very recent experimental results[6] for linear N_2S is found for most parameters; however, the estimated experimental bending harmonic vibrational frequency is 100 cm^{-1} below the two most reliable theoretical estimates (obtained using the DZP CASSCF and DZP CCSD methods). Protonation of the linear isomer is favored at sulfur, and will weaken the N–S bond. Unlike P_2O, protonation does not dramatically lower[13] the relative energy of cyclic N_2S. Protonation of N_2S lowers the relative energy of the cyclic form by only 3.1 kcal mol^{-1} at the DZP CISD+Q level (Q refers to Davidson's correlation for quadrupole excitations[24]). For cyclic P_2O, protonation disrupts the weak P–P bond, whereas the strong N–N bond is disrupted in N_2S. Although protonation gives little thermodynamic stabilization to cyclic N_2S, it may, in a way similar to excitation to the triplet state, provide kinetic stabilization. The N–S bonds are the most easily broken, and protonation of cyclic N_2S strengthens those bonds. One may, therefore, have a better chance of observing cyclic N_2S by protonating the parent compound. Linear N_2S, on the other hand, is more likely to fall apart upon protonation, because protonation will most likely occur at sulfur, leading to faster loss of N_2.

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Ion Association and Electric Field Effects on Electron Hopping in Redox Polymers. Application to the $Os(bpy)_3{}^{3+/2+}$ Couple in Nafion

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Abstract: The high ionic content and low dielectric constant that prevail in the interior of many redox polymers might be expected to accentuate the extent of ionic association within the polymers. The present study is an attempt to investigate the effects of ionic association on the dynamics of electron hopping within such materials. The general concepts of the treatment are exemplified by the experimental system chosen for study: the $Os(bpy)_3{}^{3+/2+}$ redox couple incorporated in Nafion films on electrode surfaces. Extensive ion association between both halves of the redox couple and the fixed anionic groups in the Nafion is argued to be responsible for the irreversibility of the incorporation. The apparent diffusion coefficient, which reflects the dynamics of electron propagation in the films, exhibits a remarkably sudden increase as the quantity of the redox couple in the film approaches electrostatic saturation with respect to the fixed anionic sites present. The observed behavior is not satisfactorily accounted for by previous models which have been proposed, even those that take account of the presence of electric fields within the films. The introduction of ionic association into the model for electron propagation leads to predictions that are in accord with the observed behavior. A key ingredient in the successful model is the assumption that the predominant forms of the electroactive counterions incorporated in Nafion are neutral aggregates resulting from association with several of the fixed anionic sites. Dissociation of the fully associated, neutral, oxidized half of the redox couple into a singly charged species which is associated with the same number of fixed anionic sites as the predominant form of the reduced half of the redox couple prior to electron self-exchange appears to be the lowest energy pathways for this process. The presence of ionic association equilibria which control such prior dissociation provides a satisfactory explanation for the steep increase in the apparent diffusion coefficient, i.e., in the rate of electron self-exchange between pairs of the incorporated redox couple, as the concentration approaches the saturation value. The steep increase results from a shift in the ion association equilibrium to produce more of the partially dissociated, oxidized half of the redox couple, which is the best partner for accepting an electron from the fully associated, reduced half of the redox couple. The inevitable electric fields present within the polyelectrolyte films also affect the observed behavior, especially as the concentration of incorporated electroactive counterions is increased, but the simultaneous presence of ionic association is required to produce predicted behavior which matches that observed experimentally.

The mechanisms that determine the rates of charge propagation within polymers containing covalently, coordinatively, or electrostatically bound redox centers have attracted active attention since the earliest applications of these materials as electrode coatings.[2-15] Besides their intrinsic interest, these mechanisms are also important in view of the electrocatalytic properties[16] of such films, because charge propagation (together with the rate

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of permeation of the substrate and the kinetics of the catalytic reaction) is one of the key possible rate-limiting factors.[17]

In sharp contrast with the usual behavior observed in solution, the magnitudes of the diffusion coefficients that result from charge propagation mediated by redox reactants confined to polymer films typically exhibit large variations as the reactant concentrations are changed. Although a number of proposals have been presented to try to explain the observed behavior, the previous analyses suffer from unreasonably restrictive assumptions or from conceptual or interpretative shortcomings. The model that we will develop attempts to deal explicitly and quantitatively with the types of ionic interactions that must prevail in the interior of redox polymers where ionic concentrations are high, dielectric constants are low, and the quantities of solvent available for the solvation of ions are limited. The model accounts for otherwise very puzzling experimental data and allows one to anticipate how changes in the chemical compositions of the films may affect the rate of charge propagation within them.

We begin with a brief recapitulation of the interpretations that have been offered for charge propagation rates in redox polymers. Following a description of the experimental protocols that are required to obtain the most diagonistically useful data with a particularly widely studied polymeric coating material, Nafion, the essential aspects of the new model are presented. The consequences of the model are analyzed and calculations are performed that allow the predictions it permits to be compared with previous experimental data and with an extensive set of new data obtained as a part of this study.

In most cases, propagation of charge in redox polymers has been investigated in the presence of a concentration gradient of the oxidized and reduced forms of the redox centers. Under these conditions, potential-step transient or steady-state electrochemical techniques have most often been used to measure the rates of charge transport.[18] In all cases, the rate of charge propagation as derived from the variation of the charge (or the current) with time following a potential step has been found to obey the Cottrell equation;[19a] i.e., the instantaneous charge or current is proportional to the square root of time or to its inverse, respectively, provided the time scale is short enough so that the region of space adjacent to the electrode surface in which a sizeable concentration gradient exists is small compared to the film thickness.[19b] Such observations led to the notion that charge transport can be regarded as equivalent to a diffusional process to which an apparent diffusion coefficient, D_{ap}, applies.

The way in which electron hopping between pairs of attached oxidized and reduced molecules can result in a diffusion-like behavior was first explained by means of a stochastic quasi-lattice model in which the redox centers are regarded as randomly distributed over a *fictitious* cubic lattice whose characteristic length is equal to the hopping distance, δ.[14a,20] Fick's laws than appear to give good approximate descriptions of the rate of electron hopping under a concentration gradient of the redox centers with a diffusion coefficient given by eq 1[14a,20]

$$D_{\mathrm{E}} = k_{\mathrm{pair}}\delta^2 C_{\mathrm{E}} = (k/6)\delta^2 C_{\mathrm{E}} \tag{1}$$

where k_{pair} is the volume rate constant of electron transfer for a pair of adjacent sites and $k = 6k_{\mathrm{pair}}$ is the conventional electron-transfer volume rate constant, taking into account that each node of the lattice is surrounded by six neighbors. C_{E} is the total concentration of redox centers.

This model applies to immobile redox sites. In the case of electrostatically bound redox centers, physical diffusive displacement may make a significant contribution to the charge propagation in addition to electron hopping between pairs of oxidized and reduced centers. The apparent diffusion coefficient in this case is the sum of the physical displacement and electron-hopping diffusion coefficients:[21]

$$D = D_{\mathrm{pd}} + (k/6)\delta^2 C_{\mathrm{E}} \tag{2}$$

Attempts to observe variations in the apparent diffusion coefficient with the concentration of redox sites as predicted by eqs 1 and 2 have led to a variety of results, only some of which appeared to follow eq 2. Improvements in the theory seemed called for.

One step in this direction is made by recognizing that the maintenance of electroneutrality means that the electron movement is necessarily coupled to the physical displacement of electroinactive counterions. The situation is analogous to that involved

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$$D = D_{\mathrm{pd}} + (\pi/4)k\delta^2 C_{\mathrm{E}}$$

originally derived in the framework of a thermodynamic model of the possible enhancement of the physical displacement diffusion in solution by transfer reaction between the diffusing species.[21b,c] The numerical coefficient of $\pi/4$ has been recently corrected to $1/6$ on the basis of the same thermodynamic model which was shown to be equivalent with the stochastic model.[21d–f] (b) Ruff, I.; Friedrich, V. J. *J. Phys. Chem.* **1971**, *75*, 3297. (c) Dahms, H. *J. Phys. Chem.* **1968**, *72*, 362. (d) Ruff, I.; Botar, L. *J. Chem. Phys.* **1985**, *83*, 1292. (e) Botar, L.; Ruff, I. *Chem. Phys. Lett.* **1986**, *126*, 348. (f) Botar, L.; Ruff, I. *Chem. Phys. Lett.* **1988**, *149*, 99.

with ordinary solutions of electroactive reactants in the presence of little or no supporting electrolyte where the migration of charged reactants in the electric field affects the charge propagation rates. Theoretical analysis[22] of such systems involves the addition of classical Nernst–Planck terms to Fick's diffusion laws to obtain equations which show that the smaller the concentration or mobility of the electroinactive ions present, the more pronounced is the effect of the migration. However, the "migration" of electrons is not governed by the Nernst–Planck–Fick equation. The fluxes are given instead by the equations[23a–e]

$$J_A = -J_B = -D_E\left[\frac{\partial C_A}{\partial x} + \frac{\mathcal{F}}{RT}C_A\left(1 - \frac{C_A}{C_E}\right)\frac{\partial \Phi}{\partial x}\right] = D_E\left[\frac{\partial C_B}{\partial x} - \frac{\mathcal{F}}{RT}C_B\left(1 - \frac{C_B}{C_E}\right)\frac{\partial \Phi}{\partial x}\right] \quad (3)$$

(A,B, oxidized and reduced forms of the redox couple; Φ, potential; *J*'s, fluxes; *C*'s, concentrations; *D*'s, diffusion coefficients), whereas the Nernst–Planck equation

$$J = -D\left[\frac{\partial C}{\partial x} + \frac{z\mathcal{F}}{RT}C\frac{\partial \Phi}{\partial x}\right] \quad (4)$$

applies for the electroinactive counterions or for the electroactive ions in the case where physical displacement prevails over electron hopping. Analyses of the responses expected in both steady-state[23f] and transient[23g] experiments showed that the presence of migration always enhances the rate of electron hopping and the enhancement grows as the mobility of the electroinactive counterions decreases. Thus, earlier suggestions[2b,7,8a–c,10a] that charge transport rates in redox polymers might be controlled by the slower of the two coupled processes of electron hopping and electroinactive counterion displacement seem inappropriate. On the contrary, the slower the movement of the electroinactive ions, the faster the electron hopping and the larger the resulting current density (at least within the limits of the quasi-electroneutrality assumption). In all cases, the potential-step current or charge shows a Cottrellian behavior from which apparent diffusion coefficients can be evaluated which contain the effect of the field created by any mismatch between the rates of electroinactive counterion displacement and electron hopping.[23g] These apparent diffusion coefficients increase with the concentration of redox centers more steeply than the simple proportionality indicated in eq 2. This feature has been used to interepret[23g,h] previous observations made with poly(vinylpyridine) copolymers containing coordinatively attached osmium and ruthenium ions.[12c]

All the models recalled above ignore activity effects on the dynamics of electron hopping under concentration gradients and electric fields in that they implicitly assume that the interactions between each ion and all the others remain the same as the ionic composition of the redox polymer is changed.[24] Since redox polymer coatings contain large ion concentrations, as large as moles per liter, such an assumption seems quite unlikely to hold when the total amount of electroactive material or the redox state of the film is changed, as occurs in electrochemical applications of such films. Activity effects on the equilibrium properties of redox polymer films have been analyzed in a few cases by introducing phenomenological interaction parameters,[14b,24] but their likely role in electron-hopping dynamics has been considered only recently.[23e,25]

In view of the high ionic content of typical redox polymers and of the weak polarity of large sections of their structure, association between ions of opposite charge is expected to be an important mode of ionic interaction inside of them.[26] A large part of activity effects may thus be treated in terms of ion association equilibria. Specifically, the interactions between an individual ion and the other ions may be divided in two categories: formation of ion pairs with ions of opposite charge on the one hand and diffuse interactions with all of the other ions on the other. The ion-paired and the (relatively) "free" ions are then regarded as engaged in a chemical equilibrium governed by an association constant. The influence of the association constant on the dynamics of charge propagation then depends on the relative role of ion-paired and "free" electroactive ions in the electron-hopping process.

The basic relationships governing the ways in which ion association affects electron-hopping rates in redox polymers in the presence of electric fields have recently been established for steady-state conditions.[23e,25] They predict apparent diffusion coefficients that show steep increases with the concentration of redox sites when the ion association equilibrium constants are large.[23e]

The goals of the work reported here were to test experimentally the effect of ion association on the dynamics of electron hopping and to extend the relevant theoretical treatments. For these purposes, redox polymers in which the electroactive ions are electrostatically attached to polyelectrolyte films in an irreversible fashion seemed particularly attractive systems since the very existence of their irreversible attachment implies strong association between the electroactive counterions and the fixed ionic sites (What else would prevent the loss of the incorporated counterions when the coatings are transferred to pure supporting electrolytes?). Electrode coatings prepared from the polyelectrolyte Nafion, in which cationic reactants can be incorporated by ion exchange, were chosen for this study. The good stability and high ionic permselectivity exhibited by such coatings have contributed to their attractiveness, although problems with reproducibility depending upon the source of the solutions of Nafion and the deposition procedures have been noted.[11b] In attempts to identify the mechanisms by which electronic and ionic charges move across Nafion coatings, the dependence of charge propagation rates on the concentration of the incorporated redox couple within the film is a diagnostically useful, experimentally accessible parameter. The most extensive previous measurements have involved electroactive counterions consisting of cationic complexes of 2,2′-bipyridine (bpy) with transition metals (e.g., Fe, Co, Ru, Os) which are particularly strongly, and essentially irreversibly, bound by Nafion coatings.[4b,5b,c,11a] In one of the first studies, the diffusion coefficients of the $\mathrm{Ru(bpy)_3^{3+/2+}}$ couple in Nafion were reported to show little dependence on the quantities of the complexes incorporated into the coating, but large fractions of the incorporated complexes were found to be electroinactive.[5b] By contrast, in more recent studies of the same system, a very strong dependence of the diffusion coefficients on the concentration of the incorporated $\mathrm{Ru(bpy)_3^{3+/2+}}$ was observed, and the same was reported for the $\mathrm{Os(bpy)^{3+/2+}}$ couple.[9,15] In an extensive set of measurements, we have observed similar behavior for the latter system. The results were quite sensitive to the procedures employed to prepare the coatings of Nafion on polished glassy carbon electrodes. After an experimental protocol that yielded satisfactorily reproducible behavior was established, apparent diffusion coefficients for the $\mathrm{Os(bpy)_3}$–Nafion system were evaluated by potential-step chronocoulometry over a wide range of concen-

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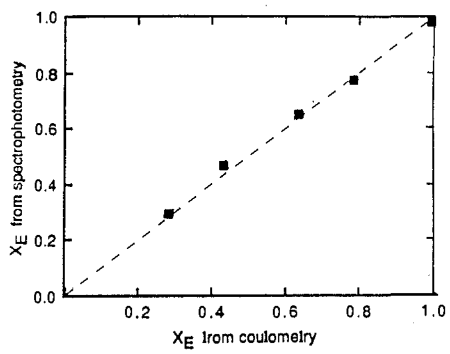

Figure 1. Fractional loading of Nafion coatings with $Os(bpy)_3^{2+}$ as determined by spectrophotometry after dissolution of the coating (see text) vs the fractional loading determined by coulometric assays. The dashed line, drawn through the origin, has unit slope.

trations. Particular care was taken to measure the molar fraction of the electroactive material in the coatings and especially to determine the conditions under which the film contained one osmium complex per three sulfonate groups. The results were used to test the predicted effects of ion association and the electric field on the rate of electron hopping after adaptation of previous models[23e,25] to polymers containing electrostatically bound redox centers and to the analysis of transient responses resulting from potential steps.

Experimental Section

Materials. Solutions of Nafion (eq wt = 1110) in an alcoholic solvent (5 wt %) were obtained from Aldrich Chemical Co. The concentration of sulfonate groups present in the solutions was determined by titration of the proton countercations to be 34.2 mM. This value was not too far from that corresponding to the concentration specified by the supplier (39.7 mM) and agrees with the concentration estimated from the sulfur content of a dried sample of Nafion obtained by evaporation of an aliquot of the stock solution. $Os^{II}(bpy)_3Cl_2\cdot 6H_2O$ was prepared as described in the literature[27] with slight modification: 1.0 g of K_2OsCl_6 and 1.28 of 2,2′-bipyridine were added to 10 mL of glycerol, and the mixture was heated at 240 °C for 1 h. The volume was reduced to ca. 1 mL by heating at 180 °C under vacuum. The residue was extracted with ether to remove excess 2,2′-bipyridine followed by dissolution in the minimum quantity of water. Dark green, lustrous crystals were obtained from this solution upon cooling in the refrigerator.

Glassy carbon electrodes (Tokai Carbon Co) were mounted and polished as previously described.[28]

Instrumentation and Procedures. Chronocoulometric measurements used to evaluate diffusion coefficients[28] were performed with a BAS 100 electrochemical analyzer (Bioanalytical Systems, Inc.). Cyclic voltammetry was carried out with a PAR instrumentation (EG&G Instruments, Inc.) and an *x*–*y* recorder.

Nafion coatings were applied to the glassy carbon electrode surfaces either by spin coating or by transfer of aliquots of the stock solution to the surface with a microsyringe. In both cases, the solvent was allowed to evaporate at room temperature to obtain adherent films. The results of experiments conducted with "solution-processed"[11b] Nafion coatings were essentially similar to those obtained with unprocessed coatings.

The quantities of $Os(bpy)_3^{2+}$ present in the coatings were measured by coulometric assays. The assays consisted of exhaustive oxidation of the complex to $Os(bpy)_3^{3+}$ followed by integration of the current required to reduce the oxidized complex to $Os(bpy)_3^{2+}$. This procedure was preferable to the simple oxidation of $Os(bpy)_2^{2+}$ because corrections for background currents were smaller and more reproducible. That all of the osmium complex incorporated in the coatings was electroactive at all loading levels was demonstrated by spectrophotometric measurements. Measured quantities of Nafion coatings were applied to platinum flag electrodes, from which detachment of the films is easier than from glassy carbon. The films were loaded with $Os(bpy)_3^{2+}$, and a coulometric assay of the quantity of electroactive complex present was carried out. The coating was then dissolved in dimethylformamide by ultrasonically agitating the coated electrode in the absence of air. The concentrations of $Os(bpy)_3^{2+}$ in the resulting solution was determined from its absorbance at 482 nm with $\epsilon = 1.4 \times 10^4$ M^{-1} cm^{-1} as determined in separate calibration measurements. The quantities of $Os(bpy)_3^{2+}$ in the solution were found to be in excellent agreement with those obtained from the coulometric assays as shown in Figure 1, thus confirming the complete electroactivity of the incorporated osmium complex.[29] In addition, the coulometric assay for $Os(bpy)_3^{3+}$ obtained with the saturated coating corresponded closely to one-third of the known, total quantity of sulfonate groups present in the coating.

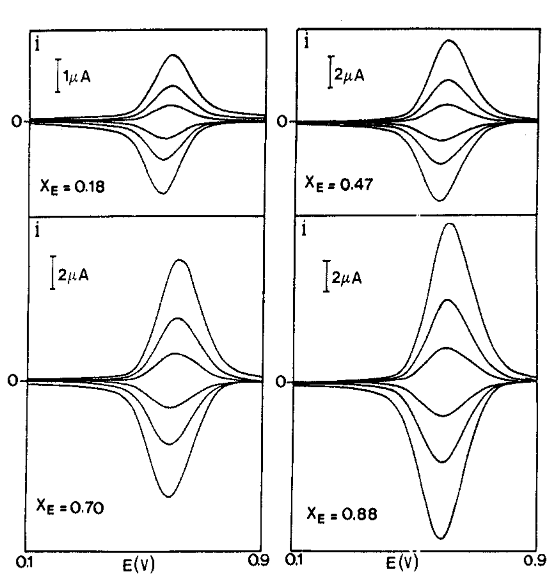

Figure 2. Slow-scan cyclic voltammetry of the $Os(bpy)_3^{3+/2+}$ couple in a Nafion film spin-coated on a glassy carbon electrode as a function of the molar fraction of Os, X_E (eq 5). Solution: 0.05 M H_2SO_4. Scan rate: 2, 5, 10 mV/s. Anodic currents are represented upward.

When the coatings were loaded to saturation with $Os(bpy)_3^{2+}$, the quantity of charge consumed during the first coulometric oxidation of the incoporated complex was greater than that required for the reduction of the resulting $Os(bpy)_2^{3+}$ and for all subsequent oxidation–reduction cycles, which produced essentially equal anodic and cathodic charge consumption. This behavior is that expected by the expulsion from the saturated coating of a portion of the incorporated $Os(bpy)_3^{2+}$ during its oxidation to $Os(bpy)_3^{3+}$ to maintain electroneutrality within the coating. (The alternative incorporation of anions into the Nafion is strongly disfavored by its high cation permselectivity.) If electroneutrality were maintained entirely by expulsion of $Os(bpy)_3^{3+}$ during the oxidation of the incorporated $Os(bpy)_3^{2+}$, one would expect the first coulometric assay to consume 1.5 times as much charge as all subsequent assays, anodic or cathodic. However, if electroneutrality were maintained by expulsion of $Os(bpy)_3^{2+}$ near the coating/electrolyte interface as $Os(bpy)_3^{3+}$ was generated at the electrode/coating interface, there would be no difference between the first anodic and all subsequent coulometric assays. Experimentally, the ratio of the charges consumed in the first (anodic) and all subsequent coulometric assays was 1.4 ± 0.1. It thus appears that electroneutrality is maintained primarily by the expulsion of $Os(bpy)_3^{3+}$ during the oxidation of $Os(bpy)_3^{2+}$ in saturated films. The charge obtained in the subsequent cathodic coulometric assays, Q_t^0, was taken as a measure of the quantity of the osmium comlex in the film that corresponds to saturation of all of the SO_3^- groups by $Os(bpy)_3^{3+}$ and thus to $X_E = 1$. The values of X_E for loadings below saturation were then obtained from $X_E = Q_t/Q_t^0$, where Q_t was the measured cathodic charge.

The spin-coated films exhibited the most reproducible behavior and were employed for measurements of apparent diffusion coefficients of $Os(bpy)_3^{2+}$. The complex was incorporated into coatings by immersing them for controlled times in 0.5 mM solutions of $Os(bpy)_3^{2+}$ in 0.05 M H_2SO_4. Measurements were started with the lowest concentrations of $Os(bpy)_3^{2+}$ in the coatings. The concentration was increased gradually by re-exposure of the coating to the $Os(bpy)_3^{2+}$ solution for controlled periods. In this way a series of diffusion coefficients was obtained for a wide range of reactant concentrations with a single Nafion coating. After each successive loading, the coating was soaked for 30 min in pure supporting electrolyte to allow the reactant concentration profile to become uniform before the diffusion coefficient was measured.

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(27) Creutz, C.; Chou, M.; Netzel, T. L.; Okumura, M.; Sutin, N. *J. Am. Chem. Soc.* **1982**, *104*, 1309.

(28) (a) Oyama, N.; Anson, F. C. *J. Am. Chem. Soc.* **1980**, *101*, 3450.

(29) An early study of $Ru(bpy)_3^{2+}$ in Nafion coatings reported that significant portions of the incorporated complexes were not electroactive.[5b] These results, which depended upon the mixing of the complexes with nonaqueous solutions of Nafion before deposition of coatings on electrode surfaces, may have resulted in significantly different internal structures in which pockets of reactants were insulated from the electrode.

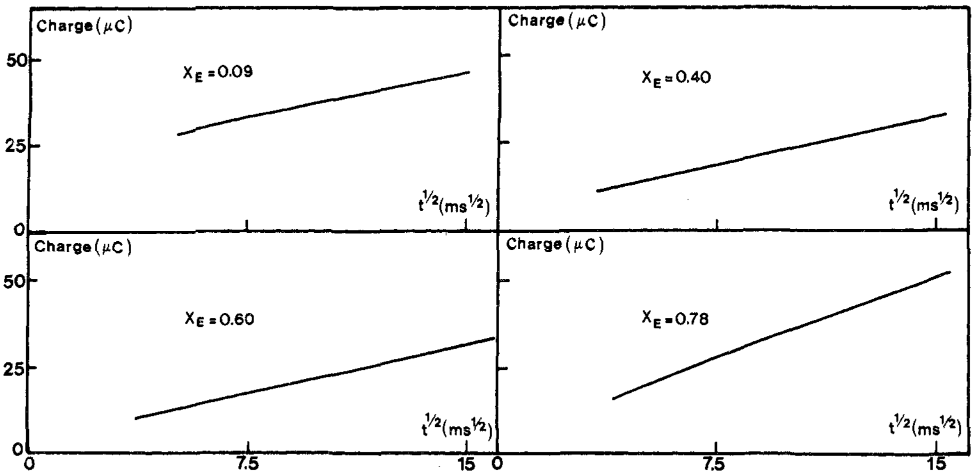


Figure 3. Potential-step chronocoulometry of the $Os(bpy)_3^{3+/2+}$ couple in a Nafion film spin-coated on a glassy carbon electrode as a function of the molar fraction of Os, X_E (eq 5). Solution: 0.05 M H_2SO_4. Nafion coverage: 9.7 × 10^{-8} mol cm^{-2} of sulfonate groups. The potential was stepped from 0.2 to 0.9 V.

Results and Discussion

Diffusion Coefficients for the $Os(bpy)_3^{3+/2+}$–Nafion System. The voltammetric behavior of the $Os(bpy)_3^{3+/2+}$ couple incorporated in Nafion films is shown in Figure 2. The couple exhibits reversible electrochemistry, and the formal potential of the 3+/2+ transition is well separated from background reactions so that accurate values of the quantities of $Os(bpy)_3^{2+}$ present in the coatings can be obtained from coulometric assays.

Apparent diffusion coefficients for the $Os(bpy)_3^{3+/2+}$–Nafion system were evaluated over a wide range of concentrations. Particular care was taken in measurements of the molar fraction of electroactive material in the coatings, X_E, defined as

$$X_E = 3C_E/C_F^0 \qquad (5)$$

where C_E and C_F^0 are the concentration of the osmium complex (in both oxidation states) and the total concentration of fixed sulfonate sites in the coatings, respectively. X_E was obtained from coulometric assays of the quantities of $Os(bpy)_3^{2+}$ present in the coatings as described under Experimental Section, where it was also demonstrated that the maximum quantity of $Os(bpy)_3^{3+}$ that can be incorporated in the coating corresponds to the complete replacement of the unipositive counterions by the osmium complex.

The apparent diffusion coefficient was measured by potential-step chronocoulometry for a series of X_E values. The chronocoulometric plots of charge vs (time)$^{1/2}$ that resulted when the potential of the spin-coated electrodes was stepped from 0.2 V, where no current flowed, to 0.9 V, where the incorporated $Os(bpy)_3^{2+}$ was oxidized to $Os(bpy)_3^{3+}$, were linear (Cottrell behavior) for all values of X_E (Figure 3). Measurement times were typically from 10 to 225 ms with film thicknesses of the order of 0.85 μm. Apparent diffusion coefficients were obtained from the slopes, Sl ($Cs^{-1/2}$), of the linear plots according to

$$D_{ap} = \pi\left[\frac{Sl}{2FSC_E}\right]^2 = \pi\left[\frac{Sl}{Q_l}\right]^2\left[\frac{Q_l}{2FS\frac{C_F^0}{3}X_E}\right]^2 = \pi\left[\frac{Sl}{Q_t}\right]^2\left[\frac{Q_t^0}{2FS\frac{C_F^0}{3}}\right]^2 \qquad (6)$$

where Q_l is the charge obtained in the coulometric assays and S is the electrode area. For a given coating, containing successively increasing amounts of the osmium complex, the quantity $Q_l/[2FS(C_F^0/3)X_E]$ is independent of the fractional loading. As shown in the last term in eq 6, its value was conveniently obtained from the total charge, Q_t^0 measured at X_E = 1. Experimental uncertainties in obtaining values of Q_t^0 resulted in corresponding uncertainties in the absolute values of D_{ap}, but the relative values of D_{ap} for a single coating with varying fractional loadings could be reproduced to ca. 10%. The assumption that the coating thickness, and hence C_F^0, did not change significantly with the fractional loading was based on previous measurements in which Nafion coatings were loaded with varying quantities of $Co(bpy)_3^{2+}$.[4e] The evaluation of the absolute values of D_{ap} required that C_F^0, the total concentration of sulfonate groups within the Nafion coating, be known. A value of 1.2 M was chosen.[11c] Uncertainties in C_F^0 result in corresponding uncertainties in the absolute values of D_{ap} but leave unaffected the relative variation in D_{ap} with changes in X_E, which was the central point of interest in the present investigation.

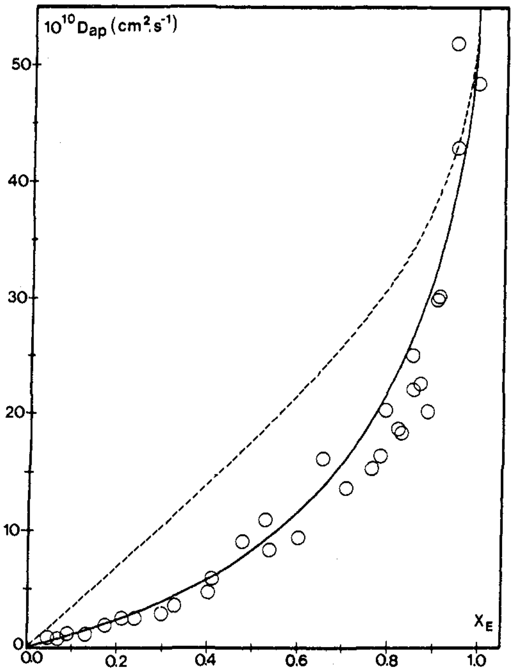


Figure 4. Apparent diffusion coefficient, D_{ap}, as a function of the osmium fractional loading, X_E. Supporting electrolyte: 0.05 M H_2SO_4. Solid line: simulation according to the ion pair dissociation–electron-hopping model (with KC_F^0 = 7). Dashed line: simulation ignoring the effect of ion pairing but taking the effect of the electric field into account.

The results of a large number of measurements of D_{ap} for a range of X_E values are shown in the data points plotted in Figure 4. The general trend in the data is similar to that reported recently for similar experimental conditions.[9] The present, more extensive data set makes it clearer that the diffusion coefficient becomes very small as the loading approaches zero, that there is a relatively small region of intermediate loadings where it increases proportionally to the concentration of incorporated $Os(bpy)_3^{2+}$, and that it increases in a strikingly steep manner as the molar fraction approaches unity.[30] Similar behavior has been very recently reported[15] for the $\mathrm{Os(bpy)_3}^{2+}$–Nafion system when sodium instead of hydrogen ion was the electroinactive counterion. The features evident in Figure 3 are not in accord with the simple model based on eq 2[21] that has often been utilized in previous studies to account for the observed variations in apparent diffusion coefficients.[4b,5b,21] However, these previous studies have not included as wide a range of loadings as the present measurements, nor has the electroactivity of all the incorporated complexes been independently verified. The ion-pair dissociation model described below is one attempt to rationalize the unusual behavior exhibited by the data in Figure 4.

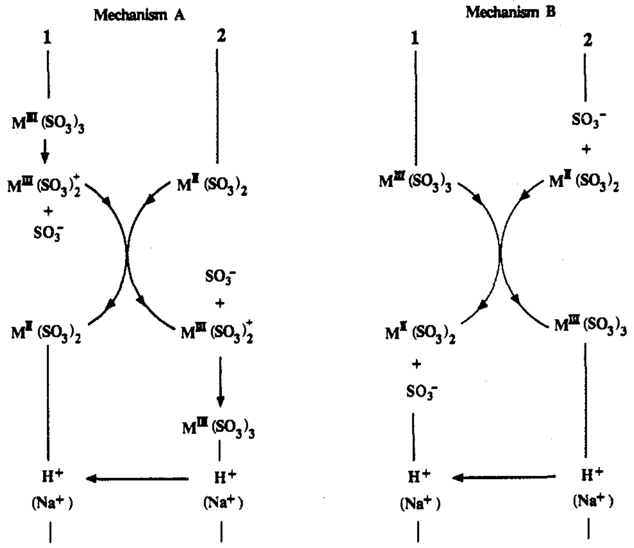
Modeling of the Effects of Ion Association. Ions in polyelectrolyte films such as Nafion are likely to associate strongly because of their large concentration, the reduced availability of water compared to concentrated ionic aqueous solutions, and the low dielectric constant of the organic polymer matrix which contributes to increased anion–cation coulombic attraction.[31a] This association is particularly likely for ions such as $\mathrm{Os(bpy)_3}^{3+/2+}$ because their organic ligands cause them to be located closer to the organic phase of the Nafion than are cations such as sodium or hydrogen ions. The two-phase structure envisioned for Nafion (organic plus aqueous ionic clusters)[31b] leads one to expect cations such as $\mathrm{Os(bpy)_3}^{3+/2+}$ to be located in the interfacial region between the two phases[31c] where the local environment is likely to favor strong ion association. One of the most striking features of dipositive transition-metal complexes of 2,2′-bipyridine incorporated in Nafion coatings is the persistence of the complexes within the film for long periods after they are transferred to pure electrolyte solutions. This lack of physical mobility is believed to be a result of the stable ionic aggregates that they form with the pendant $\mathrm{SO_3}^-$ groups. This is consistent with the large value measured for the selectivity coefficient of the closely related $\mathrm{Ru(bpy)_3}^{2+}$ vs Na^+ in Nafion.[31g] At equilibrium, we expect the predominant forms of the electroactive ions, $\mathrm{M}^{\mathrm{III}}$ and M^{II}, to be the uncharged aggregates $\mathrm{M}^{\mathrm{III}}(\mathrm{SO_3})_3$ and $\mathrm{M}^{\mathrm{II}}(\mathrm{SO_3})_2$. Electron propagation through such systems can thus only result from electron hopping between pairs of electroactive species and not from physical displacement. The various possible ion association equilibrium are depicted in eqs 7 and 8 in which the dissociation constant

$$\mathrm{M}^{\mathrm{III}}(\mathrm{SO_3})_3 \underset{-\mathrm{SO_3}^-}{\overset{+\mathrm{SO_3}^-}{\rightleftarrows}} \mathrm{M}^{\mathrm{III}}(\mathrm{SO_3})_2{}^+ \underset{-\mathrm{SO_3}^-}{\overset{+\mathrm{SO_3}^-}{\rightleftarrows}} \mathrm{M}^{\mathrm{III}}(\mathrm{SO_3})^{2+} \underset{-\mathrm{SO_3}^-}{\overset{+\mathrm{SO_3}^-}{\rightleftarrows}} \mathrm{M}^{\mathrm{III}3+} \quad (7)$$

$$\mathrm{M}^{\mathrm{II}}(\mathrm{SO_3})_2 \underset{-\mathrm{SO_3}^-}{\overset{+\mathrm{SO_3}^-}{\rightleftarrows}} \mathrm{M}^{\mathrm{II}}(\mathrm{SO_3})^+ \underset{-\mathrm{SO_3}^-}{\overset{+\mathrm{SO_3}^-}{\rightleftarrows}} \mathrm{M}^{\mathrm{II}2+} \quad (8)$$

decreases from left to right. Consequently, to a first approximation, we consider that only the first equilibrium may have a significant effect on the electron-hopping rate. Electron transfer inside a pair of $\mathrm{M}^{\mathrm{III}}(\mathrm{SO_3})_3$ and $\mathrm{M}^{\mathrm{II}}(\mathrm{SO_3})_2$ molecules located in two adjacent planes implies the dissociation of one sulfonate group in the first plane and the association of one sulfonate group in the second plane. Such a reaction may occur in a stepwise manner, the dissociation, electron-transfer, and association steps taking place successively (mechanism A in Scheme I) or concertedly (mechanism B in Scheme I). In both cases, the physical displacement of the electroinactive counterions accompanies the electron-hopping reaction so as to maintain electroneutrality. Any mismatch between the two processes creates an electric field that accelerates the electron-hopping reaction.

Scheme I[a]



[a] For clarity the scheme represents the reaction in one direction, namely, the transfer of one electron, one sulfonate, and one electroinactive counterion from plane 2 to plane 1. The system can work in the reverse direction as well.

In the case where mechanism B would prevail over mechanism A, the apparent diffusion coefficient, D_{ap}, would vary with the fractional loading X_{E} in the manner represented by the slightly upward bending dashed line in Figure 4. The only cause of deviation from the linear variation predicted for a purely diffusive behavior would be the effect of the electric field resulting from the mismatch between electron hopping and electroinactive counterion displacement. Since our goal is to unravel the causes of steeper variations such as those exhibited by the $\mathrm{Os(bpy)_3}$–Nafion films, we analyze in what follows the $D_{\mathrm{ap}} - X_{\mathrm{E}}$ variations predicted for mechanism A.

Although likely to be located in the aqueous portion of the two-phase structure evoked earlier, the electroinactive counterions also interact with the pendant sulfonate groups,[31a,b,h] albeit to a lesser extent than the electroactive ions. Electroactive and electroinactive counterions will thus compete for association with the fixed sulfonate groups depending on their relative concentrations. To proceed, we adopted the following strategy: First, we discuss a model based on mechanism A for electron hopping that neglects the possible variations of the interactions of the electroinactive counterions with the sulfonate groups as the ionic composition of the film is changed. As will be shown, this model is able to account for the main feature of the experimental data in Figure 4, i.e., the steep rise in the variation of the apparent diffusion coefficient with the molar fraction of redox centers present. The effect of the variations of the interactions of the electroinactive counterions with the fixed sulfonate groups is then discussed qualitatively. A quantitative treatment of these effects would be feasible in principle, but it would require the use of additional adjustable parameters that are not independently available at present to describe quantitatively the interactions between electroinactive counterions and sulfonate groups.

With the notations A $[\mathrm{M}^{\mathrm{III}}(\mathrm{SO_3})_2{}^+]$, B $[\mathrm{M}^{\mathrm{II}}(\mathrm{SO_3})_2]$, C $[\mathrm{M}^{\mathrm{II}}\mathrm{I}(\mathrm{SO_3})_3]$, F $[\mathrm{SO_3}^-$ (i.e., sulfonate groups not involved in ion pairs)], H $[\mathrm{Na}^+(\mathrm{H}^+)]$, x (distance from the electrode), t (time),

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(30) (a) In a very recent paper, measurements have been presented of the diffusion coefficient for a singly charged ferrocenylammonium cation and for $\mathrm{Fe(bpy)_3}^{2+}$ in Nafion coatings on ultramicroelectrodes.[11c] The results show a sharp increase in diffusion coefficients at very low loadings, a region not investigated extensively in the present and in the other recent[9,15] studies. The experimental conditions employed were quite different, including the use of much higher concentrations of the supporting electrolyte. The cationic permselectivity of the coatings was compromised, while in the present study the permselectivity was high as demonstrated previously.[30b] (b) Redepenning, J. G.; Anson, F. C. *J. Phys. Chem.* **1987**, *91*, 4549.

(31) (a) Mauritz, K. A.; Hopfinger, A. J. *Modern Aspects of Electrochemistry*; Bockris, J. O'M., Conway, B. E., White, R. E., Eds.; Plenum: New York, 1982; No. 14, Chapter 6, pp 441–452. (b) Yeager, H. L.; Steck, A. *J. Electrochem. Soc.* **1981**, *128*, 1880. (c) This expectation is supported by luminescence studies of the closely related $\mathrm{Ru(bpy)_3}^{2+}$ in Nafion showing that it is located in the interfacial region of the Nafion structure[31d,e] unlike the hydrophilic Fe^{2+}, Fe^{3+}, Eu^{3+} ions which are located in the aqueous phase.[31e,f] (d) Lee, P. C.; Meisel, D. *J. Am. Chem. Soc.* **1980**, *102*, 5477. (e) Szentirmay, M. N.; Prieto, N. E.; Martin, C. R. *J. Phys. Chem.* **1985**, *89*, 3017. (f) Rodmacq, B.; Pineri, M.; Coey, J. M. D.; Meagher, A. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 603. (g) Szentirmay, M. N.; Martin, C. R. *Anal. Chem.* **1984**, *56*, 1898. (h) Yeager, H. L.; Yeo, R. S. In *Modern Aspects of Electrochemistry*; Bockris, J. O'M., Conway, B. E., White, R. E., Eds.; Plenum: New York, 1985; No. 16, Chapter 6, pp 437–504.

and Φ (potential), the transient behavior of the system under potentiostatic conditions is described by the set of equations[23e,32a]

$$\frac{\partial(C_A + C_C)}{\partial t} = \frac{k\delta^2}{6}\frac{\partial}{\partial x}\left[C_B\frac{\partial C_A}{\partial x} - C_A\frac{\partial C_B}{\partial x} + \frac{\mathcal{F}}{RT}C_AC_B\frac{\partial \Phi}{\partial x}\right] \tag{9}$$

$$\frac{\partial C_B}{\partial t} = \frac{k\delta^2}{6}\frac{\partial}{\partial x}\left[C_A\frac{\partial C_B}{\partial x} - C_B\frac{\partial C_A}{\partial x} - \frac{\mathcal{F}}{RT}C_AC_B\frac{\partial \Phi}{\partial x}\right] \tag{10}$$

$$\frac{\partial C_H}{\partial t} = D_I\frac{\partial}{\partial x}\left[\frac{\partial C_H}{\partial x} + \frac{\mathcal{F}}{RT}C_H\frac{\partial \Phi}{\partial x}\right] \tag{11}$$

k and δ are the bimolecular rate constant and optimal average distance[32c] of electron hopping, respectively, and D_I is the diffusion coefficient of the mobile electroinactive counterion.

conservation of fixed ions:

$$2C_A + 2C_B + 3C_C + C_F = C_F^0 \tag{12}$$

conservation of electroactive ions:

$$C_A + C_B + C_C = C_E \tag{13}$$

(This equation is not independent from eqs 9 and 10 since it results from the integration of their sum.)

conservation of charge:

$$C_A + C_H = C_F \tag{14}$$

The association of the oxidized form of the electroactive counterion (the only reaction considered to alter the concentrations of the reactant species) is assumed to remain at equilibrium within the time scale of the experiment (i.e., it is fast compared to the rate of electron hopping)

$$C_C/C_AC_F = K \tag{15}$$

K is the ion association equilibrium constant.

$t = 0$, $x \geq 0$ and $x = \infty$, $t \leq 0$: $C_B = C_E$ and the other concentrations have the values resulting from the application of eqs 12–15.

$x = 0$, $t \geq 0$: $C_B = 0$, the values of the other concentrations are derived from eqs 12–15.

In addition

$$\frac{\partial C_H}{\partial x} + \frac{\mathcal{F}}{RT}C_H\frac{\partial \Phi}{\partial x} = 0 \tag{16}$$

because the electroinactive counterions are not oxidized at the electrode surface.

The current, i, is given by

$$\frac{i}{FS} = \frac{k\delta^2}{6}\left[C_A\frac{\partial C_B}{\partial x} - \frac{\mathcal{F}}{RT}C_AC_B\frac{\partial \Phi}{\partial x}\right]_0 \tag{17}$$

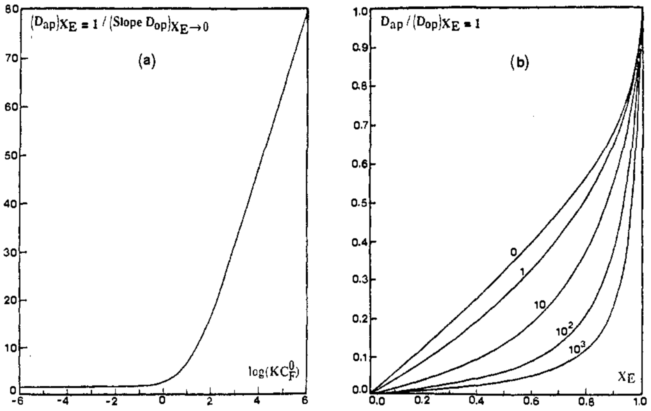

Figure 5. (a) Variation of the ratio between the value of the apparent diffusion coefficient at $X_E = 1$ and the slope of the initial linear region with KC_F^0. (b) Variation with X_E of the apparent diffusion coefficient normalized with respect to its value for $X_E = 1$. The number of each curve is the value of KC_F^0.

The subscript 0 refers to $x = 0$; anodic currents are taken as positive. Since diffusion coefficients of sodium ions in Nafion[33] are at least 100 times larger than the highest values of the apparent diffusion coefficients found here (Figure 3) and since protons doubtless diffuse even more rapidly, $D_I \gg D_E$. Thus[23e]

$$\frac{\mathcal{F}}{RT}\frac{\partial \Phi}{\partial x} = -\frac{1}{C_H}\frac{\partial C_H}{\partial x} \tag{18}$$

and eqs 9, 10, and 17 can be replaced by

$$\frac{\partial C_A + C_C}{\partial t} = \frac{k\delta}{6}\frac{\partial}{\partial x}\left[C_B\frac{\partial C_A}{\partial x} - C_A\frac{\partial C_B}{\partial x} - \frac{C_AC_B}{C_H}\frac{\partial C_H}{\partial x}\right] \tag{19}$$

$$\frac{\partial C_B}{\partial t} = \frac{k\delta^2}{6}\frac{\partial}{\partial x}\left[C_A\frac{\partial C_B}{\partial x} - C_B\frac{\partial C_A}{\partial x} + \frac{C_AC_B}{C_H}\frac{\partial C_H}{\partial x}\right] \tag{20}$$

$$\frac{i}{FS} = \frac{k\delta^2}{6}\left[C_A\frac{\partial C_B}{\partial x} + \frac{C_AC_B}{C_H}\frac{\partial C_H}{\partial x}\right]_0 \tag{21}$$

A detailed account of the algebraic and numerical solution of the problem posed by the above equations is given in the Appendix. The main results are the following.

The chronoamperometric and chronocoulometric responses are predicted to obey the Cottrell equation throughout the whole range of X_E values. The potential-step response may therefore be characterized by an apparent diffusion coefficient, D_{ap}, related to the diffusion coefficient in the absence of ion association and electric field effects, D_E, by means of a dimensionless function ψ

$$D_{ap}/D_E = \pi\psi^2 \tag{22}$$

defined as

$$\psi = \frac{it^{1/2}}{FSC_ED_E^{1/2}} = \frac{Q}{2FSC_ED_E^{1/2}t^{1/2}} \tag{23}$$

where i and Q are the chronoamperometric and chronocoulometric current and charge, respectively. ψ depends only upon the fractional loading, X_E, and the dimensionless association equilibrium contant, KC_F^0, and is calculated as described in the Appendix.

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[32] (a) These are based on the stochastic description of electron hopping recalled in the introduction. In the cubic quasi-lattice model thus employed, the system is regarded as a completely disordered structure. Thus, the probability of finding one particular species at one node of the lattice is proportional to its concentration. In a recent discussion of electron hopping in redox polymers, a quite different approach was proposed.[32b] The analysis presented amounts to assuming that the redox centers are individually located at the nodes of an actual perfect cubic lattice. The lattice characteristic distance is taken as equal to the average distance between two nearest neighbors and the probability of electron hopping between them as an exponentially decaying function of this distance. The resulting, diffusion-like charge propagation is then predicted to increase with the concentration of redox sites more rapidly than proportionally. However, it does not seem likely that such a perfect crystal ordering of the electroactive sites could exist in redox polymers. For such systems, the stochastic model decribed above strikes us as more realistic. (b) Fritsch-Faules, I.; Faulkner, L. R. *J. Electroanal. Chem.* **1989**, *263*, 237. (c) A simple estimate of the hopping distance is the separation between the redox centers when the equivalent hard spheres are in contact. It would be possible to allow electron transfer to occur at greater distances in consideration of significant overlap of the electron-transferring and -receiving orbitals ("extended electron transfer"[32b]) and/or because each redox center may oscillate out of its equilibrium location. In both cases, integration over a distance-dependent probability distribution (a decaying exponential would be the simplest model) would lead to an increase of the average hopping distance, δ, in eqs 9 and 10.

[33] Komorski, R. A.; Mauritz, K. A. *J. Am. Chem. Soc.* **1978**, *100*, 7487.

[34] (a) The protonated form of Nafion is a strong acid, and, with the exception of Li^+, the relative incorporation constants are slightly in favor of alkali cations over protons, the more so the larger the cation.[39b] This preference is essentially a reflection of the decreased solvation of the cation by water upon passing from the solution to the interior of Nafion. It does not imply that the sulfonate–cation interaction be weaker for H^+ than for Na^+. It is entirely conceivable that H-bonding may favor SO_3^-, H^+ interactions as compared to SO_3^-, Na^+. (b) Steck, A.; Yeager, W. L. *Anal. Chem.* **1980**, *52*, 1215.

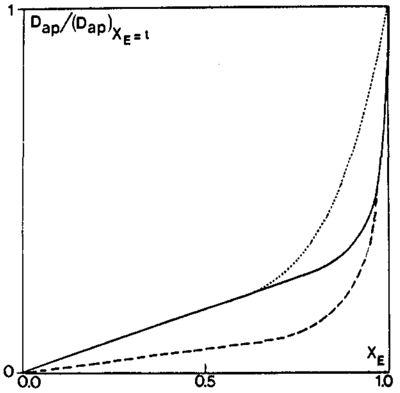

Figure 6. Qualitative representation of the effect of the interactions between the sulfonate ions and the electroinactive counterions. Dotted line: constant interactions. Dashed line: negligible interactions. Full line: predicted behavior.

Two portions of the $D_{ap} - X_E$ curve are of particular interest, namely, the behavior when $X_E \rightarrow 0$ and the value of D_{ap} at $X_E = 1$. When $X_E \rightarrow 0$, the electroinactive counterions are in excess, the effect of the electric field vanishes, and the fraction of M^{III} present in the dissociated form, $C_A/(C_A + C_C)$, becomes constant. Under these conditions

$$D_{ap} = \frac{D_E}{1 + KC_F^0} = \frac{k\delta^2}{18}\frac{C_F^0}{1 + KC_F^0}X_E \qquad (24)$$

As X_E increases toward unity, the fraction of M^{III} present as $M^{III}(SO_3)_2^+$ increases because the quantity of fixed ions available for association becomes smaller and smaller. As a result, the apparent diffusion coefficient increases with X_E, more rapidly than corresponds to simple proportionality. The variation with KC_F^0 of the ratio of $(D_{ap})_{X_E=1}$ to the slope of the plot of D_{ap} vs X_E as $X_E \rightarrow 0$ is represented in Figure 5 together with the variations of $D_{ap}/(D_{ap})_{X_E=1}$ with X_E for several values of KC_F^0. The curve in Figure 5a provides a means to estimate the association constant K from the measured values of D_{ap}. The curves in Figure 5b make it clear that steeper and steeper increases of D_{ap} with X_E are expected as ion association becomes stronger and stronger. We can now discuss in qualitative terms the expected consequences of the fact that the interactions between the electroinactive counterions and the fixed ions may vary with X_E. Figure 6 gives a schematic representation of the expected changes in the variation of D_{ap} with X_E. The dashed curve represents the D_{ap} vs X_E variation in the case where the interactions between the electroinactive counterions and the fixed ions are neglected; i.e., the activity coefficient of the fixed ions that are not associated with the redox centers is regarded as equal to unity. The dotted line represents the D_{ap} vs X_E variation in the case where significant interactions between the electroinactive counterions and the fixed ions are present but remain constant as X_E varies and keep the same magnitude as they have in the $X_E \rightarrow 0$ region. The fact that the dotted line lies above the dashed line is a result of the decreased availability of the fixed ions for association with $M^{III}(SO_3)_2^+$. In other words, both curves obey the assumptions of the model developed so far, the dotted curve corresponding to an *apparent* association constant which is smaller than the true association constant that governs the dashed curve. As X_E increases, the extent of association of $M^{III}(SO_3)_2^+$ with the sulfonate ions decreases. It is thus predicted that, upon increasing X_E, the actual $D_{ap} - X_E$ curve should pass from the situation approximated by the dotted line to that depicted by the dashed line, resulting in a somewhat steeper increase than anticipated on the basis of the model developed above. It is also predicted that the slope at $X_E \rightarrow 0$ may vary according to the nature of the electroinactive counterions: the larger the specific interactions with the SO_3^- groups, the larger the slope and vice versa.

Comparison with Experimental Data. As discussed in the preceding section, the model based on mechanism A predicts that the larger the association constant, the steeper the rise of the apparent diffusion coefficient with increasing fractional loading. A satisfactory fit is obtained for $KC_F^0 = 7$, implying that $K = 5.8$ M^{-1}. The fitting of the absolute values of D_{ap} leads to $k\delta^2C_F^0 = 5.2 \times 10^{-8}$ cm^2 s^{-1}, i.e., to $k = 3 \times 10^6$ M^{-1} s^{-1}, assuming that δ is equal to the contact distance (1.3 nm) between two $Os(bpy)_3^{3+/2+}$ centers.

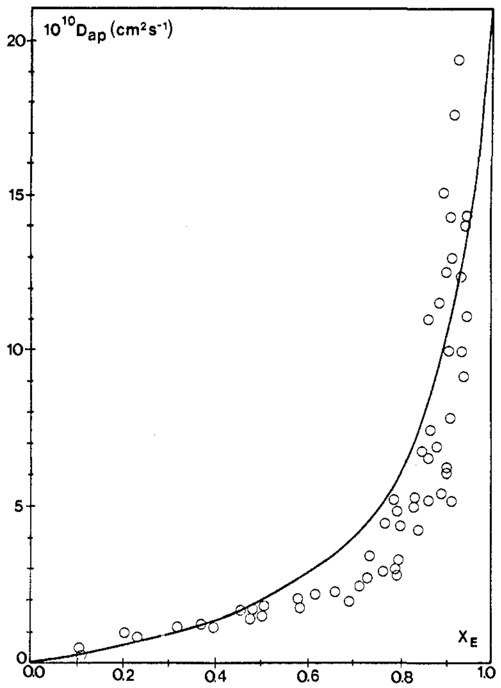

Figure 7. Apparent diffusion coefficient, D_{ap}, as a function of the osmium fractional loading, X_E. Supporting electrolyte: 0.05 M Na_2SO_4 (from ref 15). Solid line: simulation according to the ion-pairing–electron-hopping model with $KC_F^0 = 45$.

The same model should also apply to the data obtained recently for the $Os(bpy)_3^{3+/2+}$–Nafion system where Na^+ instead of H^+ served as the mobile electroinactive counterion.[15] A fit of the model to these data is shown in the curve in Figure 7 which corresponds to a somewhat larger value of KC_F^0 ($KC_F^0 = 45$).

The same analysis as applied in the preceding case leads to $k\delta^2C_F^0 = 5.7 \times 10^{-8}$ cm^2 s^{-1} and $k = 4 \times 10^6$ M^{-1} s^{-1}. While the hopping rate constant is nearly the same in both cases, the larger value of KC_F^0 means that the association of a third sulfonate group with $Os(bpy)_3(SO_3)_2^+$ is about sixfold more extensive in the presence of Na^+ than in the presence of H^+ as the electroinactive counterion. This ordering implies that the H^+ ions interact more strongly with SO_3^- groups than do Na^+ counterions in the $Os(bpy)_3^{3+/2+}$–Nafion system.[33] Another manifestation of the interaction between the sulfonate groups and the electroactive counterions is the observation that the experimental $D_{ap} - X_E$ plots are somewhat steeper than the modeled curve as predicted by the qualitative analysis given at the end of the preceding section.

On the whole, a satisfactory agreement between the experimental data and the predictions of the ion-pair dissociation model[35] is obtained. The sharp rise of the apparent diffusion coefficient observed when the concentration of electroactive counterions comes close to saturation with the Os(III) complex is essentially a reflection of the rise in the fraction of the $M^{III}(SO_3)_2^+$ species that is the important electron acceptor in the electron-hopping process. The contribution of the electric field to the observed behavior increases with X_E because fewer and fewer electroinactive coun-

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(35) In this model, dissociation of the $M^{III}(SO_3)_3$ ion pair into $M^{III}(SO_3)_2^+$ and SO_3^- is the key ingredient that allowed the rationalization of the experimental data, whereas the dissociation of $M^{II}(SO_3)_2$ into $M^{II}(SO_3)^+$ and SO_3^-, which should be of the same order as the former, was ignored. This is because the reduced half of the redox couple that participates in the hopping reaction is $M^{II}(SO_3)_2$, not $M^{II}(SO_3)^+$, and because $M^{II}(SO_3)_2$ predominates over $M^{II}(SO_3)^+$ in the ion-pairing equilibrium, whereas the situation is exactly opposite for the oxidized half of the redox couple.

terions (H^+ or Na^+) are available to screen the field as they are replaced by the osmium complex. Mechanism B of Scheme I does not appear to contribute significantly to the electron-hopping process in the $Os(bpy)_3^{3+/2+}$–Nafion system in spite of the fact that all of the Os^{III} centers would then be involved, as opposed to mechanism A where only the $M^{III}(SO_3)_2^+$ form participates in the electron transport. We are thus led to conclude that the activation barrier is much higher for the concerted process than for the stepwise process. The formation of the activation barrier for the concerted process (Scheme I) involves the same $M^{III}(SO_3)_3$ dissociation (facilitated by the passage of one SO_3^- from the organic to the aqueous phase) in plane 1 as the first step in the stepwise process. However, the concerted approach of one SO_3^- toward $M^{II}(SO_3)_2$ in plane 2 involves both the unfavorable converse passage of this SO_3^- ion from the aqueous to the organic phase and strong repulsive van der Waals terms. It is not therefore surprising that the resulting activation barrier is so high as to eliminate the participation of mechanism B in electron transport.[36]

Other Models. Although the ion-pairing model discussed above is in good agreement with the experimental data, it is worth considering whether the observed variation of D_{ap} with X_E could have a different origin. Curved $D_{ap} - X_E$ plots have been predicted in an alternative analysis which amounts to assuming that the redox centers are individually located at the nodes of a real, perfect cubic lattice.[32b] As already noted, redox polymers such as those involved in the present study do not seem likely to have structures that match this model.[32a] Another (quite different) model that has been recently proposed to explain the sharp rise of the $D_{ap} - X_E$ plots observed with the $Os(bpy)_3^{3+/2+}$ and $Ru(bpy)_3^{3+/2+}$ couples in Nafion[9] is based on the notion of charge propagation being the result of a diffusion process that combines physical displacement of the redox centers and electron hopping between them.[21b] The overall diffusion coefficient is expressed[21] by

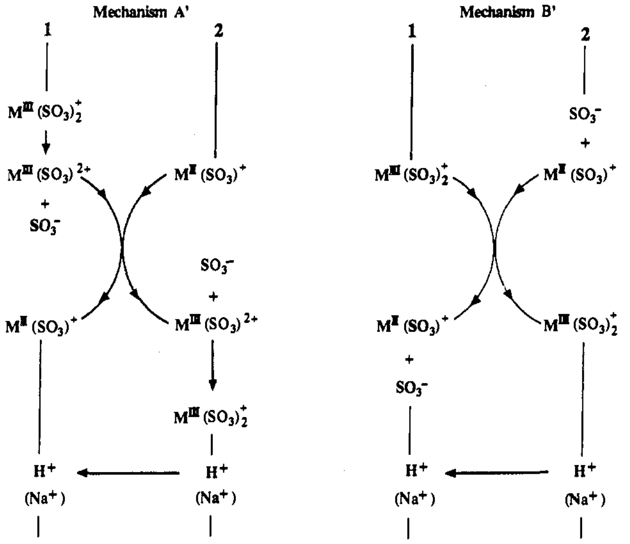
$$D_{ap} = D_{pd} + (\pi/4)k\delta^2 C_E \tag{25}$$

but the rate constant, k, is regarded, itself, as possibly limited either by electron transfer between redox centers or by their diffusion, one toward the other, according to

$$\frac{1}{k} = \frac{1}{k_E} + \frac{1}{k_D} \tag{26}$$

where k_E is the activation-limited electron self-exchange rate constant and k_D is the diffusion-limited bimolecular rate constant. The suggestion was[9] that the kinetic control of electron hopping passes from diffusion to activation, as the concentration of the redox couple in the film increases. However, this reasoning is difficult to understand because both k_E and k_D are bimolecular rate constants; the combination of these two rate constants in eq 26 should therefore be independent of the concentration of redox sites. Interestingly, this same problem had been previously addressed by using the concept that the diffusion-limited bimolecular rate constant might be increased by electron transfer.[21b] However, the rate constant k in eq 25, or better[21a] in eq 2, is merely the activation-limited electron-exchange volume rate constant, and diffusion by physical displacement is entirely taken into account by the first term on the right-hand side of eq 2.[37] We thus conclude that the observed dependences of the apparent diffusion coefficient upon the fractional loading shown in Figures 3 and 6 is not satisfactorily explained by these alternative models.

Scheme II



Returning to ion association effects, in addition to the mechanism we have envisaged so far, other possibilities exist a priori, which involve the other ion-pairing equilibria represented in eqs 7 and 8. We now consider if their occurrence could explain the observed $D_{ap} - X_E$ variations. One possibility is the following: let us suppose that, contrary to what we have assumed so far, the $Os^{III}(bpy)_3(SO_3)_2^+$ and $Os^{II}(bpy)_3(SO_3)^+$ ions are not strongly ion paired but that the $Os^{III}(bpy)_3(SO_3)^{2+}$ and $Os^{II}(bpy)_3^{2+}$ are. Then, among the two possible electron-hopping mechanisms (A′ and B′) shown in Scheme II, mechanism A′ should prevail over mechanism B′ for the same reasons that, in the preceding case, mechanism A prevailed over mechanism B. From the conservation conditions

$$C_{A'} + C_{B'} + 2C_{C'} + C_F = C_F^0 \tag{27}$$

$$C_{A'} + C_{B'} + C_{C'} = C_E \tag{28}$$

$$C_{A'} + C_E + C_H = C_F \tag{29}$$

[A′, $M^{III}(SO_3)^{2+}$; B′, $M^{II}(SO_3)^+$; C′, $M^{III}(SO_3)_2^+$], the ion-pairing equilibrium condition

$$C_{C'}/C_{A'}C_F = K' \tag{30}$$

becomes

$$\frac{C_{C'}}{C_{A'}\left(C_F^0\dfrac{X_E}{3} + C_{A'} + C_H\right)} = K' \tag{31}$$

whereas in the preceding case it was

$$\frac{C_C}{C_A(C_A + C_H)} = K \tag{32}$$

The essential cause of the steep rise in the $D_{ap} - X_E$ plot was that, at the electrode surface, C_A becomes much larger than C_H as X_E

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[36] (a) Self- and cross-exchange rate constants of electron transfer in solution involving the $Os(bpy)_3^{3+/2+}$ couple or similar transition-metal complexes have been shown to increase with the concentration of anions (e.g., ClO_4^-, PF_6^-) present, up to concentrations of the order of 0.1 M.[36b–e] This increased reactivity is presumably caused by ion–ion interactions increasing the driving force of the electron-transfer reaction and decreasing the Coulombic repulsive work terms as a result of both diffuse-type interactions and formation of ion pairs between the multiply charged reactants and one anion. Under these conditions, if ion pairs do participate in the electron-transfer mechanism, there is no reason to envisage that electron transfer could occur between species containing a different number of anions and would thus require the concerted exchange of one of these anions. The observations cited above do not therefore contradict our analysis of the reasons why such a concerted electron–transfer process should have a higher activation barrier than the outer-sphere electron transfer between two species in the same state of ionic aggregation. (b) Stalnaker, N. D.; Solenberger, J. C.; Wahl, A. C. *J. Phys. Chem.* **1977**, *81*, 601. (c) Chan, M.-S.; Wahl, A. C. *J. Phys. Chem.* **1978**, *82*, 2542. (d) Braga, T. G.; Wahl, A. C. *J. Phys. Chem.* **1985**, *89*, 5822. (e) Chan, M.-S.; Wahl, A. C. *J. Phys. Chem.* **1985**, *89*, 5829.

[37] (a) Anson, F. C.; Blauch, D. N.; Savéant, J-M. Unpublished results. (b) It should be borne in mind, when comparing the electron-hopping rate constant to the self-exchange rate constant of the same redox couple in solution, not only that the intrinsic barriers may be different because of differences in the reorganization energies but also that the pre-exponential factors are likely to be different: collisions between bound molecules in the first case; translational collisions in the second (alternatively, in the framework of transition-state theory, the partition functions for the reactants and the transition state are different in the two cases).

approaches 1 since $C_H \rightarrow C_B = 0$. Thus, in mechanism A the amount of the non-ion-paired, electron-accepting species, A, as $X_E \rightarrow 1$ and $C_H \rightarrow 0$ was given by

$$C_A = (C_C/K)^{1/2} \tag{33}$$

and was thus, for strong ion pairing, much bigger than the amount present for small X_E's

$$C_A = C_C/KC_F^0 \tag{34}$$

(the smaller the larger K).

In the present case, the amount of A′ at the electrode surface when X_E approaches 1 is, for strong ion pairing, given by

$$C_{A'} = \frac{C_{C'}}{K'\dfrac{C_F^0}{3}} \tag{35}$$

whereas when $X_E \rightarrow 0$

$$C_{A'} = \frac{C_{C'}}{K'C_F^0} \tag{36}$$

The fraction of non-ion-paired charge carrier, A′, is thus of the same order of magnitude at small and at large X_E's. Thus, only a small upward bending of the $D_{ap} - X_E$ plot is expected if such a mechanism were prevailing, which is not in accord with the experimental results.

Still another ion pair dissociation–electron-hopping mechanism could be envisaged, namely

$$\mathrm{M^{III}(SO_3)^{2+} \leftrightharpoons SO_3^- + M^{III3+},\ M^{III3+} + e^- \leftrightharpoons M^{II2+}} \tag{37}$$

However, this possibility can be ruled out for the same physical reasons as in the case just discussed: there is no dramatic change in the fraction of non-ion-paired electron acceptor at the electrode surface upon going from small to large X_E, and thus no steeply rising $D_{ap} - X_E$ plots are expected. In addition, this mechanism implies that the $\mathrm{Os(bpy)_3^{2+}}$ complex is not ion paired at all, which would lead to rapid leaking of the electroactive material from the coatings, which does not match the experimental observations.

Conclusions

In view of the high ionic content and low dielectric constant prevailing in the interior of most redox polymers, the dynamics of electron-hopping processes occurring within them are expected to be influenced by ion association. The present study was an attempt to investigate the effect of ion association between electroactive and electroinactive ions incorporated in polymers on the dynamics of electron hopping. The $\mathrm{Os(bpy)_3^{3+/2+}}$–Nafion system was chosen as a good test system for this study because ion association was expected to play a major role in the incorporation and retention of the osmium complexes by Nafion scattering. The strikingly nonlinear increase in the apparent diffusion coefficient of the incorporated redox counterions as their concentration increases, particularly as saturation of the sulfonate groups by the osmium complex is approached, was accounted for by the model proposed. Previous theoretical treatments of the dynamics of electron hopping, including those that take into account the influence of the electric fields present within redox polymers, have not resulted in satisfying explanations for the observed behavior. However, incorporation of ion association effects into the previous treatments, as described in this study, did provide a satisfactory explanation for the variation of D_{ap} with X_E over the entire range $0 < X_E \leq 1$.

When the ion association equilibria result in conversion of both halves of incorporated redox couples into fully associated, uncharged species, electron hopping from the reduced to the oxidized ionic aggregate is opposed by the high activation barrier for the simultaneous transfer of the associated, fixed ionic site. Prior dissociation of the neutral, oxidized half of the redox couple into a form associated with the same number of fixed ionic sites as the reduced half of the couple, followed by simple, outer-sphere electron transfer, appears to be an energetically more favorable process. The sharp rise in the apparent diffusion coefficient as the concentration of the redox couple in the film nears saturation is the expected consequence of the shifting of the ionic association equilibrium to produce larger concentrations of the form of the oxidized half of the redox couple which is well-matched for rapid electron acceptance from the reduced half of the couple. Electric fields present in films also contribute to the sharp increase of D_{ap} with X_E, but, by themselves, the calculated effects of the electric fields are too small to account for the observed behavior.

Ion association effects of the type we have invoked would also be expected to influence the dependence of apparent diffusion coefficients on the concentration of redox centers in other systems where the centers are electrostatically confined within polyelectrolyte films. Similar effects may also be anticipated in systems where charged redox centers are covalently or coordinatively bound to polymeric coatings, if ionic association between the redox centers and mobile, electroinactive counterions is strong.[38]

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Appendix

A simpler formulation of the problem posed by eqs 9–21 is obtained by means of the normalizations

$$a = \frac{C_A}{C_E};\ b = \frac{C_B}{C_E};\ c = \frac{C_C}{C_E};\ f = \frac{C_F}{C_E};\ h = \frac{C_H}{C_E};\ \kappa = KC_F^0 \tag{38}$$

and introduction of the Boltzman transformation:

$$u = x/(D_E t)^{1/2} \tag{39}$$

The resulting boundary value problem is

$$\frac{u}{2}\frac{da + c}{du} + \frac{d}{du}\left[b\frac{da}{du} - a\frac{db}{du} - \frac{ab}{h}\frac{dh}{du}\right] = 0 \tag{40}$$

with

$$a = b + c = 1 \tag{41}$$

$$a + c + h = 1 + 3\frac{1 - X_E}{X_E} \tag{42}$$

$$-b + h = 3\frac{1-X_E}{X_E} \tag{43}$$

$$\frac{c}{a(a + h)} = \kappa\frac{X_E}{3} \tag{44}$$

It follows from eqs 40 through 44 that

$$\frac{u}{2}\frac{dh}{du} + \frac{d}{du}\left[a\frac{db}{du} - b\frac{da}{du} + \frac{ab}{h}\frac{dh}{du}\right] = 0 \tag{45}$$

Substitution of eqs 46–49

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[38] For example, the variation of the apparent diffusion coefficient with the concentration of redox centers is then steeper than simple proportionality in poly(vinylpyridine) copolymers containing coordinatively attached osmium and ruthenium ions.[12c] This has been interpreted and modeled as a field effect resulting from the coupling by electroneutrality of electron hopping and displacement of the mobile electroinactive counter ions.[23g] However, the observed effect is so larger that it was necessary to assume, without strong supporting evidence, that the displacement of the mobile electroinactive counterions is slower than electron hopping. An alternative explanation could rely on the effect of ion association between the charged redox centers and the mobile electroinactive counterions.

$$\frac{db}{du} = \frac{dh}{du} \tag{46}$$

$$\frac{da}{du} = \frac{1 + \kappa\frac{X_E}{3}a}{1 + \kappa\frac{X_E}{3}(2a + h)}\frac{dh}{du} \tag{47}$$

$$b = h - 3\,\frac{1 - X_E}{X_E} \tag{48}$$

$$a = \frac{1}{2\kappa}\frac{3}{X_E}\left[\left[\left(1 + \frac{3\kappa}{X_E}h\right)^2 + 4\kappa\frac{X_E}{3}\left(1 + 3\frac{1 - X_E}{X_E}\right)\right]^{1/2} - \left(1 + \frac{3\kappa}{X_E}h\right)\right] \tag{49}$$

into eq 45 leads to a differential equation that involves only h and dh/du, with the following boundary conditions:

$$h_0 = 3\frac{1 - X_E}{X_E} \tag{50}$$

$$h_\infty = 1 + 3\frac{1 - X_E}{X_E} \tag{51}$$

The dimensionless current function, ψ (eqs 22–23), is obtained from

$$\psi = \left[a\frac{dh}{du}\right]_0 = a_0\left[\frac{db}{du}\right]_0 \tag{52}$$

where a_0 is obtained by evaluation of eq 49 with $h = h_0$ (defined in eq 50)

$$a_0 = \frac{3}{2\kappa X_E}\left[\left[(1 + \kappa(1 + X_E))^2 + \frac{4\kappa X_E}{3}\right]^{1/2} - [1 + \kappa(1 - X_E)]\right] \tag{53}$$

The gradient, $(dh/du)_0$, is obtained from the numerical solution of system (45) through (50). The above equations are valid for all fractional loadings except $X_E = 1$.

There is a singularity in eqs 46 and 52 when $X_E = 1$. In this case, eq 45 is replaced by

$$\frac{u}{2}\frac{dh}{du} + \frac{d}{du}\left[2a\frac{dh}{du} - h\frac{da}{du}\right] = 0 \tag{54}$$

and eqs 47 and 49 become

$$\frac{da}{du} = \frac{1 + \frac{\kappa a}{3}}{1 + \frac{\kappa}{3}(2a + h)}\frac{dh}{du} \tag{55}$$

$$a = \frac{3}{2\kappa}\left[\left[(1 + 3\kappa h)^2 + \frac{4}{3}\kappa\right]^{1/2} - (1 + 3\kappa h)\right] \tag{56}$$

The relevant boundary conditions are

$$h_0 = 0,\ h_\infty = 1 \tag{57}$$

and the dimensionless current function is given by

$$\psi = \left[2a\frac{dh}{du}\right]_0 \tag{58}$$

Equations 45 through 51 simplify considerably when the fractional loading is very small, i.e., $X_E \rightarrow 0$. In this limit, the concentration of free sulfonate ions, C_F, is essentially equal to the total concentration of sulfonate groups, C_F^0. For this reason, eq 15 may be rewritten as

$$c = \kappa a \tag{59}$$

Substitution of eq 59 into eq 41 produces

$$b = 1 - (1 + \kappa)a \tag{60}$$

Because the ions H are present in large excess, their concentration is essentially independent of the oxidation state of the electroactive centers and the term $(ab/h)(dh/du)$ in eq 40 becomes negligibly small. On the basis of this observation, eq 40 reduces to

$$\frac{d^2a}{du^2} + (1 + \kappa)\frac{u}{2}\frac{da}{du} = 0 \tag{61}$$

with boundary conditions

$$a_0 = \frac{1}{1 + \kappa}a_\infty = 0 \tag{62}$$

The analytical solution of the above boundary value problem produces eq 24.

The above derivations lead to boundary value problems of the general form

$$\frac{u}{2}\frac{dh}{du} + \frac{d}{du}\left[G(h)\frac{dh}{du}\right] = 0 \tag{63}$$

Its numerical computation was performed, taking into account the appropriate boundary conditions, according to the following procedure. The difficulties posed by the fact that, for certain values of κ and X_E, eq 63 is stiff were partially circumvented by means of an exponential transformation applied to u:

$$z = 3\frac{1 - X_E}{X_E} + \exp(-\alpha u) \tag{64}$$

The scaling factor, α, is a positive number whose magnitude was chosen so that $-dh/dz$ at the electrode surface ($u = 0$, $z = 1 + [3(1 - X_E)/X_E]$ was approximately unity. Equation 63 is thus converted into

$$0 = \left[G(h) + \frac{1}{2\alpha^2}\ln\left[z - 3\frac{1 - X_E}{X_E}\right]\right]\frac{dh}{\mathrm{d}z} + \left[z - 3\frac{1 - X_E}{X_E}\right]\left[G(h)\frac{d^2h}{dz^2} + \frac{dG}{dh}\left[\frac{dh}{dz}\right]^2\right] \tag{65}$$

and

$$\left[\frac{dh}{du}\right]_{u=0} = -\alpha\left[\frac{dh}{dz}\right]_{z=1+3[(1-X_E)/X_E]} \tag{66}$$

The nonlinear boundary value problem represented by eq 65 was solved numerically by means of a finite technique utilizing the standard centered-different approximations[39] for the first and second derivatives of $G(h)$. In all cases, dG/dh was obtained by explicit differentiation of the appropriate expression of $G(h)$. Newton's method[39] was employed to solve the nonlinear system of equations resulting from the substitution of the finite difference formulas into the boundary value problem. The Jacobian for this system of equations was tridiagonal, thereby permitting use of fast direct factorization methods.[39]

Calculations were performed on a Digital Equipment VAX 11/750 or MicroVAX 3500 using programs written in VAX FORTRAN V4.7. The number of mesh points varied between 100 and 5000. Computations were performed to a precision of 0.01%.

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[39] Burden, R. L.; Faires, J. D.; Reynolds, A. C. *Numerical Analysis*, 2nd ed.; Prindle-Webster-Schmidt: New York, 1981.