}_6)_2$ ¹⁸ were prepared as described in the cited references. (Ferrocenylmethyl)trimethylammonium hexafluoro-

phosphate, $[\text{CpFeCp-CH}_2\text{N}(\text{CH}_3)_3]\text{PF}_6$ (Cp = cyclopentadienide or substituted cyclopentadienide) was obtained by metathesis of

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[†] Contribution No. 7142.

the corresponding bromide (Research Organic/Inorganic) using NH_4PF_6 . The crude product was recrystallized from water. *N*-(4-picolinyl)ferrocenylformamide (PFF), $\text{CpFeCp-C(=O)-NHCH}_2\text{C}_5\text{H}_4\text{N}$ ($\text{C}_5\text{H}_4\text{N} = 4\text{-pyridyl}$), was prepared by slight modifications in conventional procedures for peptide synthesis:^{19,20} 11 mmol of *N,N'*-dicyclohexylcarbodiimide (Aldrich) dissolved in 10 mL of CH_2Cl_2 was added slowly to a well-stirred mixture of 10 mmol of ferrocenylcarboxylic acid (Aldrich) and 10 mmol of 4-(aminomethyl)pyridine (Aldrich) in 10 mL of CH_2Cl_2 . The resulting mixture was allowed to react for 48 hours at 0 °C. Most of the solvent was removed by evacuation and the residue was dissolved in CHCl_3 . A small amount of acetic acid was added to convert the excess carbodiimide to the corresponding urea which precipitated and was removed by filtration. The filtrate was extracted with several portions of 1 M hydrochloric acid. The combined aqueous extracts were neutralized with NaOH to pH > 10 to precipitate the crude product which was dissolved in CHCl_3 and the extraction-precipitation-redissolution procedure repeated 5–6 times. The final CHCl_3 solution was extracted with several portions of aqueous NaOH (1 M) followed by H_2O . The product obtained by evaporation of the CHCl_3 was recrystallized from toluene, washed with ethyl ether, and dried at 70 °C in a vacuum oven. Elemental analysis: C, 63.79; H, 5.10; N, 8.71. Calcd for $\text{FeC}_{17}\text{H}_{16}\text{N}_2\text{O}$: C, 63.78; H, 5.04; N, 8.75. The ^1H NMR spectrum was consistent with the proposed structure.

$[(\text{NH}_3)_5\text{RuC}_5\text{H}_4\text{NCH}_2\text{NHC(=O)-CpFeCp}](\text{PF}_6)_3$ was prepared by adaptation of the procedure of Sutton and Taube for similar substituted pyridine complexes¹⁸ except that the oxidation of the Ru(II) product to Ru(III) was performed electrochemically instead of chemically in order to avoid the oxidation of the ferrocene center: an excess of PFF (3 mmol) was reacted with 0.6 mmol of $[(\text{NH}_3)_5\text{RuOH}_2](\text{PF}_6)_2$ in 30 mL of (1:1) acetone-ethanol in an argon atmosphere and in absence of light for 6 h. The reaction was monitored by means of an absorption band at 415 nm.²¹ The product was collected by adding the reaction solution to a large volume (250 mL) of rapidly stirred ether. The precipitate was dissolved in 20 mL of 1 M HCl and oxidized at a platinum gauze electrode maintained at 0.23 V until the current had decreased to background levels. The desired Ru(III) product was precipitated as the chloride by pouring the electrolysis solution into ~200 mL of rapidly stirred acetone. The resulting solid was converted to the PF_6^- salt by metathesis with NH_4PF_6 and recrystallization from water. To prepare a solution for voltammetric experiments, the solid salt was dissolved in water and passed through a Sephadex-SPC25-120 cation exchange column in the Na^+ form. Residual impurities were eluted with 0.15 M NaCl followed by the desired complex, $[(\text{NH}_3)_5\text{RuPFF}]^{3+}$, with 0.6 M NaCl. Isolation of the purified complex as a solid was unsuccessful because of the apparent decomposition of the ferrocene moiety at the temperature required to remove the solvent. The purified complex was therefore stored as a solution at ~5 °C.

Nafion coatings were cast from 5.2 wt % solutions of a soluble form of the polymer (equiv wt = 970) obtained from E. I. DuPont de Nemours Co. a number of years ago. Similar material is presently available from C. G. Processing Inc. (Rockland, DE). Solutions were prepared from distilled water that was further treated by passage through a purification train (Barnsted Nanopure). Electrodes were prepared from basal plane pyrolytic graphite obtained from Union Carbide Co. (Chicago).

Procedures. Electrodes were cut and mounted as previously described^{12a} to yield areas of 0.17 cm². Nafion coatings were

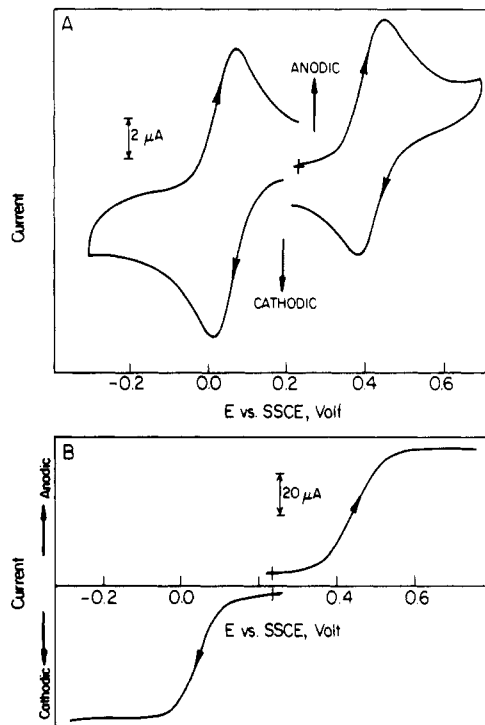


Figure 1. (A) Cyclic voltammograms for a 0.28 mM $\text{Ru}^{\text{III}}\text{LFe}^{\text{II}}$ solution at a bare graphite electrode. Scan rate: 100 mV s^{-1} . (B) Normal pulse voltammograms for a 0.7 mM $\text{Ru}^{\text{III}}\text{LFe}^{\text{II}}$ solution at a bare graphite electrode. Scan rate: 2 mV s^{-1} . Supporting electrolyte: 0.6 M NaCl + 0.05 M CH_3COONa at pH 4.5 for both curves.

obtained by transferring 2 μL of the stock solution to a freshly cleaved electrode and allowing the solvent to evaporate. Metal complexes were incorporated in the coatings by soaking them in aqueous solutions of the complexes (~1 mM). The quantities of complex incorporated were measured coulometrically as previously described.^{2b} Cyclic and normal pulse voltammetry and coulometry were conducted with appropriate combinations of PAR instruments (E G & G, Inc.). Chronocoulometry was conducted with a computer-controlled apparatus previously described.²² All experiments were conducted at ambient temperatures (22 ± 2 °C) in solutions that had been deaerated with prepurified argon. Potentials are quoted with respect to a sodium chloride-saturated calomel electrode, SSCE.

Results and Discussion

The binuclear complex, $[(\text{NH}_3)_5\text{RuC}_5\text{H}_4\text{NCH}_2\text{NHC(=O)-CpFeCp}]^{3+}$, which we will denote $\text{Ru}^{\text{III}}\text{LFe}^{\text{II}}$ hereafter, contains one oxidized and one reduced redox center. Uncotated electrodes placed in solutions of this complex assume open circuit potentials near 0.2 V. Cyclic voltammograms initiated from the open circuit potential contain an anodic peak (with its cathodic counterpart) when scanned to more positive potentials and a cathodic peak (with its anodic counterpart) when scanned to more negative potentials (Figure 1A). The response at 0.4 V corresponds to the one-electron oxidation of the ferrocene center in the complex and that at 0.05 V can be assigned to the one-electron reduction of the $[\text{Ru}(\text{NH}_3)_5(\text{py})]^{3+}$ center because its formal potential matches that of the corresponding mononuclear complex in which a phenyl group replaces the ferrocene moiety.²³ To obtain reliable estimates of the diffusion-limited currents corresponding to each of the peaks in Figure 1A normal pulse voltammograms²⁴ were also recorded (Figure 1B). The anodic and cathodic plateau currents in Figure 1B are identical (within the experimental precision of 1%) as expected because the same molecule diffuses to the electrode surface whether it is oxidized or reduced there.

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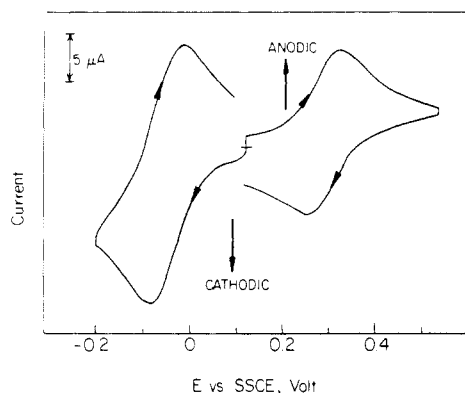


Figure 2. Cyclic voltammograms for 6.6×10^{-9} mol cm^{-2} of $\text{Ru}^{\text{III}}\text{LFe}^{\text{II}}$ incorporated in a Nafion coating on a graphite electrode containing 6.0×10^{-7} cm^{-2} of sulfonate groups. Supporting electrolyte = 0.1 M CF_3COONa + 0.1 M CH_3COONa at pH 4.5. Scan rate: 100 mV s^{-1} .

This simple symmetrical pattern was broken when the same $\text{Ru}^{\text{III}}\text{LFe}^{\text{II}}$ complex was incorporated in a Nafion coating on the graphite electrode as shown in Figure 2. The cathodic peak for the reduction of the Ru^{III} center is now significantly larger than the anodic peak for the oxidation of the Fe^{II} center. Despite the differences in peak currents, coulometric measurements demonstrated, as expected, that exactly as much charge was required to oxidize all of the Fe^{II} centers as to reduce all of the Ru^{III} centers in the coating. The shapes of the voltammograms in Figure 2 indicate that the currents are controlled by the diffusion of the complex within the coating^{2b,11} so that the unequal peak currents must reflect unequal rates of diffusional charge transport even though the same molecule is "diffusing" in both cases. If we denote by $D_{\text{III}^{\text{a}}-\text{II}}$ and $D_{\text{III}^{\text{a}}-\text{II}^{\text{a}}}$ the diffusion coefficients corresponding to the reduction of the Ru^{III} center and the oxidation of the Fe^{II} center, respectively, the peak currents in Figure 2 indicate that $D_{\text{III}^{\text{a}}-\text{II}} > D_{\text{III}^{\text{a}}-\text{II}^{\text{a}}}$.

Evaluation of Diffusion Coefficients. To allow more quantitative comparisons of diffusion rates, diffusion coefficients were measured by potential-step chronocoulometry.²⁵ The measured parameter was the slope, S , of linear chronocoulometric charge-(time)^{1/2} plots recorded at times short enough to ensure that the conditions for semiinfinite linear diffusion were obtained despite the finite volume of the thin Nafion coatings to which the diffusion was confined.^{10a,15a} Equation 1 gives the relationship between S and the corresponding diffusion coefficient

$$D = \left[\frac{S\phi\pi^{1/2}}{2F\Gamma} \right]^2 \quad (1)$$

where F is Faraday's constant, ϕ is the thickness of the electrode coating (assumed to be uniform), and Γ is the total quantity of the diffusing reactant in the coating (assumed to be uniformly distributed). Coating thicknesses were estimated from the quantity of Nafion present in the coatings and the previous profilometer measurements of Buttry on similar coatings.^{2b} The quantity of reactant incorporated in the coatings was obtained by coulometric assay.^{2d}

The binuclear complex can be prepared in three different combinations of oxidation states of the two metal centers: $\text{Ru}^{\text{III}}\text{LFe}^{\text{III}}$, $\text{Ru}^{\text{III}}\text{LFe}^{\text{II}}$, and $\text{Ru}^{\text{II}}\text{LFe}^{\text{III}}$ (the $\text{Ru}^{\text{II}}\text{LFe}^{\text{III}}$ state is unstable with respect to $\text{Ru}^{\text{III}}\text{LFe}^{\text{II}}$). Four diffusion coefficients can therefore be measured for these three oxidation states: $D_{\text{III}^{\text{a}}-\text{II}}$ and $D_{\text{III}^{\text{a}}-\text{II}^{\text{a}}}$, defined above; $D_{\text{III}^{\text{a}}-\text{III}^{\text{a}}}$, corresponding to the reduction of the Fe^{III} center in the $\text{Ru}^{\text{III}}\text{LFe}^{\text{III}}$; and $D_{\text{II}^{\text{a}}-\text{II}}$, corresponding to the oxidation of the Ru^{II} center in $\text{Ru}^{\text{II}}\text{LFe}^{\text{II}}$. Values were obtained for these four diffusion coefficients by adjusting the initial potential of the coated electrode to convert the incorporated complex into each of the possible oxidation states. The results, listed in Table I, are remarkable for several reasons. The measured diffusion coefficients differ by as much as a factor of 4.5 even

TABLE I: Diffusion Coefficients for the RuLFe Complex within a Nafion Coating^a

expt no.	E_i^b , mV	E_f^c , mV	oxidation state		$10^9 D^d$, $\text{cm}^2 \text{s}^{-1}$	symbol for D
			initial	final		
1	0.12	-0.20	$\text{Ru}^{\text{III}}\text{LFe}^{\text{II}}$	$\text{Ru}^{\text{II}}\text{LFe}^{\text{II}}$	(1.3 ± 0.2)	$D_{\text{III}^{\text{a}}-\text{II}}$
2	-0.20	0.12	$\text{Ru}^{\text{II}}\text{LFe}^{\text{II}}$	$\text{Ru}^{\text{III}}\text{LFe}^{\text{II}}$	(2.1 ± 0.2)	$D_{\text{II}^{\text{a}}-\text{II}}$
3	0.55	0.12	$\text{Ru}^{\text{III}}\text{LFe}^{\text{III}}$	$\text{Ru}^{\text{III}}\text{LFe}^{\text{II}}$	(0.46 ± 0.05)	$D_{\text{III}^{\text{a}}-\text{III}^{\text{a}}}$
4	0.12	0.55	$\text{Ru}^{\text{III}}\text{LFe}^{\text{II}}$	$\text{Ru}^{\text{III}}\text{LFe}^{\text{III}}$	(0.57 ± 0.06)	$D_{\text{III}^{\text{a}}-\text{III}^{\text{a}}}$

^a The Nafion coating contained 6×10^{-7} mol cm^{-2} of sulfonate groups and 4.9×10^{-9} mol cm^{-2} of the RuLFe complex. ^b Initial electrode potential. ^c Final electrode potential. ^d Calculated from eq 1 with $\phi = 1.2 \times 10^{-4}$ cm. The indicated uncertainties are based on the observed precision of $\pm 5\%$ in the measurements of chronocoulometric slopes for a given coating.

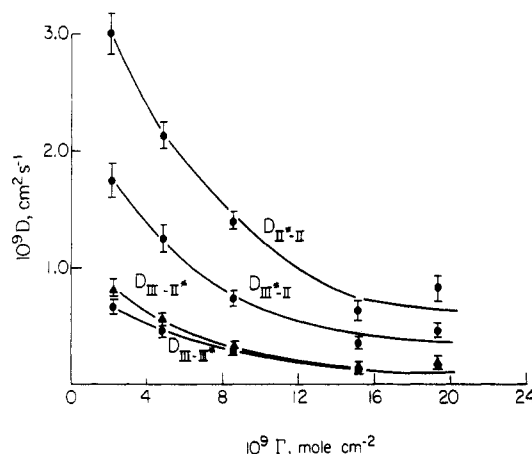


Figure 3. Concentration dependences of the four diffusion coefficients evaluated for the binuclear RuLFe complex (see text). Supporting electrolyte as in Figure 2.

though the diffusing species differ only in their net charges. The diffusing species in experiments 1 and 4 are, in fact, identical in all respects yet the values of $D_{\text{III}^{\text{a}}-\text{II}}$ and $D_{\text{III}^{\text{a}}-\text{III}^{\text{a}}}$ differ by a factor of 2.3. There is no apparent correlation between the total charge carried by the diffusing species and its diffusion coefficient as might have been anticipated if electrostatic cross-linking of the polyelectrolyte by the multiply charged complexes^{2c,f,4a,10,12a,g} had a dominating effect on the measured values of D .

The larger values of D obtained when the ruthenium center is the site of the electron-transfer reaction ($D_{\text{III}^{\text{a}}-\text{II}}$ and $D_{\text{II}^{\text{a}}-\text{II}}$) suggests that rapid electron exchange between oxidized and reduced forms of the complex may enhance the measured diffusional rates as proposed by Dahms²⁶ and Ruff et al.²⁷ and demonstrated for $\text{Co}(\text{bpy})_3^{2+}$.^{2b} This possibility is not supported by the concentration dependences of $D_{\text{III}^{\text{a}}-\text{II}}$ and $D_{\text{II}^{\text{a}}-\text{II}}$ shown in Figure 3 because the measured diffusion coefficients decrease as the concentration of the complex is increased instead of increasing in the manner predicted by Dahms and Ruff.^{26,27} However, almost all previously reported diffusion coefficients for redox couples in Nafion coatings^{2a,b,3a,b,8,16b} have exhibited similar decreases as the reactant concentration is increased. These decreases have been attributed to the effects of electrostatic cross-linking^{2c,f,4a,10,12a,g} and/or of single-file diffusion.^{2b,28} With larger and more highly charged redox couples such as $[\text{RuLFe}]^{4+/3+}$ the factors responsible for decreases in diffusion coefficients with concentration may become dominant so that the contributions of electron self-exchange, which act in the opposite direction, may be masked. Thus, while measured diffusion coefficients that increase with concentration seem a reliable indicator of the presence of contributions

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from electron self-exchange to the diffusional process, the converse is not necessarily true. Diffusion coefficients that decrease as the reactant concentration increases may nevertheless be enhanced by contributions from electron self-exchange reactions.

Although it has been instructive in previous studies^{2b,3a,b,4b,c} to employ the simplest version of the equation of Dahms and Ruff^{26,27} to compare measured and calculated values of diffusion coefficients when contributions from electron self-exchange are suspected, we elected not to do so for the present system because the disparate magnitudes and concentration dependences of the diffusion coefficients obtained seemed incompatible with the assumptions that underlie the Dahms–Ruff analysis. For example, the rate constants governing self-exchange reactions for such intrinsically reactive couples as Ru(III/II) and ferrocenium/ferrocene^{29,30} are apt to be close to the diffusion-controlled limit in Nafion coatings.^{2b} Since the diffusion coefficients of the couples decrease with concentration, the diffusion-controlled rate constants must also decrease, so that the assumption of a concentration-independent self-exchange rate constant in the Dahms–Ruff equation will be invalid.

Another difficulty is posed by the fact that significant differences were observed between D_{III^*-II} and D_{II^*-II} and between $D_{III-III^*}$ and $D_{III-III^*}$ (Table I). The Dahms–Ruff equation employed heterotofore^{2b,3a,b,4b,c} is valid only when $D_{Ox} = D_{Red}$. If this is not the case, a more complex equation results^{27c} that has yet to be solved and tested.

A further factor that may produce deviations from the predictions of the simplest form of the Dahms–Ruff equation is coupling between the diffusion fluxes of the oxidized and reduced forms of the redox couple when both are confined within polyelectrolyte matrices by electrostatic forces. As the concentration of a multiply charged diffusants increases to the point that the number of available electrostatic binding sites is limited, one might well expect the diffusive motion of one half of a redox couple to be influenced by that of the other half which proceeds in the opposite direction. Such coupling is not encountered when diffusion coefficients in homogeneous solution are measured by electrochemical techniques or in cases where only half of a redox couple is present during the measurement (by nonelectrochemical methods). The existence of this type of coupling could help to explain the, otherwise puzzling, large difference between D_{III^*-II} and $D_{III-III^*}$ (Table I) which both apply to the same $Ru^{III}LFe^{II}$ complex. D_{III^*-II} is measured by converting $Ru^{III}LFe^{II}$ to the less highly charged $Ru^{II}LFe^{II}$ so that the electrode reaction product would require fewer electrostatic binding sites than the reactant from which it originated. As a result the diffusion of the reactant might be affected less than when $D_{III-III^*}$ is measured and the more highly charged $Ru^{III}LFe^{III}$ complex is the reaction product. The situation is further complicated by the likelihood that contributions to ion transport in polymer coatings by migration may not be easy to eliminate^{31,32} especially when highly charged diffusants are involved.

Comparison with Mononuclear Complexes. For the purpose of comparison, diffusion coefficients were also evaluated for various concentrations of mononuclear complexes that were structurally analogous to either end of the binuclear $RuLFe$ complex. The results, summarized in Figure 4, show the mononuclear complexes to diffuse more rapidly than the binuclear complex under all conditions but both types of complex have diffusion coefficients that decrease with concentration. The much smaller concentration dependence of the diffusion coefficient for the singly charged, reduced form of the monomeric ferrocene derivative may be the result of its low cationic charge which causes the effects of electrostatic cross-linking and (possible) electron self-exchange to be more nearly balanced. The large difference in the mag-

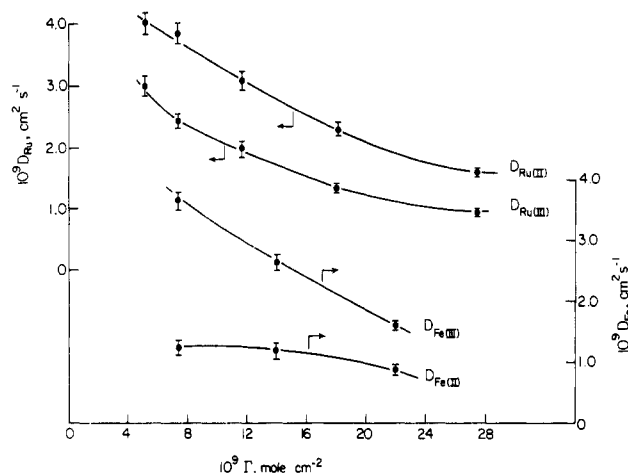


Figure 4. Concentration dependence of diffusion coefficients for mononuclear (ferrocenylmethyl)trimethylammonium and ruthenium pentaammine pyridine complexes. Supporting electrolyte as in Figure 2.

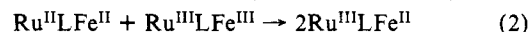
TABLE II: Chronocoulometric Slopes for the Reduction of $Ru^{III}LFe^{III}$ in Nafion Coatings by One- or Two-Electron Steps

$10^3 \Gamma,^a$ mol cm ⁻²	$S_1,^{b,c}$ $\mu C\ cm^{-2}\ s^{-1/2}$	$2S_1,^{b,c}$ $\mu C\ cm^{-2}\ s^{-1/2}$	$S_2,^{c,d}$ $\mu C\ cm^{-2}\ s^{-1/2}$	$(S_2)_{calcd},^e$ $\mu C\ cm^{-2}\ s^{-1/2}$
2.23	53	106	164	154
4.86	94	188	325	280
8.58	132	264	423	381
15.1	159	318	514	468
19.4	235	470	760	690

^a Quantity of $[Ru^{III}LFe^{III}]^{4+}$ incorporated in the Nafion coating which contained 6×10^{-7} mol cm⁻² of sulfonate groups. ^b Slope measured for the electrode reaction: $Ru^{III}LFe^{III} + e \rightarrow Ru^{III}LFe^{II}$. ^c For a given coating slopes could be measured with a precision of ca. $\pm 5\%$. ^d Slope measured for the electrode reaction: $Ru^{III}LFe^{III} + 2e \rightarrow Ru^{II}LFe^{II}$. ^e Calculated from eq 3 by using the diffusion coefficients evaluated at the same values of Γ (Figure 3).

nitudes of diffusion coefficients for the oxidized and reduced forms of the monomeric ferrocene complex has been previously reported⁸ and attributed to differences in hydrophobic interactions between the two complexes and the hydrophobic portions of the Nafion matrix.³³

Effect of Electron-Transfer Cross-Reactions on Diffusion Coefficients. In several recent studies the ability of rapid electron-transfer reactions to couple the diffusional rates of pairs of reacting redox couples with disparate individual diffusion coefficients^{4b,16a,b} has been described. The effect was considered in earlier investigations³⁴ but the advent of polymer-coated electrodes has renewed interest in the phenomenon because it is more likely to be encountered within such coatings.^{16b} The widely differing diffusion coefficients exhibited by the binuclear complex prepared in this study (Table I) are expected to result in the same type of coupling of diffusion fluxes by electron transfer in the appropriate experiments. To test this expectation, the chronocoulometric slope for the one-electron reduction of $Ru^{III}LFe^{III}$ to $Ru^{III}LFe^{II}$ was compared with the slope obtained in an experiment where the potential was stepped across both reduction waves so that a two-electron reduction to $Ru^{II}LFe^{II}$ proceeded at the electrode. Since D_{II^*-II} is much greater than $D_{III-III^*}$ (Table I) one expects the slope measured in the single two-electron step, S_2 , to be larger than twice the slope of the one-electron step, S_1 , if the rate of reaction 2 is large.¹⁶ If reaction 2 proceeded negligibly on the



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TABLE III: Chronocoulometric Slopes for the Oxidation of Ru^{II}LFe^{II} in Nafion Coatings by One- or Two-Electron Steps

10 ⁹ Γ, ^a mol cm ⁻²	S ₁ , ^{b,c} μC cm ⁻² s ^{-1/2}	2S ₁ , μC cm ⁻² s ^{-1/2}	S ₂ , ^{c,d} μC cm ⁻² s ^{-1/2}	(S ₂) _{calcd} , ^e μC cm ⁻² s ^{-1/2}
2.23	111	222	166	164
4.86	204	408	314	300
8.58	293	586	470	434
15.2	350	700	523	511
19.4	511	1022	760	736

^aQuantity of [Ru^{II}LFe^{II}]²⁺ incorporated in the Nafion coating which contained 6 × 10⁻⁷ mol cm⁻² of sulfonate groups. ^bSlope measured for the electrode reaction: Ru^{II}LFe^{II} → Ru^{III}LFe^{II} + e. ^cFor a given coating slopes could be measured with a reproducibility of ca. ±5%. ^dSlope measured for the electrode reaction: Ru^{II}LFe^{II} → Ru^{III}LFe^{III} + 2e. ^eCalculated from eq 3 by using the diffusion coefficients evaluated at the same values of Γ (Figure 3).

time scale of the experiment the two slopes should differ by a factor of 2 whatever the relative values of the diffusion coefficients.³⁵ Table II summarizes data for experiments conducted with several concentrations of incorporated complex. The anticipated enhancement in the slope for the two-electron step is observed: compare the third and fourth columns of Table II.

The magnitude of the enhanced slope to be expected in the two-electron step was calculated from eq 3 which was derived by a procedure analogous to that employed recently by Andrieux et al. for the case of two coupled, mononuclear redox couples.^{16a} (The derivation is given in the Appendix)

$$\frac{S_2}{2S_1} = \frac{\left(\frac{d_1}{d_2}\right)^{1/2} \operatorname{erfc}[(d_3)^{1/2}\beta]}{[\operatorname{erf}(\beta/R)] \operatorname{erfc}[(d_4)^{1/2}\beta]} \left\{ 1 - \frac{\exp[\beta^2(d_3 - R^2)]}{2 \exp[\beta^2(d_3 - 1)]} \right\} \exp[(d_3 - d_4)\beta^2] \quad (3)$$

where $d_1 = D_{\text{III}^*\text{-II}}/D_{\text{III-III}^*}$, $d_2 = D_{\text{III-III}^*}/D_{\text{III-III}^*}$, $d_3 = D_{\text{II}^*\text{-II}}/D_{\text{III-III}^*}$, $d_4 = D_{\text{II}^*\text{-II}}/D_{\text{III-III}^*}$, $R = (d_1/d_4)^{1/2}$, and β is given implicitly by eq 4.

$$\operatorname{erf}(\beta/R) =$$

$$R(d_3)^{1/2} \operatorname{erfc}[\beta(d_3)^{1/2}]\{2 \exp[\beta^2(d_3 - 1)] - \exp[\beta^2(d_3 - R^2)]\} \quad (4)$$

It is noteworthy that eq 3 and 4 (unlike their counterparts that apply to coupling between two separate redox couples) are independent of the concentration of the binuclear complex. The final column of Table II lists the calculated values of S_2 for comparison with the experimental values in the fourth column. Although the calculated and experimental values differ somewhat, the general trend of the experimental results is matched by the calculated values. We regard the agreement as reasonable considering the number of independent experimental parameters that are required in the calculation. That substantial enhancement in the overall diffusional rate results from the occurrence of reaction 2 within the diffusion layer at the coating/electrode interface seems clearly established by the data.

Equations 3 and 4 (with appropriate redefinition of the symbols) can also be used to calculate the depressions in the overall diffusional rate that are to be expected¹⁶ if the experiment is repeated in the reverse order, i.e., if Ru^{II}LFe^{II} is oxidized to Ru^{III}LFe^{III}. Table III summarizes data obtained in a series of such experiments. The agreement between observed and calculated slopes is satisfactory and gives added evidence of the important effect that reaction 2 exerts on the diffuse flux of reactant that arrives at the electrode surface.

Conclusions

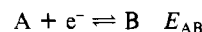
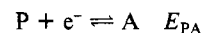
The results obtained in this study have revealed more problems in accounting for diffusional processes in Nafion coatings on

electrodes than they have resolved. To identify the origins of the differences in the magnitudes of the diffusion coefficients in Figures 3 and 4 and of their concentration dependences will require considerably more quantitative data to be obtained. On the other hand, the agreement between the calculated and measured slopes in Tables II and III indicates that, despite the remarkable differences in their magnitudes, the diffusion coefficients evaluated in this study do provide accurate measures of the disparate diffusional rates exhibited by the three different oxidation states of the RuLFe complex. The large amount that remains to be learned about diffusional processes within Nafion coatings on electrodes is evident from the uncertainties that remain, despite the fact that more data have been reported on diffusion within Nafion than for any other type of coating.

Acknowledgment. This work was supported by the U. S. Army Research Office. Discussions with Prof. J.-M. Saveant aided our endeavors.

Appendix

Consider a molecule, P, containing two electroactive groups that undergo the following reversible half-reactions



where P is the fully oxidized species, A is the partially reduced species, B is the fully reduced species, and the corresponding formal potentials are E_{PA} and E_{AB} . The diffusion coefficient of P as measured by its reduction to A, that of A as measured by its oxidation to P, that of A as measured by its reduction to B, and that of B as measured by its oxidation to A are D_P , D_A' , D_A , and D_B , respectively. We suppose $E_{PA} \gg E_{AB}$ and wish to calculate the chronoamperometric current-time response that results when the electrode potential is stepped from a value well positive of E_{PA} to a value well negative of E_{AB} , i.e., across both reduction waves, in a solution containing only P. The cross reaction $P + B \rightarrow 2A$ is assumed to be irreversible and to proceed at a high rate at all points within the diffusion layer. The initial conditions are $t = 0$, $C_P = C_P^0$, and $C_A = C_B = 0$, where C_i is the concentration of species i and C_P^0 is the initial uniform concentration of P.

Dimensionless parameters are defined as follows: $p = C_P/C_P^0$; $a = C_A/C_P^0$; $b = C_B/C_P^0$; $d_a = D_A/D_P$; $d_a' = D_A'/D_P$; $d_b = D_B/D_P$; $\tau = t/\theta$ where θ is the total duration of the potential step, $y = x/\delta$ where x is the distance from the electrode surface, $\delta = (D_P\theta)^{1/2}$, $\psi = i [F(D_P)^{1/2}C_P^0/\theta^{1/2}]^{-1}$.

By analogy with the previous treatment of a system containing two unattached electroactive species,¹⁶ P and B are assumed to react so rapidly they do not coexist anywhere within the diffusion layer and μ represents the spatial position where the concentrations of both P and B are zero.

Writing Fick's Law in terms of the dimensionless parameters:

$$0 < y < \mu$$

$$\partial a / \partial \tau = d_a (\partial^2 a / \partial y^2) \quad (A1)$$

$$\partial b / \partial \tau = d_b (\partial^2 b / \partial y^2) \quad (A2)$$

$$p = 0 \quad (A3)$$

$$y < \mu < \infty$$

$$\partial a / \partial \tau = d_a' (\partial^2 a / \partial y^2) \quad (A4)$$

$$\partial p / \partial \tau = \partial^2 p / \partial y^2 \quad (A5)$$

$$b = 0 \quad (A6)$$

$$\text{with } \tau = 0, y > 0$$

$$a = b = 0, \quad p = 1 \quad (A7)$$

$$\tau > 0, y = 0$$

$$a = p = 0 \quad (A8)$$

$$d_a(\partial a/\partial y) = -d_b(\partial b/\partial y) \quad (\text{A9})$$

$$y = \infty$$

$$p = 1 \quad (\text{A10})$$

$$y = \mu$$

$$b = p = 0; \quad (\partial p/\partial y) = -d_b(\partial b/\partial y) \quad (\text{A11})$$

Following the previous successful approach¹⁶ the solution of eq A1-A11 was assumed to be of the form:

$$0 < y < \mu$$

$$b = \left\{ 1 - \frac{\operatorname{erf}\left(\frac{y}{2(d_b\tau)^{1/2}}\right)}{\operatorname{erf}\left(\frac{\mu}{2(d_b\tau)^{1/2}}\right)} \right\} C \quad (\text{A12})$$

$$a = \left\{ \frac{\operatorname{erf}\left(\frac{y}{2(d_a\tau)^{1/2}}\right)}{\operatorname{erf}\left(\frac{\mu}{2(d_a\tau)^{1/2}}\right)} \right\} C' \quad (\text{A13})$$

$$y < \mu < \infty$$

$$a = \left\{ \frac{\operatorname{erfc}\left[\frac{y}{2(d_a'\tau)^{1/2}}\right]}{\operatorname{erfc}\left[\frac{\mu}{2(d_a'\tau)^{1/2}}\right]} \right\} C'' \quad (\text{A14})$$

$$p = \left\{ 1 - \frac{\operatorname{erfc}\left(\frac{y}{2\tau^{1/2}}\right)}{\operatorname{erfc}\left(\frac{\mu}{2\tau^{1/2}}\right)} \right\} \quad (\text{A15})$$

where (A7), (A8), and (A10) have been applied. Since a is continuous at μ

$$C' = C'' \quad (\text{A16})$$

Substitution of (A12) and (A13) into (A9) leads to

$$C = C'(d_a/d_b)^{1/2} \left\{ \frac{\operatorname{erf}\left[\frac{\mu}{2(d_b\tau)^{1/2}}\right]}{\operatorname{erf}\left[\frac{\mu}{2(d_a\tau)^{1/2}}\right]} \right\} \quad (\text{A17})$$

Conservation of matter in the cross-reaction ($P + B \rightarrow 2A$) at $y = \mu$ requires that

$$y = \mu$$

$$d_a(\partial a/\partial y)_{\mu^-} - d_a'(\partial a/\partial y)_{\mu^+} = 2(\partial p/\partial y) \quad (\text{A18})$$

Combining (A13), (A14), and (A18) leads to

$$C' \left\{ \frac{(d_a)^{1/2} \exp\left(-\frac{\mu^2}{4d_a\tau}\right)}{\operatorname{erf}\left[\frac{\mu}{2(d_a\tau)^{1/2}}\right]} + \frac{(d_a')^{1/2} \exp\left(\frac{-\mu^2}{4d_a'\tau}\right)}{\operatorname{erfc}\left[\frac{\mu}{2(d_a'\tau)^{1/2}}\right]} \right\} = 2 \left[\frac{\exp\left(\frac{-\mu^2}{4\tau}\right)}{\operatorname{erfc}\left(\frac{\mu}{2\tau}\right)^{1/2}} \right] \quad (\text{A19})$$

Substitution of this expression into (A17), combination with (A11), (A12), and (A15), and rearrangement yields:

$$1 = \frac{(d_a/d_a')^{1/2} \operatorname{erfc}\left[\frac{\mu}{2(d_a'\tau)^{1/2}}\right]}{\operatorname{erf}\left[\frac{\mu}{2(d_a\tau)^{1/2}}\right]} \left\{ 2 \exp\left[\frac{\mu^2}{4d_b\tau}\left(\frac{d_b}{d_a'} - 1\right)\right] - \exp\left[\frac{\mu^2}{4d_b\tau}\left(\frac{d_b}{d_a'} - \frac{d_b}{d_a}\right)\right] \right\} \quad (\text{A20})$$

By making the following identifications: $P \equiv \text{Ru}^{\text{III}}\text{LFe}^{\text{III}}$, $A \equiv \text{Ru}^{\text{III}}\text{LFe}^{\text{II}}$, $B \equiv \text{Ru}^{\text{II}}\text{LFe}^{\text{II}}$, $d_1 = d_a$, $d_2 = d_a'$, $d_3 = d_b/d_a'$, $d_4 = d_b$, and $\mu/2(d_b\tau)^{1/2} = \beta$, eq A20 becomes eq 4 in the text. As before,¹⁶ β is a function that is independent of τ and can be evaluated from the diffusion coefficients by means of eq 4.

The dimensionless current, ψ , is obtained as follows:

$$\psi = -d_b \left(\frac{\partial b}{\partial y} \right)_{y=0} \quad (\text{A21})$$

$$\psi = \frac{2(d_1/d_2)^{1/2} \exp[(d_3 - d_4)\beta^2]}{(\pi\tau)^{1/2} \operatorname{erf}\left(\frac{\beta}{R}\right)} \left\{ 1 - \frac{\exp[\beta^2(d_3 - R^2)]}{2 \exp[\beta^2(d_3 - 1)]} \right\} \frac{\operatorname{erfc}[(d_3)^{1/2}\beta]}{\operatorname{erfc}[(d_4)^{1/2}\beta]} \quad (\text{A22})$$

where $R = (d_1/d_4)^{1/2}$. Substitution of (A22) into $i = \psi\{FD^{1/2}Cp^0/\theta^{1/2}\}$ and recasting the result in terms of the chronocoulometric slopes, lead to eq 3 in the text.

Registry No. $[(\text{NH}_3)_5\text{Ru}(\text{PFF})]^{2+}$, 97042-92-7; $[(\text{NH}_3)_5\text{Ru}(\text{PFF})]^{3+}$, 97042-93-8; $[(\text{NH}_3)_5\text{Ru}(\text{PFF})]^{4+}$, 97042-94-9; $[\text{CpFeCp} \cdot \text{CH}_2\text{N}(\text{CH}_3)_3]^+$, 33039-48-4; $[\text{Ru}(\text{NH}_3)_5\text{py}]^{3+}$, 33291-25-7; Nafion, 39464-59-0.