

Influence of Supporting Electrolyte Concentration and Composition on Formal Potentials and Entropies of Redox Couples Incorporated in Nafion Coatings on Electrodes

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The potentials (often termed Donnan potentials) present at the interface between polyelectrolyte coatings on electrodes and the solutions in which they are used contribute to the formal potentials measured for redox couples incorporated in the coatings. The dependence of the Donnan potentials on the concentration of supporting electrolyte causes the apparent formal potentials to shift with concentration in predictable ways that are discussed. With pH-dependent redox couples, shifts in formal potential reflect both the concentration and the pH of the supporting electrolytes. Spectral and electrochemical measurements with pH-dependent couples incorporated in Nafion coatings allowed the changes in pH inside the coatings resulting from changes in the supporting electrolyte pH to be monitored. Comparisons with the changes calculated on the basis of Donnan equilibrium and ion-exchange selectivity coefficients are presented. The contributions of Donnan potentials to apparent formal potentials prevent simple correlations of differences in formal potentials of redox couples inside and outside polyelectrolyte coatings with their intrinsic strengths as reducing or oxidizing agents in the two environments. The temperature dependences of formal potentials measured in polyelectrolyte coatings include an entropy of transfer as well as the reaction entropy of the redox couple involved. The two components of the measured entropies can have comparable magnitudes under common experimental conditions.

It is commonplace in reports on the behavior of electrodes coated with polymers to find comparisons of formal potentials for redox couples incorporated within the coatings with those in solution as measured at bare electrodes.¹⁻¹⁰ Differences in reaction entropies accompanying the incorporation of redox couples in polymer and polyelectrolyte coatings have also been reported and analyzed recently.^{9,10} That the ionic strength and composition of the supporting electrolytes employed in such studies can influence their outcome has been recognized,⁹ but no quantitative discussion of the effects to be expected has appeared. Although the concepts involved are well-known^{11,12} and are employed routinely in the analysis of the behavior of ion-selective electrodes, to cite one common example,¹³ it seemed desirable to apply them explicitly to the case of polyelectrolyte-coated electrodes to demonstrate their importance in this context.

Experimental Section

Materials. The following chemicals were prepared according to the references cited: [Ru(NH₃)₅Cl]Cl₂,¹⁴ [Os(bpy)₃]I₂¹⁵ (bpy = 2,2'-bipyridine), [Fe(Cp)C₅H₄CH₂N(CH₃)₃]I¹⁶ (Cp = cyclopentadienide); iodides were converted to hexafluorophosphates by metathesis with NH₄PF₆, [Ru(NH₃)₅pz](PF₆)₂ (pz = pyrazine)¹⁷ and [Ru(tpy)(bpy)OH₂](PF₆)₂ (tpy = 2,2',2''-terpyridine)¹⁸ (substituting NH₄PF₆ for NaClO₄). Membranes of Nafion (EW 1100, Aldrich) were 0.43 mm thick. They were rinsed with acetone, soaked briefly in 0.1 M HCl, and stored in deionized water.

Nafion coatings employed in electrochemical experiments were prepared by applying 25 μ L of a 5% alcoholic solution of Nafion 1100 (Aldrich) to a polished 0.46-cm² pyrolytic graphite electrode mounted on an inverted rotator (Pine Instruments) and immediately spinning the electrode at 2000 rpm to remove the solution. The thicknesses of the coatings prepared similarly with a spin-coating apparatus (Headway Research, Inc.) were estimated to be 0.05–0.2 μ m from profilometer (Dektak) measurements on dry films. Complexes were incorporated into Nafion coatings by immersing the coated electrodes in 0.1 mM solutions of the complex of interest and the appropriate supporting electrolyte.

Apparatus and Procedure. Electrochemical measurements were conducted in conventional H-type cells by using a PAR Model 173 potentiostat, Model 175 universal programmer (EG&G Instruments Co.), and an x-y recorder (Houston Instruments Model 2000). The quantities of electroactive complexes incorporated were determined by graphically integrating the charge passed

during the recording of voltammograms at low scan rates (10 mV/s). (It was determined that the spin-coating procedure described above yielded coatings in which cyclic voltametric peak currents were linearly dependent on scan rate up to 100 mV/s.) Formal potentials were equated with the average of the anodic and cathodic peak potentials of cyclic voltammograms recorded at 10 mV/s with coated electrodes and 100 mV/s with bare electrodes. All potentials are reported with respect to a sodium chloride saturated calomel electrode (SSCE).

Electronic spectra were recorded on a Hewlett-Packard Model 8450 spectrophotometer. Nafion membranes, 2 cm² in area, were mounted between two lucite brackets that slipped into a 5-mL cuvette mounted in the sample beam of the spectrometer. Reactants were incorporated into the mounted membrane by soaking in millimolar solutions in the appropriate supporting electrolyte. The membranes were then transferred to the 5-mL cuvette containing the supporting electrolyte of interest. The electrolyte was removed and replaced several times, and the spectra were recorded until they became constant. Spectral experiments were also performed with Nafion coatings prepared by evaporating

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[†]Contribution No. 7408.

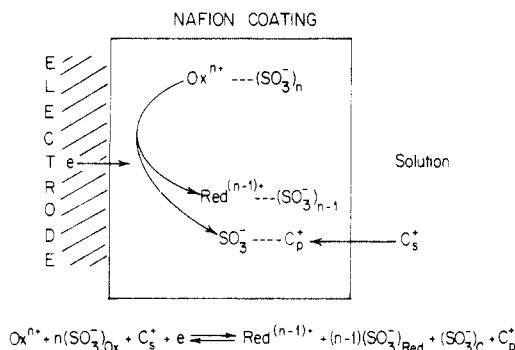
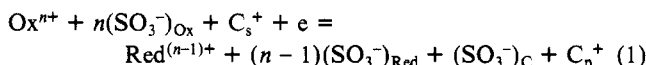


Figure 1. Schematic representation of the counterion transfer that accompanies electron transfer to a redox couple incorporated in Nafion coatings on electrodes. (SO_3^-) are fixed charge sites within the Nafion; C^+ is the counterion of the supporting electrolyte with which the coating is bathed.

aliquots of the soluble Nafion solution on glass slides. The results with coatings cast on glass were similar to those obtained with Nafion membranes, but the cast coatings suffered from poor adherence and occasional buckling when subjected to large changes in ionic strength. For this reason the results reported here were restricted to measurements with the Nafion membranes.

Results and Discussion

The electrochemical situation we wish to consider is depicted schematically in Figure 1. The cationic redox couple, $\text{Ox}^{n+}/\text{Red}^{(n-1)+}$, is incorporated within a polyanionic Nafion coating where its electrochemical behavior is monitored, typically by means of cyclic voltammetry. The Nafion coating exhibits a high degree of permselectivity¹⁹ so that anions are excluded from the coating. Electroneutrality is maintained during cyclic voltammetric measurements by the incorporation (reductive half-cycle) or ejection (oxidative half-cycle) of counterions, C^+ , from the supporting electrolyte solution. The complete half-reaction responsible for the observed voltametric responses includes the counterions transferred between the solution and polyelectrolyte phases



where $(\text{SO}_3^-)_{\text{Ox}}$, $(\text{SO}_3^-)_{\text{Red}}$, and $(\text{SO}_3^-)_C$ represent sulfonate groups within the polyelectrolyte coating associated with counterions Ox^{n+} , $\text{Red}^{(n-1)+}$, and C^+ , respectively. C_s^+ and C_p^+ are supporting electrolyte cations in the solution and polyelectrolyte phases, respectively. The apparent formal potential exhibited by the redox couple within the coating, $(E_p^f)_{\text{app}}$, will be given by eq 2 where

$$(E_p^f)_{\text{app}} = E_p^f + \frac{RT}{F} \ln \frac{[\text{C}^+]_s}{[\text{C}^+]_p} \quad (2)$$

E_p^f is the formal potential of the couple in the coating and ionic activities have been approximated by their concentrations. The concentration of C^+ within a permselective Nafion coating, $[\text{C}^+]_p$, should remain essentially constant during electrochemical measurements when the concentration of the redox couples incorporated in the coating is much smaller than $[\text{C}^+]_p$. In such cases, $[\text{C}^+]_p$ can be regarded as essentially equal to $[\text{SO}_3^-]_p$, the total concentration of sulfonate groups in the coating, a quantity that should be independent of $[\text{C}^+]_s$, when changes in the supporting electrolyte concentration produce negligible changes in the swelling of the coatings. As a result, $(E_p^f)_{\text{app}}$ is expected to change by 59 mV at 25 °C for every 10-fold change in $[\text{C}^+]_s$. The values of $(E_p^f)_{\text{app}}$ plotted in Figure 2 for three redox couples are in reasonable accord with eq 2.

Similar changes in $(E_p^f)_{\text{app}}$ are observed with other electrolytes (Table I). With electrolytes consisting of dipositive counterions (Mg^{2+} , Zn^{2+}), the slopes of lines such as those in Figure 2 are only half as large, as expected because the logarithmic term in eq 2

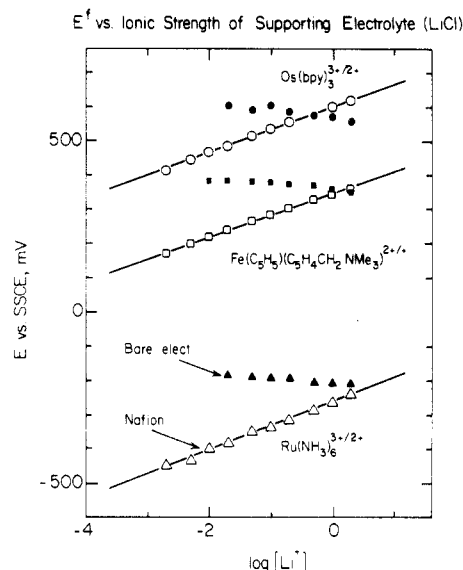


Figure 2. Dependence of the apparent formal potentials for three redox couples on the concentration of the LiCl supporting electrolyte. Solid symbols: Bare electrode, couples in solution. Open symbols: Electrode coated with Nafion in which the couples were incorporated. The quantities of the redox couples incorporated in the Nafion coatings represented less than 5% of the saturation values. The slopes of the lines (in mV/decade) are 67 (Os), 64 (Fe), and 70 (Ru).

TABLE I: Effect of Supporting Electrolyte Cations on Slopes of Semilogarithmic Plots of $(E_p^f)_{\text{app}}$ vs. Cation Concentration for $\text{Os}(\text{bpy})_3^{3+/2+}$

cation ^a	slope, ^b mV/decade	$(E_p^f)_{\text{app}}^{\circ}$, mV ^c	corr. coeff ^d
Li^+	67	599	0.999
H^+	61	624	0.999
Na^+	61	619	0.998
K^+	65	656	0.999
Mg^{2+}	27	618	0.997
Zn^{2+}	28	625	0.989

^a Chloride salts; concentration range as in Figure 2. ^b Least-squares slope of linear plots of $(E_p^f)_{\text{app}}$ vs. $\log [\text{cation}]$. ^c Value of $(E_p^f)_{\text{app}}$ at $[\text{cation}] = 1 \text{ M}$. ^d Correlation coefficient of the least-squares analysis.

should be multiplied by the reciprocal of the charge carried by the counterions. The small scatter in the values of $(E_p^f)_{\text{app}}^{\circ}$ listed in Table I for 1 M electrolyte concentrations could be the result of a variety of factors. If the coatings swelled to different extents in the different electrolytes, the value of $[\text{C}^+]_p$ would not remain constant which would be reflected in changes in $(E_p^f)_{\text{app}}^{\circ}$. Variation in the ratio of activity coefficients for the counterions in solution and in the Nafion with the identity of the counterion is another factor that could contribute to variations in $(E_p^f)_{\text{app}}^{\circ}$. In light of these possibilities, the good linearity and relatively constant values of $(E_p^f)_{\text{app}}$ obtained for the electrolytes used in Table I were a pleasant surprise.

When formal potentials, E_s^f , for the redox couples are measured at uncoated electrodes in homogeneous solution, the values obtained are much less sensitive to the composition of the supporting electrolyte solution (solid points in Figure 2). $(E_p^f)_{\text{app}}$ changes with ionic strength because of the changes in free energy associated with transfer of the supporting electrolyte cation from the solution to the Nafion phase. It is evident from Figure 2 that the difference between E_s^f and $(E_p^f)_{\text{app}}$ also changes with ionic strength. This difference, ΔE^f , is therefore not a direct measure of changes in the intrinsic oxidizing or reducing strength of a redox coupling that result from its incorporation in Nafion.

If the interactions between redox couples and the coating involved only the electrostatic attraction resulting from the Donnan potential at the coating/solution interface, the differences between $(E_p^f)_{\text{app}}$ and E_s^f at each concentration of LiCl in Figure 2 should be close to the Donnan potential. In that case, ΔE^f should be the

same for all three of the couples at each concentration of LiCl. It is evident that this is not true for the couples shown in Figure 2. It may be inferred that additional interactions are involved in the binding of the redox couples to the Nafion coatings. These probably include hydrophobic interactions of the osmium and iron complexes as well as specific electrostatic interactions between the fixed sulfonate groups and the more polarizable osmium complex. These additional interactions can produce contributions to the apparent formal potentials comparable to, or even larger than, those resulting from the Donnan potential. The change in sign of ΔE^f for the osmium couple at the higher concentrations of supporting electrolyte is an example of this effect. The presence and magnitude of mutually compensating interactions between redox couples and Nafion are revealed by measurements such as those displayed in Figure 2. It is more difficult to speculate convincingly about such compensatory effects on the basis of measurements of ΔE^f that are commonly reported for only a single electrolyte concentration. It may be worth emphasizing that the slopes of the lines in Figure 2 constitute good evidence that the thin films of Nafion 1100 prepared by the spin-coating possess permselectivity comparable to that of much thicker Nafion membranes.

Mixtures of Supporting Electrolyte. The situation becomes somewhat more complex when supporting electrolytes containing more than one cation are employed. In such cases it is necessary to take into account the selectivity coefficients that govern the ion-exchange equilibria to determine the relative amounts of each type of cation that are incorporated in the coating.³ It is instructive to consider the case in which just two unipositive cations, C^+ and D^+ , are present in the supporting electrolyte and the concentration of the incorporated redox couple is much less than the concentrations of C^+ and D^+ in the coatings which are required by electroneutrality to satisfy eq 3.

$$[C^+]_p + [D^+]_p = [SO_3^-]_p = \text{constant} \quad (3)$$

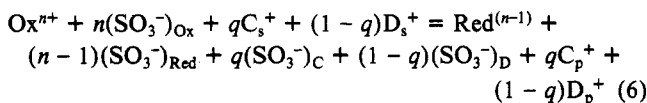
The ion-exchange equilibria involving C^+ and D^+ are governed by the ion-exchange selectivity coefficient, $K_{D^+}^{C^+}$, which may be defined as²⁰

$$K_{D^+}^{C^+} = \frac{[C^+]_p [D^+]_s}{[C^+]_s [D^+]_p} \quad (4)$$

Hence,

$$[D^+]_p = \frac{[D^+]_s [SO_3^-]_p}{K_{D^+}^{C^+} [C^+]_s + [D^+]_s} \quad (5)$$

The complete half-reaction associated with the reduction of a one-electron redox couple incorporated in Nafion can be formulated as



where q and $(1-q)$ are the fractions of the changes in the counterion content of the coating arising from C^+ and D^+ cations, respectively:

$$q = \frac{K_{D^+}^{C^+} [C^+]_s}{K_{D^+}^{C^+} [C^+]_s + [D^+]_s} \quad (7)$$

$$1 - q = \frac{[D^+]_s}{K_{D^+}^{C^+} [C^+]_s + [D^+]_s}$$

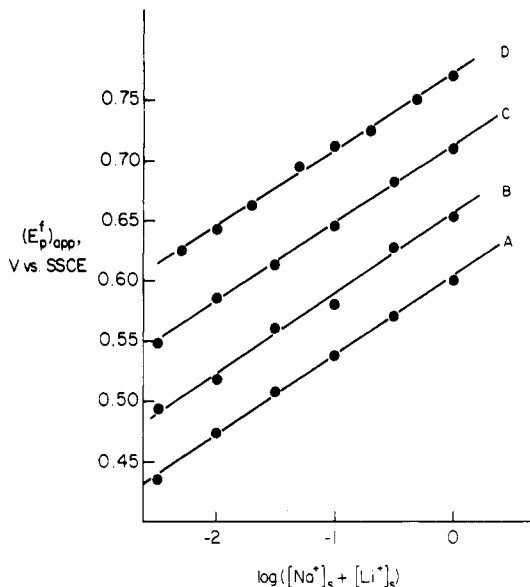


Figure 3. Apparent formal potentials for the $Os(bpy)_3^{3+/2+}$ couple incorporated in Nafion coatings. The supporting electrolyte consisted of mixtures of NaCl and LiCl with $[Na^+]_s/[Li^+]_s = (A) 0.1, (B) 0.25, (C) 0.50,$ and $(D) 1.0$. Lines B, C, and D are displaced by 50, 100, and 150 mV, respectively, for clarity. The slopes of the lines A, B, C, and D are 66, 65, 65, and 61 mV/decade, respectively.

The value of $(E_p^f)_{app}$ to be expected for half-reaction 6 can be expressed as

$$(E_p^f)_{app} = E_p^f + \frac{RT}{F} \ln \left[\left(\frac{[C^+]_s}{[C^+]_p} \right)^q \left(\frac{[D^+]_s}{[D^+]_p} \right)^{1-q} \right] \quad (8)$$

Substitution of eq 4 and 7 yields

$$(E_p^f)_{app} = E_p^f + \frac{RT}{F} \left[\ln \frac{[C^+]_s}{[C^+]_p} + \frac{[D^+]_s}{K_{D^+}^{C^+} [C^+]_s + [D^+]_s} \ln K_{D^+}^{C^+} \right] \quad (9)$$

According to eq 9, plots of $(E_p^f)_{app}$ vs. $\ln [C^+]_s$ (or $\ln [D^+]_s$) at constant ionic strength will be nonlinear. However, there are two special cases where linear plots are to be expected. If the concentration of supporting electrolyte is changed while maintaining the ratio $[D^+]_s/[C^+]_s \equiv X$ constant, eq 10 applies.

$$(E_p^f)_{app} = E_p^f + \frac{RT}{F} \left[\ln [C^+]_s + \ln \frac{K_{D^+}^{C^+} + X}{K_{D^+}^{C^+} [SO_3^-]_p} + \frac{X}{K_{D^+}^{C^+} + X} \ln K_{D^+}^{C^+} \right] \quad (10)$$

For this case, linear plots of $(E_p^f)_{app}$ vs. $\ln [C^+]_s$ are expected with slopes of 59 mV per decade change in $[C^+]_s$. Experiments of this type were conducted with the $Os(bpy)_3^{3+/2+}$ couple incorporated in Nafion with a series of mixed electrolytes consisting of Na^+ and Li^+ . Linear plots were obtained with slopes reasonably close to 59 mV/decade (Figure 3). Thus, the system behaved as expected on the basis of eq 10.

A second special case of interest is that for which $K_{D^+}^{C^+} [C^+]_s \gg [D^+]_s$. Equation 11 applies under these conditions. The second term inside the brackets in eq 11 will usually be negligible com-

$$(E_p^f)_{app} = E_p^f + \frac{RT}{F} \left[\ln \frac{[C^+]_s}{[SO_3^-]_p} + \frac{[D^+]_s}{K_{D^+}^{C^+} [C^+]_s} \ln K_{D^+}^{C^+} \right] \quad (11)$$

pared to the first so that essentially linear plots of $(E_p^f)_{app}$ vs. $\ln [C^+]_s$ are expected with slopes of 59 mV/decade. An example of this special case will be encountered in the following analysis of the behavior of pH-dependent redox couples.

pH Changes within Nafion Coatings. When the hydrogen ion forms of Nafion coatings or membranes are equilibrated with

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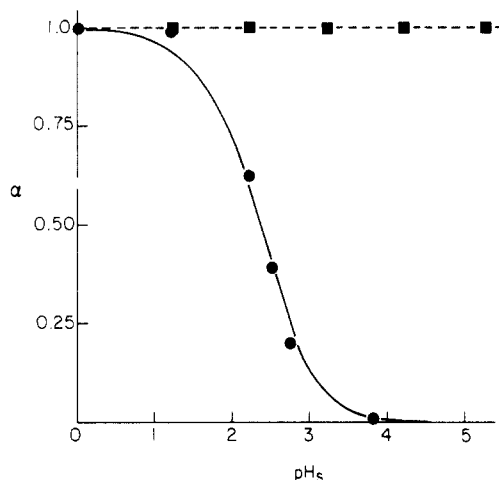


Figure 4. pH dependence of the ratio $[\text{Ru}(\text{NH}_3)_5\text{pz}]^{2+}/[\text{Ru}(\text{NH}_3)_5\text{pzH}^+]^{3+}$. Dashed line: $[\text{Ru}(\text{NH}_3)_5\text{pzH}^+]^{3+}$ incorporated in a Nafion membrane that was subsequently equilibrated with solutions containing only protons at the pH values shown. Solid line: $\sim 10^{-5}$ M $[\text{Ru}(\text{NH}_3)_5\text{pz}]^{2+}$ dissolved in the same solutions.

solutions containing differing concentrations of protons but no other cations, the proton concentration within the Nafion cannot change in response to changes in the solution composition. Thus, acid-base indicators incorporated within Nafion membranes or coatings are not expected to respond to changes in the pH of the bathing solution that produce large changes when the same indicator is dissolved in the bathing solution. A useful "indicator" for use in this type of experiment proved to be the cationic complex $[\text{Ru}(\text{NH}_3)_5\text{pz}]^{2+}$ that changes color when the exposed nitrogen atom of the pyrazine ligand is protonated:¹⁷



Both the protonated and unprotonated forms of the complex are strongly incorporated by Nafion membranes and coatings, and the significant spectral differences between the two forms¹⁷ facilitate the evaluation of the ratio of their concentrations within the Nafion as a function of the concentration of protons in the bathing solutions. In Figure 4 the changing ratio of the unprotonated to the protonated complex in solution is contrasted with the essentially constant ratio within a Nafion membrane equilibrated with the same solutions which contained only HCl.

When a second cation is present in the supporting electrolyte, changes in the proton concentration in the bathing solution, $[\text{H}^+]_s$, do produce changes in the ratio of the acid to the basic form of indicators incorporated in Nafion. The behavior can be analyzed quantitatively. The concentration of protons within Nafion coatings equilibrated with solutions containing both $[\text{C}^+]_s$ and $[\text{H}^+]_s$ as calculated from eq 5 is

$$[\text{H}^+]_p = \frac{[\text{H}^+]_s[\text{SO}_3^-]_p}{K_{\text{H}^+}^{\text{C}^+}[\text{C}^+]_s + [\text{H}^+]_s} \quad (12)$$

where the ion-exchange selectivity coefficient is defined as

$$K_{\text{H}^+}^{\text{C}^+} = \frac{[\text{H}^+]_s[\text{C}^+]_p}{[\text{H}^+]_p[\text{C}^+]_s} \quad (13)$$

The ratio of the acid to basic forms of the indicator provides an experimental measure of $[\text{H}^+]_p$

$$[\text{H}^+]_p = \frac{K_d^{\text{HIn}}[\text{HIn}]_p}{[\text{In}]_p} \quad (14)$$

where K_d^{HIn} is the acid dissociation constant for the indicator within the coating. Combination of eq 12 and 14 yields eq 15. Thus, a plot of the measured ratio $[\text{In}]_p/[\text{HIn}]_p$ vs. $[\text{C}^+]_s/[\text{H}^+]_s$

$$\frac{[\text{In}]_p}{[\text{HIn}]_p} = \frac{K_d^{\text{HIn}}}{[\text{SO}_3^-]_p} + \frac{K_d^{\text{HIn}}K_{\text{H}^+}^{\text{C}^+}[\text{C}^+]_s}{[\text{SO}_3^-]_p[\text{H}^+]_s} \quad (15)$$

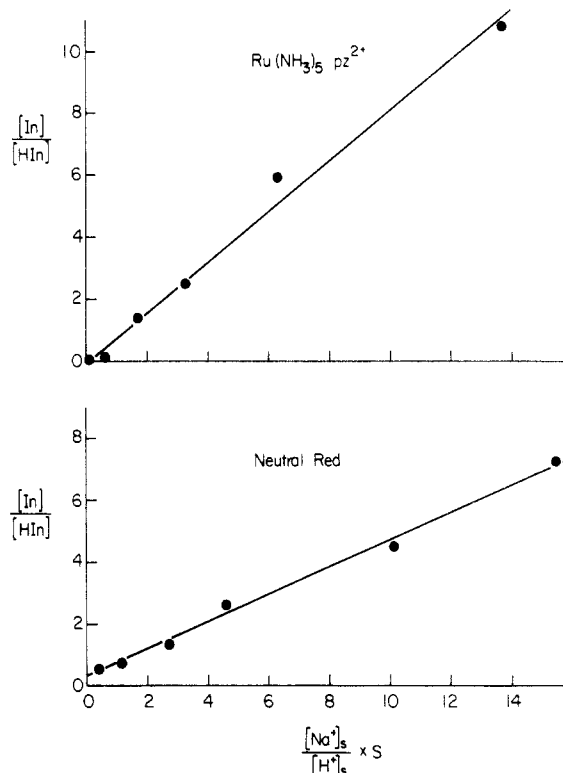
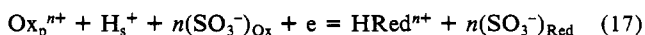
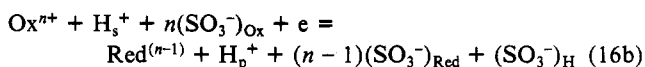
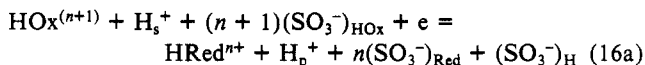


Figure 5. Acid-base indicator ratios in Nafion membranes plotted according to eq 15. The electrolytes bathing the membranes consisted of NaCl-HCl mixtures with $[\text{H}^+]_s = 10^{-5.5}$ (Ru complex) and $10^{-10.5}$ (neutral red). Scale factor: $S = 10^{-4}$ (Ru complex); $S = 10^{-9}$ (neutral red).

should be linear. Examples of this type of plot are shown in Figure 5 for the $[\text{Ru}(\text{NH}_3)_5\text{pz}]^{2+}$ "indicator" as well as a conventional acid-base indicator, neutral red. The anticipated linearity is observed in both cases. Although the form of eq 15 suggests that the slopes and intercepts of such plots might be used to estimate $[\text{SO}_3^-]_p$ and K_d^{HIn} within the Nafion membrane, we have refrained from doing so because of the possibility that both $K_{\text{H}^+}^{\text{Na}^+}$ and $[\text{SO}_3^-]_p$ change with the sodium concentration as the degree of membrane swelling changes.¹⁹

pH-Dependent Redox Couples. It is interesting to consider the behavior within Nafion coatings of redox couples having pH-dependent formal potentials. With coatings equilibrated with supporting electrolytes containing only protons, the pH within the Nafion coating is not altered by changes in the pH of the solution (dashed line in Figure 4). Nevertheless, the measured $(E_p^f)_{\text{app}}$ values for incorporated redox couples—pH-dependent as well as pH-independent couples—change in response to the changes in the proton concentration in solution because the changes in ionic strength affect the Donnan potential at the coating/solution interface (Figure 2).

The half-reactions that describe the electrode reactions of proton-dependent redox couples in Nafion coatings depend upon the pH of the supporting electrolyte solution and the $\text{p}K_a$ values of the oxidized and reduced forms of the couple. Examples are given in half-reactions 16 and 17. Half-reaction 16a or 16b is



equivalent to half-reaction 1 (with $\text{C}^+ = \text{H}^+$), and the redox couple induces, but does not participate in, the proton-transfer process. One proton per electron is transferred from the solution to the coating as the half-reaction proceeds, and $(E_p^f)_{\text{app}}$ is expected to change by 59 mV per pH unit because of the changes in the

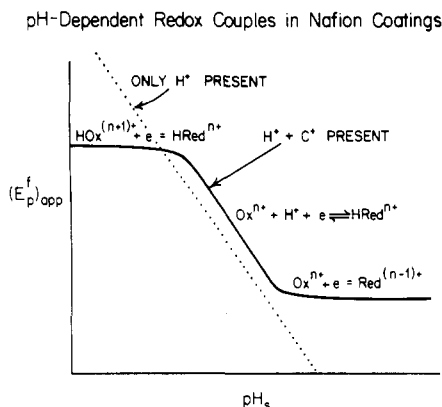
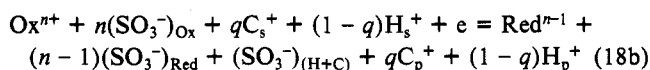
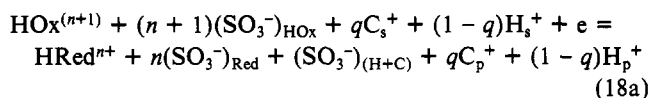


Figure 6. pH dependence of apparent formal potentials to be expected for proton-consuming redox couples incorporated in permselective coatings such as Nafion (dotted line). Supporting electrolyte: dotted line, protons the only cations present; solid line, protons plus a second cation, C^+ , present. The solid line also depicts the behavior expected at uncoated electrodes. However, the pK_a values measured in solution and within Nafion could differ substantially.

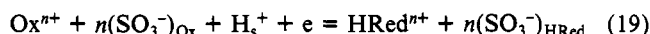
Donnan potential caused by the changes in ionic strength that result from the pH changes. Note that in solution the E_s^f values for the $HOx/HRed$ or Ox/Red couples would show no pH dependence.

In half-reaction 17, a proton is consumed by the redox couple itself. $(E_p^f)_{app}$ is again expected to change by 59 mV per pH unit as would E_s^f values measured at a bare electrode in homogeneous solutions. Thus, redox couples whose half-reactions do not involve protons and which, therefore, yield pH-independent values of E_s^f measured at bare electrodes in solution are expected to exhibit pH-dependent values of $(E_p^f)_{app}$ when incorporated in Nafion. The $(E_p^f)_{app}$ values measured in Nafion are expected to change by 59 mV per 10-fold change in $[H^+]_s$ no matter what the pH of the solution is when protons are the only cations present. The dotted line in Figure 6 displays the expected behavior.

Different behavior is to be expected when the solution bathing the Nafion coating contains another cation, C^+ , as well as protons. The situation is similar to the one analyzed above for the case of supporting electrolytes consisting of two univalent salts. However, with pH-dependent redox couples the behavior to be expected will depend upon the pH inside the coating. It is useful to consider two cases. In case i the redox half-reaction itself does not involve protons ($pH_p < pK_a^{Ox}$, half-reaction 18a, or $pH_p > pK_a^{Red}$, half-reaction 18b).



In case ii the contrary is true ($pK_a^{Red} > pH_p > pK_a^{Ox}$; half-reaction 19):



For case i ($pH_p < pK_a^{Ox}$), an expression for $(E_p^f)_{app}$ can be obtained from eq 9:

$$(E_p^f)_{app} = E_p^f + \frac{RT}{F} \left[\ln \left(\frac{K_{H^+}^+ [C^+]_s + [H^+]_s}{K_{H^+}^+ [SO_3^-]_p} \right) + \frac{[H^+]_s}{K_{H^+}^+ [C^+]_s + [H^+]_s} \ln K_{H^+}^+ \right] \quad (20)$$

For case ii a much simpler result is obtained

$$(E_p^f)_{app} = E_p^f + \frac{RT}{F} \ln [H^+]_s \quad (21)$$

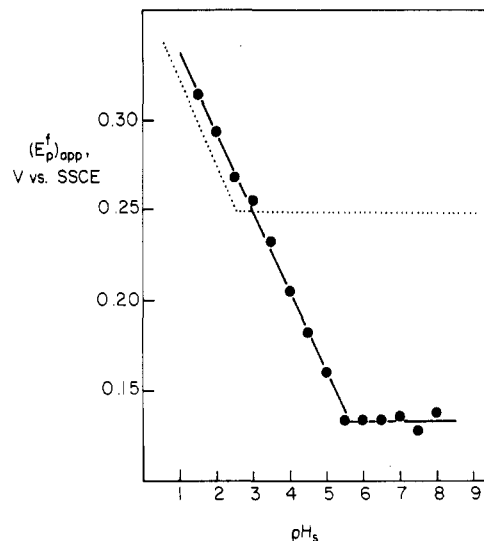
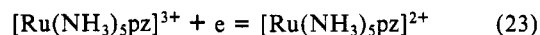
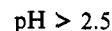
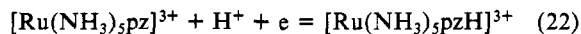
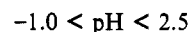


Figure 7. pH dependence of the apparent formal potential of the $[Ru(NH_3)_5pzH]^{3+}/[Ru(NH_3)_5pzH]^{2+}$ (x and $y = 0$ or 1) couple incorporated in Nafion coatings. All solutions contained 0.2 M Na^+ and appropriate anionic buffers: HSO_4^-/SO_4^{2-} ($pH \leq 2.5$); HOx/Ox^{2-} ($3 \leq pH \leq 5$; Ox = oxalate); $H_2PO_4^-/HPO_4^{2-}$ ($pH \geq 5.5$). The dotted line is the (calculated) behavior of the same couple at a bare electrode in solution.

but eq 21 applies only to a restricted pH range: $pK_a^{Red} > pH_p > pK_a^{Ox}$.

In general, it is more convenient to examine the behavior of pH-dependent redox couples in Nafion coatings under conditions such that eq 10 applies. This can be accomplished by employing anionic buffers prepared from salts of C^+ at concentrations chosen so that $K_{H^+}^+ [C^+]_s \gg [H^+]_s$ throughout the pH range of interest. For such solutions eq 10 predicts $(E_p^f)_{app}$ values that remain essentially independent of pH for case i ($pH_p < pK_a^{Ox}$) but shift by 59 mV per pH unit for case ii ($pH_p > pK_a^{Ox}$) where half-reaction 18 proceeds and eq 20 applies. The solid line in Figure 6 depicts the expected behavior with supporting electrolytes containing both protons and a second cation. Extrapolation of the pH-independent and pH-dependent potentials to their point of intersection establishes a value of $[H^+]_s$ from which an estimate of the pK_a for the components of the redox couple can be calculated from eq 12. These expectations were tested with the $[Ru(NH_3)_5pz]^{3+/2+}$ redox couple that exhibits pH-dependent formal potentials in solution in the pH range where the $Ru(II)$ but not the $Ru(III)$ complex is protonated. The half-reactions in solution are



Values of $(E_p^f)_{app}$ for this redox couple incorporated in Nafion are plotted vs. the pH of the buffered bathing solutions in Figure 7. (Sodium salts of anionic buffers were employed so that the only cationic species present in the supporting electrolyte solutions were Na^+ and H^+ .) As anticipated, a two-segment plot is obtained similar to the behavior of the same complex at bare electrodes (dotted line, Figure 7). However, the intersection of the horizontal and inclined lines occurs at a higher pH for the complex incorporated in Nafion. A pK_a for $[Ru(NH_3)_5pzH]^{3+}$ in Nafion of ca. 4.5 was calculated from eq 12. (Since the experiments were conducted at a constant concentration of sodium ion, we have more confidence in assigning constant values to $K_{H^+}^{Na^+} = 1.2^{19}$ and $[SO_3^-]_p = 1.4 M^6$ than was the case in connection with Figure 5 and eq 15 where the slopes and intercepts of the plots might otherwise have been utilized to obtain an estimate of K_d^{HIn} .) The pK_a of the complex in solution is 2.5.¹⁷ Thus, the electrochemical data indicate a significant increase in the pK_a of the complex when it

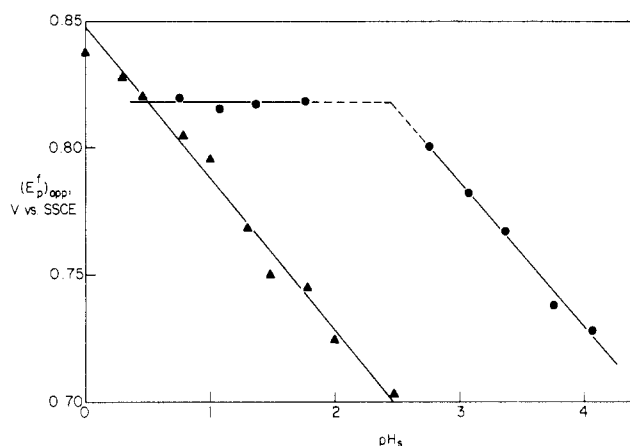


Figure 8. pH dependence of the apparent formal potential of the $[\text{Ru}(\text{tpy})(\text{bpy})\text{OH}_x]^{(1+x)+}/[\text{Ru}(\text{tpy})(\text{bpy})(\text{OH}_2)]^{2+}$ ($x = 2$ or 1) couple incorporated in Nafion coatings. Supporting electrolyte: dotted line, protons (HClO_4), the only cations present; solid line, $0.1 \text{ M NaClO}_4 + \text{HClO}_4$.

is incorporated in Nafion. The increase seems much too large to be attributed to uncertainties in the values of $[\text{SO}_3]_p$ or K_{H^+} . Similar increases in the $\text{p}K_a$ for the ruthenium complex in solution are produced by increases in ionic strength. For example, a value of $\text{p}K_a$ of 3.6 was measured in 4 M NaCl . Thus, the increases in $\text{p}K_a$ upon incorporation of the indicators in Nafion membranes seem likely to arise, at least in part, from the increase in ionic strength of the environment that they experience inside the membrane.

With supporting electrolytes containing only protons, it was not practical to measure $(E_p^f)_{\text{app}}$ for the $[\text{Ru}(\text{NH}_3)_5\text{pzH}]^{3+/2+}$ couple over the range (pH 5–7) where the pH dependence disappears in mixed electrolytes. We therefore employed a different redox couples to test the predicted behavior shown in Figure 6 for purely protonic and mixed electrolytes. The $[\text{Ru}(\text{tpy})(\text{bpy})\text{OH}_2]^{3+/2+}$ couple proved suitable for our purposes, and values of $(E_p^f)_{\text{app}}$ for this couple in both types of supporting electrolyte are shown in Figure 8.

The dotted line in Figure 8 is drawn through the data points obtained in supporting electrolyte that contained only protons. The slope is 60 mV/decade throughout the entire pH range as predicted by half-reactions 16 and 17 and displayed in the dotted line in Figure 6. In solution, the same couple exhibits pH-dependent formal potentials at pH values below 1.7 where the sixth ligand in both the oxidized and reduced complex is present as H_2O .¹⁸ When the measurements with the Nafion coatings were repeated with a supporting electrolyte that contained both protons and sodium ions, the data fell on the solid line in Figure 8. The inclined line has a slope of 57 mV/decade , and the behavior matches that anticipated by the upper portion of the solid line in Figure 6. A lack of suitable anionic buffers that did not anate the complex prevented extension of the pH measurements to values much above 4 so that the region corresponding to the lower portions of the solid lines in Figure 6 could not be examined. However, the data clearly demonstrate the significant behavioral differences to be expected when pH-dependent redox couples are examined in only protonic or mixed supporting electrolytes. The apparent $\text{p}K_a$ value for the $[\text{Ru}(\text{tpy})(\text{bpy})\text{OH}_2]^{3+}$ in Nafion obtained from the intersection of the solid lines in Figure 8 is 1.4,

a value slightly smaller than the reported $\text{p}K_a$ in solution, 1.7.¹⁸ This is somewhat surprising as the $\text{p}K_a$ for $[\text{Ru}(\text{NH}_3)_5\text{pzH}]^{3+}$ was increased upon incorporation in Nafion. However, the voltametric waves for the $[\text{Ru}(\text{tpy})(\text{bpy})\text{OH}_2]^{3+/2+}$ couple were broad and flat at pH values in the vicinity of the intersection point in Figure 8 which diminished the precision with which the $\text{p}K_a$ value could be measured.

Redox Reaction Entropies in Nafion Coatings. The reaction entropies^{9,10} of redox couples incorporated in Nafion coatings have also been the subject of recent studies.^{9,10} The reaction entropies were evaluated from the coefficient $F(dE^\circ/dT)$ where E° is the standard potential (usually approximated by the formal potential), F is the Faraday constant, and T is the temperature. This is the correct coefficient for formal potentials measured at uncoated electrodes with redox couples dissolved in solution.²¹ However, when the couple is incorporated in Nafion, the temperature dependence of the apparent formal potential will include a contribution from the entropy of transfer of the supporting electrolyte cation between the solution and the Nafion:

$$F \left[\frac{d(E_p^f)_{\text{app}}}{dT} \right] = S_{\text{rc}} + R \ln \frac{[\text{C}^+]_s}{[\text{C}^+]_p} \quad (24)$$

Thus, the measured temperature coefficient does not provide the reaction entropy desired, ΔS_{rc} , but the sum of ΔS_{rc} and the entropy of transport of the supporting electrolyte cation. If $[\text{C}^+]_p$ is taken to be 1.4 M ,²⁰ the second term in eq 24 amounts to 6 eu for $[\text{C}^+]_s = 0.1 \text{ M}$ and 11 eu for $[\text{C}^+]_s = 0.01 \text{ M}$. These values are comparable to values of ΔS_{rc} that have been reported for several redox couples in Nafion¹⁰ which shows that the correction called for in eq 24 is not negligible.

Conclusions

The data and analysis presented here make it clear that the effects of ionic composition and pH of supporting electrolytes on the electrochemical behavior of redox couples must be considered explicitly in studies directed at accounting for the formal potentials and reaction entropies of the couples when they are incorporated in Nafion coatings. This fact has not always been clearly recognized in previous publications on Nafion-coated electrodes, including our own. The necessary theoretical relationships are well-known^{11,12} and not difficult to apply. It seems possible that their application could help to account for some of the otherwise puzzling behavior often encountered with Nafion coatings.^{1,2,6,9,10}

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Registry No. $\text{Os}(\text{bpy})_3^{3+}$, 30032-51-0; $\text{Os}(\text{bpy})_3^{2+}$, 23648-06-8; $[\text{Ru}(\text{NH}_3)_5\text{pzH}^{+}]^{3+}$, 19441-21-5; $[\text{Ru}(\text{NH}_3)_5\text{pz}]^{2+}$, 19471-65-9; $[\text{Ru}(\text{NH}_3)_5\text{pz}]^{3+}$, 38139-16-1; $[\text{Ru}(\text{NH}_3)_5\text{pzH}^{+}]^{4+}$, 38192-67-5; $[\text{Ru}(\text{tpy})(\text{bpy})\text{OH}_2]^{3+}$, 89463-61-6; $[\text{Ru}(\text{tpy})(\text{bpy})(\text{OH}_2)]^{2+}$, 20154-63-6; $[\text{Ru}(\text{tpy})(\text{bpy})\text{OH}]^{2+}$, 81971-63-3; $\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4\text{CH}_2\text{NMe}_3)^{2+}$, 51150-57-3; $\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4\text{CH}_2\text{NMe}_3)^+$, 33039-48-4; $\text{Ru}(\text{NH}_3)_6^{3+}$, 18943-33-4; $\text{Ru}(\text{NH}_3)_6^{2+}$, 19052-44-9; LiCl , 7447-41-8; HCl , 7601-90-3; NaCl , 7647-14-5; KCl , 7447-40-7; MgCl_2 , 7786-30-3; ZnCl_2 , 7646-85-7; NaClO_4 , 7601-89-0; HClO_4 , 7601-90-3; Nafion EW 1100, 63496-24-2; graphite, 7782-42-5.

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