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Effects of Electron Exchange and Single-File Diffusion on Charge Propagation in Nafion Films Containing Redox Couples

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Abstract: The concentration dependence of the diffusion coefficients of redox ions that undergo rapid electron exchange predicted by Dahms and Ruff and co-workers has been observed and measured for cobalt(2,2′-bipyridine)$_3{}^{2+}$, Co(bpy)$_3{}^{2+}$, incorporated in Nafion coatings applied to graphite electrodes. The diffusion coefficient of Co(bpy)$_3{}^{2+}$ was measured both by reducing it to Co(bpy)$_3{}^{+}$ and by oxidizing it to Co(bpy)$_3{}^{3+}$. The resulting diffusion coefficients differed considerably. That measured by reduction of Co(bpy)$_3{}^{2+}$ increased linearily with its concentration while that measured by oxidation of the complex was much smaller and exhibited a concentration dependence of the opposite sign. The latter is attributed to the effects of single-file diffusion which involves competition between the diffusing species for residence sites within the coating. The surprisingly wide range of diffusion coefficients that have been reported for structurally similar cations incorporated in Nafion coatings is explained in terms of a model for the interior of Nafion coatings that includes both hydrophilic and hydrophobic phases between which incorporated reactants are partitioned. Two general classes of diffusional behavior for redox reactants in Nafion are identified and examples of each class are provided.

Kaufman and Engler[1] originally proposed that charge propagates through polymeric films with redox sites anchored to the polymeric chains by means of electron hopping between adjacent oxidized and reduced sites. It has since been shown that this mechanism may also contribute to charge propagation when ionic redox species are bound electrostatically within polyelectrolyte films.[2-4] The results of these studies have been discussed in the context of earlier analyses by Dahms[5] and Ruff and co-workers,[6] who proposed the following relation for the experimentally observed diffusion coefficient for one-half of a redox couple in homogeneous solution, D_{exptl}, in terms of the second-order self-exchange rate constant for the redox couple, k_{ex}, and the diffusion coefficient that would be measured in the absence of self-exchange, D_0:

$$D_{\text{exptl}} = D_0 + \frac{\pi}{4}k_{\text{ex}}\delta^2 C \tag{1}$$

C is the sum of the concentrations of the oxidized and reduced forms of the redox couple and δ is the distance between the centers of the reactants when the electron transfer occurs. (Equation 1 is a simplified version of a more general expression.[6c] It applies to cases where the ratio of the concentration gradients of the oxidized and reduced forms of the reactant are everywhere equal to −1. This constraint is commonly met in electrochemical experiments.)

According to eq 1, whenever electron self-exchange makes a significant contribution to the diffusion process, D_{exptl} should exhibit a linear dependence on the concentration, C. However, in previous studies of the diffusion of Ru(bpy)$_3{}^{2+}$ (bpy = 2,2′-bipyridine) within Nafion coatings (Nafion is a polyelectrolyte containing anionic sulfonate groups) on electrode surfaces, the values of D_{exptl} were essentially independent of the concentration of Ru(bpy)$_3{}^{2+}$.[2,3b]

In the present study, a different reactant, Co(bpy)$_3{}^{2+}$, was incorporated in Nafion films on graphite electrodes and its diffusion coefficient was measured electrochemically both by oxidizing it to Co(bpy)$_3{}^{3+}$ and by reducing it to Co(bpy)$_3{}^{+}$. Much larger values of D_{exptl} resulted when the Co(bpy)$_3{}^{2+/+}$ redox couple was involved than when the electroactive couple was Co(bpy)$_3{}^{3+/2+}$, even though the same species, Co(bpy)$_3{}^{2+}$, is "diffusing" in both cases. In addition, the larger values of D_{exptl} obtained with the Co(bpy)$_3{}^{2+/+}$ couple exhibited a clear concentration dependence of the type predicted by eq 1. An interpretation of this behavior is proposed that also leads to a rationalization for the absence of a concentration dependence in D_{exptl} for Ru(bpy)$_3{}^{2+}$.

Experimental Section

Materials. A 5.2 wt % solution of Nafion in a 5/1 mixture of isopropyl alcohol-water (available from a sample supplied by E. I. duPont Co. a number of years ago) was used to prepare electrode coatings.

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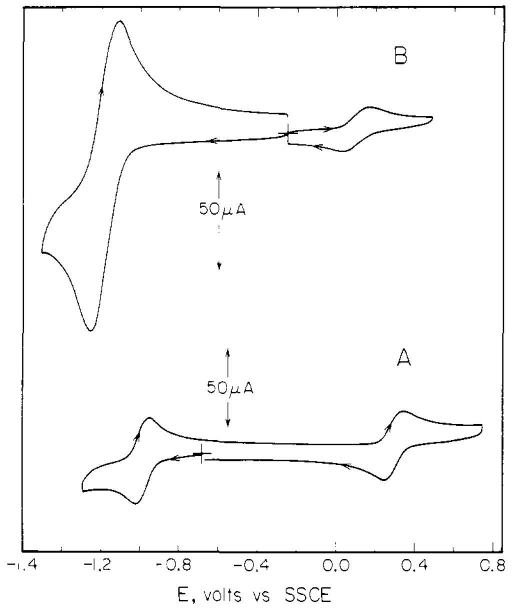

Figure 1. Cyclic voltammograms for $Co(bpy)_3^{2+}$. (A) 0.5 mM $Co(bpy)_3^{2+}$ in acetonitrile recorded at a bare graphite electrode. Supporting electrolyte: 0.1 M tetraethylammonium perchlorate. (B) $Co(bpy)_3^{2+}$ incorporated in a Nafion coating (0.6 μm) on a graphite electrode. The concentration of complex in the coating is ca. 1 M. The two voltammograms were recorded in separate experiments in pure supporting electrolyte: 0.5 M Na_2SO_4. Scan rate: 100 mV s^{-1} throughout.

$Co(bpy)_3Cl_2$ was synthesized and purified essentially as described by Burstall and Nyholm.[7] Other chemicals were reagent grade and were used as received. Basal plane pyrolytic graphite electrodes (Union Carbide Co., Chicago) were cut and mounted as previously described.[8] A standard two-compartment electrochemical cell was employed. The calomel reference electrode was saturated with sodium chloride. All potentials are quoted with respect to this reference electrode (SSCE). The supporting electrolyte was 0.5 M Na_2SO_4.

Procedures and Instrumentation. Nafion films were prepared on the graphite electrodes as described previously.[9] Incorporation of $Co(bpy)_3^{2+}$ was accomplished by exposing the coated electrodes to a 1.0 mM aqueous solution of the complex for times ranging from 10 s to 10 min. Measurements were commenced at low reactant concentrations and repeated after the concentration was increased by exposing the electrode to the reactant solution for an additional time in order to allow measurements of D_{exptl} at various reactant concentrations in the same film. After each successive loading of the film it was allowed to soak for 30 min in pure supporting electrolyte solution to allow the reactant concentration profile to become more uniform. The quantities of complex incorporated after each soaking step were determined by potential-step coulometry as previously described.[10]

For cyclic voltammetry and coulometry a Princeton Applied Research Model 173/179 potentiostat/digital coulometer was employed along with a Model 175 universal programmer. Chronocoulometric data were obtained with use of a computer-controlled apparatus previously described.[11]

The film thicknesses resulting from evaporation of both 2- and 4-μL aliquots of the 5.2% Nafion solution were measured with a Sloan Dektak profilometer. The thickness of a 4-μL film was measured both before and after loading the film with $Co(bpy)_3^{2+}$ up to concentrations of ca. 1 M. The film thickness did not depend on the concentration of the incorporated complex.

Results

Cyclic voltammograms for $Co(bpy)_3^{2+}$ recorded at uncoated electrodes in aqueous solution are distorted by the adsorption of the 2+ complex and the low solubility of the 1+ complex. For this reason its behavior at an uncoated graphite electrode was examined in acetonitrile where there is no evidence of adsorption.[12]

Figure 1A shows the voltammogram. The two sets of waves at +0.33 and -0.96 V correspond to the $Co(bpy)_3^{3+/2+}$ and $Co(bpy)_3^{2+/+}$ couples, respectively. The peak currents are all equal and reflect the diffusion coefficient of $Co(bpy)_3^{2+}$. Figure 1B shows the strikingly different response obtained when the $Co(bpy)_3^{2+}$ is incorporated in a 0.6-μm film of Nafion on the electrode and the cyclic voltammetry is repeated in an aqueous supporting-electrolyte solution containing no $Co(bpy)_3^{2+}$. The responses of the $Co(bpy)_3^{3+/2+}$ and $Co(bpy)_3^{2+/+}$ couples within the Nafion coating appear at +0.10 and -1.19 V, respectively. The peak currents are far from equal despite the fact that the same reactant, $Co(bpy)_3^{2+}$, is responsible for both waves. The magnitudes of the currents are unaffected by changes in the initial potential or scan direction. The asymmetrical shape of the waves for both couples indicates that the current is controlled by diffusion-like processes within the film. These results show that the effective diffusion coefficient of $Co(bpy)_3^{2+}$ in the presence of $Co(bpy)_3^{+}$, $D_{2/1}$, is much larger than it is in the presence of $Co(bpy)_3^{3+}$, $D_{2/3}$. We propose that this difference arises because the rate of electron exchange between $Co(bpy)_3^{2+}$ and $Co(bpy)_3^{+}$ is large enough ($k_{ex} \geq 10^8$ M^{-1} s^{-1} in homogeneous aqueous solution[13]) for there to be a significant contribution from electron hopping to the propagation of charge through the film during the reduction of $Co(bpy)_3^{2+}$.

It was shown in a recent study that electron exchange does not contribute to the diffusion of $Co(bpy)_3^{2+}$ in the presence of $Co(bpy)_3^{3+}$ in Nafion coatings[2] ($k_{ex} = 2$ M^{-1} s^{-1} for the $Co(bpy)_3^{3+/2+}$ couple[14]) and this is in accord with the much smaller peak currents exhibited by this couple in Figure 1B. This is a very useful result because it allows D_0 for $Co(bpy)_3^{2+}$ in Nafion coatings to be measured (by oxidizing it to $Co(bpy)_3^{3+}$). Then, the contribution of electron exchange to the diffusion of the same complex can be deduced by reducing it to $Co(bpy)_3^{+}$ and subtracting the contribution arising from D_0. Thus, an internal standard for D_0 is available that is immune to changes in reactant concentrations or film thicknesses. This feature is exploited extensively in the experiments to be described.

Evaluation of Diffusion Coefficients. Potential-step chronocoulometry was used to determine values of D_{exptl} from the slope of plots of charge vs. $(time)^{1/2}$.[15] Typically, measurements encompassed times from 10^{-3} to 10^{-1} s for a variety of concentrations of $Co(bpy)_3^{2+}$ and for two values of the film thickness. The concentration dependence of the slopes of the plots of charge vs. $(time)^{1/2}$ was measured with the identical film for the entire set of measurements to minimize uncertainties arising from small variations in the film thickness from coating to coating. The value of D_{exptl} was calculated from the equation

$$D_{exptl} = \left[\frac{S\Phi\pi^{1/2}}{2F\Gamma}\right]^2 = \left[\frac{S\pi^{1/2}}{2FC}\right]^2 \qquad (2)$$

where S is the chronocoulometric slope (C cm^{-2} $s^{-1/2}$), Φ is the film thickness (cm), Γ is the total quantity of $Co(bpy)_3^{2+}$ in the film (mol cm^{-2}), C is its concentration (mol cm^{-3}), and F is the Faraday constant.

Equation 2 contains the tacit assumption that the $Co(bpy)_3^{2+}$ is distributed uniformly throughout the film. For this assumption to be verified, a separate set of experiments was performed in which the linearity of chronocoulometric plots for the oxidation of $Co(bpy)_3^{2+}$ was examined over a time range wide enough for the diffusion layer thickness, $(Dt)^{1/2}$, to vary from a few percent to over fifty percent of the film thickness. The plots remained linear throughout this range of diffusion layers as expected for a reactant distributed uniformly throughout the film.

Figure 2 shows the values of $D_{2/1}$ and $D_{2/3}$ obtained as a function of C for a 0.6-μm film into which $Co(bpy)_3^{2+}$ was incrementally incorporated. $D_{2/1}$ undergoes a nearly fivefold increase over the

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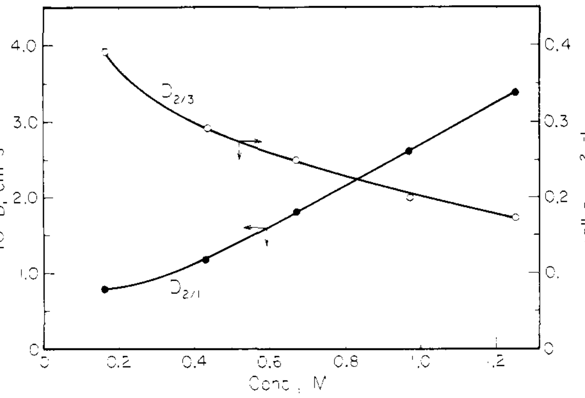

Figure 2. Concentration dependence of diffusion coefficients for Co$(bpy)_3^{2+}$ in a 0.6-μm Nafion coating: (●) $D_{2/1}$, measured by reducing Co$(bpy)_3^{2+}$ to Co$(bpy)_3^{+}$; (○) $D_{2/3}$, measured by oxidizing Co$(bpy)_3^{2+}$ to Co$(bpy)_3^{3+}$. Supporting electrolyte: 0.5 M Na_2SO_4.

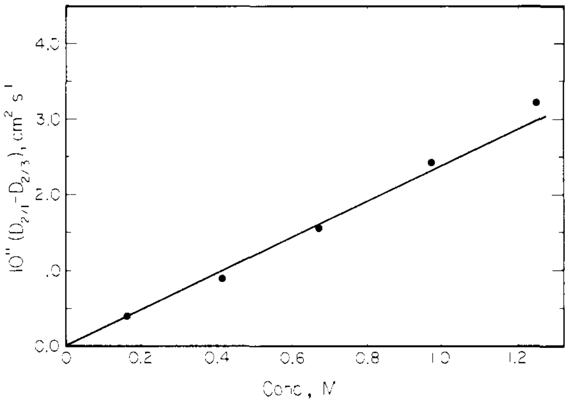

Figure 3. Concentration dependence of the difference between the values of $D_{2/1}$ and $D_{2/3}$ in Figure 2.

concentration range examined while $D_{2/3}$ decreases by a smaller factor. The values of $D_{2/1}$ and $D_{2/3}$ tend toward a common value as C approaches zero. The increase of $D_{2/1}$ with concentration and the near equality of $D_{2/1}$ and $D_{2/3}$ at low concentrations are features that are in qualitative agreement with eq 1 if $D_{2/3}$ is taken as equal to D_0. The dependence of $D_{2/3}$ (i.e., D_0) on C is not predicted by eq 1 and this aspect of the behavior will be examined further in the Discussion section. The data of Figure 2 were replotted in the form $D_{2/1} - D_{2/3}$ vs. C in Figure 3 to correct for the dependence of D_0 on C in comparing the experimental data with eq 1. A similar plot for a film thickness of 1.2 μm had the same slope and intercept within the experimental reproducibility of ca. ±30%. The fact that the plots are linear and go through the origin supports the contention that the data adhere to eq 1 and therefore provide a means of evaluating k_{ex} for electron exchange between Co$(bpy)_3^{2+}$ and Co$(bpy)_3^{+}$ inside the Nafion coating.

Discussion

The results shown in Figures 2 and 3 seem clearly to demonstrate that the diffusion coefficient for Co$(bpy)_3^{2+}$ measured in the presence of Co$(bpy)_3^{+}$ in Nafion coatings exhibits a concentration dependence of the type that Dahms[5] and Ruff and coworkers[6] predicted to be present whenever electron self-exchange is an important component of the diffusive process. The fact that the contributions from physical motion of the Co$(bpy)_3^{2+}$ cation can be easily determined from the diffusion coefficient, $D_{2/3}$, obtained in experiments where the complex is oxidized to Co$(bpy)_3^{3+}$ makes this system unusually attractive for quantitative studies. Thus, according to eq 1, the slope of the line in Figure 3 should be equal to $(\pi/4)k_{ex}\delta^2$ from which k_{ex} can be estimated if δ is taken to be the diameter of the Co$(bpy)_3^{2+}$ complex, ~14 Å. The value of k_{ex} obtained in this way, 2×10^3 M^{-1} s^{-1}, is much smaller than the value of k_{ex} obtained by Brunschwig et al.[13] from measurements in homogeneous solution, $k_{ex} \geq 10^8$ M^{-1} s^{-1}. This is not surprising when it is recognized that the rate constants measured experimentally, $(k_{ex})_{obsd}$, obey the equation

$$\frac{1}{(k_{ex})_{obsd}} = \frac{1}{k_d} + \frac{1}{k_{ex}} \qquad (3)$$

where k_d is the diffusion-controlled rate constant and k_{ex} is the true self-exchange rate constant. In homogeneous solution k_d is 10^{10}–10^{11} M^{-1} s^{-1} so that the measured rate constant, $(k_{ex})_{obsd} \geq 10^8$ M^{-1} s^{-1},[13] provides a good estimate of k_{ex}. However, the value of k_d that applies to Nafion coatings is much smaller. Its magnitude may be estimated from the measured value of $D_{2/3}$ with use of the Smoluchowski equation[16]

$$k_d = 4\pi N_A R D/10^3 \qquad (4)$$

N_A is Avagadro's number and R and D are the sum of the radii and of the diffusion coefficients, respectively, of the reactants. Taking R to be ~14 Å (twice the radius of Co$(bpy)_3^{2+}$) and D to be 2×10^{-12} cm^2 s^{-1} (twice $D_{2/3}$) gives $k_d = 4 \times 10^3$ M^{-1} s^{-1}. This value is much smaller than the measured value of k_{ex} in homogeneous solution so that it is clear from eq 3 that $(k_{ex})_{obsd}$ evaluted from eq 1 and the slope of the line in Figure 3 will be determined by k_d rather than k_{ex}. The fact that the value of k_d calculated from eq 4, 4×10^3 M^{-1} s^{-1}, is close to the rate constant obtained from the slope of the line in Figure 3, 2×10^3 M^{-1} s^{-1}, strongly supports this interpretation. The approximations involved in this calculation make quantitative conclusions unwarranted, but it does seem clear that whenever the rates of reactant diffusion inside electrode coatings are much smaller than they are in homogeneous aqueous solution (as is often the case), the values of rate constants measured for exchange reactions occurring within the coatings are expected to be correspondingly smaller than the values measured in homogeneous solutions.

Variation in $D_{2/3}$ with the Concentration of Incorporated Reactant. The decrease in $D_{2/3}$ for Co$(bpy)_3^{2+}$ shown in Figures 2 and 3 occurs in concentration ranges where the thickness of the films has been shown to remain fixed. Recalling that $D_{2/3}$ measures the diffusion rate of Co$(bpy)_3^{2+}$ by physical motion of the complex and/or counterions through the coating, we believe that the decrease results from competition between the diffusing complexes for counterionic or hydrophobic residence sites within the polyelectrolyte film. The basic phenomenon, termed "single-file diffusion", was first discussed by Hodgkin and Keynes in relation to cationic transport across membranes.[17] Subsequently, numerous theoretical and experimental investigations of the phenomenon have been carried out.[18] The essential idea is that diffusing species which must move between more or less fixed sites within a matrix may have their rate of motion limited by the decreasing availability of sites as the concentration of the diffusing species increases. The experimental result is a diffusion coefficient that decreases with the concentration of the diffusing species. A lucid discussion of the model and its consequences is given by Heckmann.[19] It seems likely that this model may prove generally useful in accounting for the motion of incorporated reactants through polymer and polyelectrolyte coatings.

Comparison with Previous Results. The diffusion coefficients that have been measured for various cations in Nafion coatings span a surprisingly large range of values. Thus, $D_{2/3}$ for Co$(bpy)_3^{2+}$ is ca. 1×10^{-12} cm^2 s^{-1} while $D_{2/3}$ for Ru$(bpy)_3^{2+}$ is ca. 5×10^{-10} cm^2 s^{-1},[6b,20] $D_{2/3}$ for Ru$(NH_3)_6^{2+}$ is ca. 2×10^{-9} cm^2

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(20) The values quoted for Ru$(bpy)_3^{2+}$ and Ru$(NH_3)_6^{2+}$ are about 20 times smaller than the values given in ref 4. The present values are more reliable because they were obtained from measurements with Nafion coatings of measured thicknesses. (Previously the film thicknesses were calculated from an assumed density that turned out to be about 4.5 times too large.) Our newly measured values of $D_{2/3}$ for Ru$(bpy)_3^{2+}$ is $(4 \pm 3) \times 10^{-10}$ cm^2 s^{-1}, which is in good agreement with the value of $(5 \pm 2) \times 10^{-10}$ cm^2 s^{-1} reported by Martin et al.[5b]

s^{-1} [2,20] and the diffusion coefficient of Na^+ is 9×10^{-7} cm^2 s^{-1}.[21] Among these ions, only the diffusion of $Ru(bpy)_3{}^{2+}$ is believed to be enhanced by electron-exchange reactions[2,3] yet its diffusion coefficient does not exhibit the concentration dependence predicted in eq 1. What is responsible for this lack of concentration dependence and why should the diffusion of Na^+ be so much faster than that of $Ru(bpy)_3{}^{2+}$ despite the lack of electron-exchange enhancement of the diffusion of Na^+? We believe the answers to these questions are to be found in the unusual structural features of Nafion that include two phases between which incorporated cations may partition. Nafion membranes are known[22] to contain regions composed mainly of fluorocarbon that are separated from largely aqueous, hydrophilic regions by a so-called interfacial region that is more hydrophobic and tends to accumulate hydrophobic cations. For example, Cs^+ ions incorporated by Nafion membranes reside primarily in this interfacial region while Na^+ ions remain in the more hydrophilic, aqueous phase.[21]. The diffusion coefficient of Cs^+ in Nafion (5×10^{-8} cm^2 s^{-1}) is much smaller than that for Na^+ ($\sim 9 \times 10^{-7}$ cm^2 s^{-1}),[21] suggesting that ions confined to the hydrophobic phase diffuse more slowly than those in the hydrophilic phase.

Both $Ru(bpy)_3{}^{2+}$ and $Co(bpy)_3{}^{2+}$ are much more hydrophobic than Na^+ and would therefore be expected to partition preferentially into the more hydrophobic interfacial regions within Nafion. Indeed, $Ru(bpy)_3{}^{2+}$ has been shown to do so.[23] This would account for the smaller diffusion coefficient of the bipyridine complexes. However, both $D_{2/3}$ for $Ru(bpy)_3{}^{2+}$ and $D_{2/1}$ for $Co(bpy)_3{}^{2+}$ are enhanced by electron exchange but only the latter shows the concentration dependence predicted by eq 1. In addition, the absolute values of the two diffusion coefficients ($D_{2/3}$ for $Ru(bpy)_3{}^{2+} = 5 \times 10^{-10}$ cm^2 s^{-1}; $D_{2/1}$ for $Co(bpy)_3{}^{2+} = 1\text{–}5 \times 10^{-11}$ cm^2 s^{-1}) are unexpectedly disparate considering that the two dipositive ions have very similar sizes and self-exchange rate constants that are large and similar.[13] We believe this apparent anomaly can also be explained on the basis of the two-phase structure within Nafion.

Cations that partition between the hydrophobic and hydrophilic phases within Nafion coatings diffuse within each phase with a diffusion coefficient characteristic of that phase. Exchange of cations between the two phases is slow compared to the times involved in the measurement of diffusion coefficients (vide infra) so that the measured values represent the sum of the contributions of diffusion in each of the phases weighted by the concentration of the cation in each phase. Hydrophilic ions such as Na^+ that remain primarily in the more aqueous phase inside the Nafion coating exhibit relatively large diffusion coefficients that reflect their motion through the hydrophilic phase. Hydrophobic cations such as $Co(bpy)_3{}^{2+}$ partition primarily in the less aqueous phase inside the coating where much smaller diffusion coefficients prevail, e.g., $1\text{–}5 \times 10^{-12}$ cm^2 s^{-1}. Diffusion in both phases may be enhanced by electron exchange between redox couples with sufficiently large self-exchange rate constants when they are present at sufficiently high concentrations. Such in-phase electron exchange between diffusing redox couples is revealed by the concentration dependence of the observed diffusion coefficients of which the $Co(bpy)_3{}^{2+/+}$ couple is the first reported example.

Now consider the behavior of $Ru(bpy)_3{}^{2+}$. This cation will also partition between the two phases within Nafion coatings to yield a composite diffusion coefficient representing the sum of the contributions from diffusion in each phase. However, with the $Ru(bpy)_3{}^{3+/2+}$ couple, unlike the $Co(bpy)_3{}^{3+/2+}$ couple, electron exchange between the oxidized and reduced forms of the complex proceeds rapidly, and when the two forms undergoing exchange are present in different phases the exchange couples the diffusional processes occurring in each phase.[24] As a result, contributions to the measured diffusion coefficient from the cations present in the more aqueous phase will be larger than is true for couples such as $Co(bpy)_3{}^{3+/2+}$ where such cross-phase (as well as in-phase) electron exchange proceeds too slowly to be important. Saveant has shown[25] that two parallel diffusional pathways that are coupled by electron exchange between the diffusing reactants will produce an apparent diffusion coefficient, D_{app}, given by

$$D_{app} = D_1 f_1 + D_2 f_2 \qquad (5)$$

where D_1 and D_2 are the diffusion coefficients appropriate for each phase and f_1 and f_2 are the fractions of the total incorporated reactant present in each phase. The equilibrium constant, K, governing the partitioning of the ions between the two phases in which the diffusion occurs is given by $K = f_2/f_1$. The measured diffusion coefficient for $Ru(bpy)_3{}^{2+}$ is $D_{app} = 5 \times 10^{-10}$ cm^2 s^{-1}. The diffusion coefficient of the (presumably small) fraction of the $Ru(bpy)_3{}^{2+}$ present in the hydrophilic phase (i.e., D_1 in eq 5) cannot be measured independently but it may be approximated roughly by the reported value for Na^+, namely 9×10^{-7} cm^2 s^{-1}. A reasonable estimate for the diffusion coefficient of $Ru(bpy)_3{}^{2+}$ within the hydrophobic phase (i.e., D_2 in eq 5) is $D_{2/1}$ for $Co(bpy)_3{}^{2+}$, say 2×10^{-11} cm^2 s^{-1}. Substitution of these values in eq 5 leads to a calculated value of $f_1 \simeq 1/K$ of 5.3×10^{-4}. Thus, this line of reasoning leads to the conclusion that even though less than 0.1% of the $Ru(bpy)_3{}^{2+}$ is present in the hydrophilic phase, it is this phase that carries most of the diffusional current because of the efficient coupling mechanism provided by cross-phase electron exchange.

Note that this interpretation also provides an immediate explanation for the lack of concentration dependence in the measured values of $D_{app} = D_{2/3}$ for $Ru(bpy)_3{}^{2+}$: If the diffusion of this ion is dominated by its relatively rapid motion in the hydrophilic phase in the Nafion where it is present at a concentration too low for in-phase electron exchange to contribute significantly to D_1, no concentration dependence of D_{app} is expected. Electron exchange doubtless *does* enhance the rate of diffusion of the majority of the $Ru(bpy)_3{}^{2+}$ that is partitioned into the hydrophobic phase but the resulting diffusion coefficient in this phase remains too small for this diffusional pathway to become quantitatively significant.

The much smaller value of k_{ex} for the $Co(bpy)_3{}^{3+/2+}$ couple means that the diffusional pathways in the hydrophobic and hydrophilic phases that contribute to the measured values of $D_{2/3}$ for this ion are not likely to be coupled by cross-phase electron exchange. In the absence of cross-phase exchange (or when it proceeds negligibly on the experimental time scale) the observed diffusion coefficient will obey eq 6.[25] If we assume for $Co(bpy)_3{}^{2+}$,

$$D_{app}{}^{1/2} = D_1{}^{1/2} f_1 + D_2{}^{1/2} f_2 \qquad (6)$$

as we did for $Ru(bpy)_3{}^{2+}$, that $D_1 \sim 9 \times 10^{-7}$ cm^2 s^{-1} and that f_1 is the same for both $Co(bpy)_3{}^{2+}$ and $Ru(bpy)_3{}^{2+}$ ($f_1 = 5.3 \times 10^{-4}$), the $D_1{}^{1/2} f_1$ term in eq 6 amounts to 0.05×10^{-6} cm s$^{-1/2}$ while $D_{app}{}^{1/2} = D_{2/3}{}^{1/2}$ for $Co(bpy)_3{}^{2+} = 1.4 \times 10^{-6}$ cm s$^{-1/2}$. Thus, the contribution to D_{app} from the small portion of the cations that reside in the hydrophilic phase is negligibly small so that the measured value of $D_{2/3}$ for $Co(bpy)_3{}^{2+}$ should provide a reasonable measure of the diffusion coefficient of the ion within the hydrophobic phase, i.e., D_2.

Note that the small measured value of $D_{2/3}$ for $Co(bpy)_3{}^{2+}$ could not be explained if eq 5 instead of eq 6 were used. Sufficiently rapid cross-phase place-exchange reactions in which ions in opposite phases trade places with each other can also couple the two diffusional pathways.[24] The fact that the D_{app} for $Co(bpy)_3{}^{2+}$ is consistent with eq 6 but not eq 5 indicates that the rate of such a place-exchange reaction is not great enough to affect the measured values of the diffusion coefficients.

In our preliminary report[4] the large difference between the values of $D_{2/3}$ for $Ru(bpy)_3{}^{2+}$ and $Co(bpy)_3{}^{2+}$ in Nafion was taken as evidence of electron-exchange enhancement of the diffusional rate of the former complex. On the basis of the interpretation presented here this conclusion requires some refinement: The

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measured value of $D_{2/3}$ for $Ru(bpy)_3^{2+}$ in Nafion is dominated by the physical motion of the ion through the hydrophilic phase within Nafion coatings. $D_{2/3}$ for $Ru(bpy)_3^{2+}$ is larger than for $Co(bpy)_3^{2+}$ because cross-phase electron exchange between the concentrated but slower moving ions in the hydrophobic phase and the dilute but rapidly moving ions in the hydrophilic phase allows the latter to carry most of the diffusional motion.

A final question to be faced is why $D_{2/1}$ for $Co(bpy)_3^{2+}$, where a high electron-exchange rate prevails, does not achieve a concentration independence by the same mechanism proposed in the case of $D_{2/3}$ for $Ru(bpy)_3^{2+}$. The answer seems likely to depend upon the greater hydrophobicity of the less highly charged $Co(bpy)_3^+$ ion. In aqueous solutions at bare graphite electrodes $Co(bpy)_3^+$ readily leaves the aqueous phase to form multiple adsorbed (or precipitated) layers on the surface.[26] If precipitation of the $Co(bpy)_3^+$ generated in the hydrophilic phase in Nafion competed with its partitioning into the hydrophobic phase this could both slow down the rate of cross-phase electron exchange and decrease the effective concentration in the hydrophilic phase of the reactant ions whose higher mobility needs to be exploited to achieve a concentration-independent diffusion coefficient.

A second factor that could slow down the rate of cross-phase exchange is a decrease in driving force. The equilibrium constant for partitioning between the hydrophobic and hydrophilic phases will be larger for $Co(bpy)_3^+$ than for $Ru(bpy)_3^{2+}$. For this reason the formal potential of the $Co(bpy)_3^{2+/+}$ couple within the hydrophobic phase will be shifted to more positive values to a greater extent than will the formal potential of the $Ru(bpy)_3^{3+/2+}$ couple. (The difference in formal potentials between redox couples in the hydrophobic and hydrophilic phases of Nafion coatings will be $(RT/F)\ln[K_{ox}/K_{red}]$ where K_{ox} and K_{red} are the equilibrium constants governing the partitioning of the oxidized and reduced halves of the redox couple, respectively.) A larger difference in formal potentials for $Co(bpy)_3^{2+/+}$ compared with $Ru(bpy)_3^{3+/2+}$ would lead to a smaller driving force for cross-phase electron exchange for the former couple. The result could be a cross-phase exchange rate too low for efficient coupling of the slow diffusion pathway within the hydrophobic phase with the faster diffusion pathway available in the hydrophilic phase. If either, or both, of these factors decrease sufficiently the rate of the cross-phase electron exchange that couples the diffusion in the two phases, the observed value of $D_{2/1}$ for $Co(bpy)_3^{2+}$ would be a measure of its relatively slow diffusion within the hydrophobic phase unenhanced by coupling to the more rapidly diffusing ions in the hydrophilic phase. In that case, it is the rate constant for in-phase electron exchange between $Co(bpy)_3^{2+}$ and $Co(bpy)_3^+$ in the hydrophobic phase that is expressed in the concentration dependence of the resulting values of $D_{2/1}$.

Conclusions

One of the primary conclusions resulting from this study is that the previously demonstrated[21,22] two-phase structure of Nafion should not be ignored in constructing mechanistic schemes to account for charge propagation through Nafion coatings. The combination of the present data with those from previous related studies[2-4] and ideas arising from investigations of diffusion in membranes[17-19] suggests that at least two classes of diffusional behavior, as measured electrochemically, are likely to be encountered with redox reactants that diffuse through Nafion coatings. The first class is comprised of reactants with electron self-exchange rates too small to affect the diffusion process significantly. Their diffusion involves physical motion of the reactant at rates that differ greatly in the hydrophilic and hydrophobic phases within the Nafion coatings. Competition between reactant species for residence sites within the coating may produce diffusion coefficients that decrease with the reactant concentration as anticipated by the model of single-file diffusion.[19] The $Co(bpy)_3^{3+/2+}$ couple (as well as the $Co(NH_3)_6^{3+/2+}$ and $Ru(NH_3)_6^{3+/2+}$ couples[2]) is an example of a reactant of this class.

The second class of possible systems involves reactants for which electron self-exchange proceeds rapidly enough to affect the diffusional rates. Because of the two-phase structure adopted by Nafion coatings the electron exchange may involve both in-phase and cross-phase exchanges. In-phase exchange involves reactants that are both present in the same phase while cross-phase electron exchange involves reactants that are in different phases inside the coating. (Cross-phase place exchange is also possible[24,25] but is apparently rather slow in Nafion coatings as judged by the behavior of the $Co(bpy)_3^{3+/2+}$ couple.) In-phase electron exchange enhances diffusional rates in the way described by Dahms[5] and Ruff et al.[6] and produces diffusion coefficients that increase with the reactant concentration. Cross-phase electron exchange couples the diffusional processes in each phase. The concentration dependence of the measured diffusion coefficients, if any, will depend on the equilibrium concentrations and relative diffusion coefficients of the reactants in each phase. $D_{2/3}$ for $Ru(bpy)_3^{2+}$ is believed to be a case in which cross-phase electron exchange enhances the measured diffusion coefficient while $D_{2/1}$ for $Co(bpy)_3^{2+}$ is the first case in which in-phase electron exchange makes its presence evident in the form of a concentration-dependent diffusion coefficient.

To the best of our knowledge, all of the electrochemically measured diffusion coefficients of redox ions in Nafion coatings so far reported can be understood in terms of appropriate combinations of these two categories.

The diffusion of reactants within polymeric coatings on electrodes is usually considerably slower than that in homogeneous solution. As a result, rate constants evaluated within polymeric coatings for inherently rapid electron-exchange reactions are often leveled to the diffusion-controlled rate constant characteristic of the polymer. In such cases the values of rate constants for electron-transfer reactions measured in homogeneous solution will exceed the values measured in polymer coatings even when the ions are equally reactive toward electron transfer in both media. This factor may be expected to affect the observed rates of both self-exchange and cross-reactions occurring in the interior of polymeric coatings.

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Registry No. $Co(bpy)_3$, 15878-95-2; Nafion, 39464-59-0; graphite, 7782-42-5.

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