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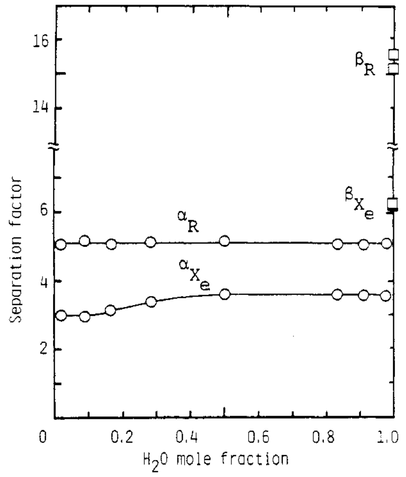

Figure 2. Concentration dependence of separation factors.

fraction of H_2O, being kept constant at 5.1 ± 0.05. β_R was 15.4 ± 0.2 for H_2O–HTO of $1.8 \times 10^4/1$ and $3.6 \times 10^4/1$. On the other hand, α_{X_e} varied with the H_2O mole fraction. At the low H_2O fraction region, it was 3.05 ± 0.05, whereas it was 3.6 ± 0.005 at the high fraction region. β_{X_e} was 6.2 ± 0.05.

With regard to the H_2O–D_2O system, the separation factor in the photoassisted decomposition has been reported as 5.3 ± 0.1 for Pt/TiO_2 catalyst.[6] The present observations (α_R) agree quite well with the above value. As for the H_2O–HTO system, the present results are the first observations in the photoassisted decomposition.

In electrolysis, the separation factors are reported as $\alpha = 5$–7 (smooth Pt surface)[14] and $\beta = 14$.[15] These values are quite close to the present observations, indicating that the photoassisted decomposition proceeds through the same mechanism as the electrolysis. In addition, the present results confirmed that the catalytic process (reaction 4) is the rate-determining step in the photoassisted decomposition, because the observed separation factors agree well with the theoretical prediction for this mechanism.[7] The kinetic model also supports this conclusion.

On the other hand, the separation factors determined from the steady state were lower than the respective values of α_R and β_R. They agree quite well with those for the gas–liquid equilibration reaction: 3.6 for H_2O–HDO,[16] 3.06 for D_2O–HDO,[17] and 7 ± 2 for H_2O–HTO.[18] It indicates that α_{X_e} and β_{X_e} observed in the present study were determined with the gas–liquid equilibration reaction.

Registry No. H_2O, 7732-18-5; D_2, 7782-39-0; T_2, 10028-17-8; Pt, 7440-06-4; TiO_2, 13463-67-7.

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Polymer Films on Electrodes. 20. An ESR Study of Several Spin Probes Incorporated into Nafion

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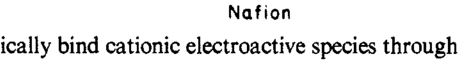
The oxidative electrochemistry of protonated 2,2,6,6-tetramethylpiperidine-1-oxyl (Tempamine, TP) has been surveyed with Pt/Nafion modified electrodes. Protonated TP was shown to incorporate into Nafion films at pH lower than 9. Its oxidation is a reversible, one-electron process occurring at $E_{1/2} = 0.54$ V vs. SCE on Pt/Nafion electrodes (ca. 120 mV less positive than $E_{1/2}$ on bare Pt) and independent of the pH in the range 4–8. The ESR spectrum of Nafion-confined TP showed that the rotational correlation time was in the slow tumbling region and was estimated to be 1.2×10^{-8} s. This reveals an unusual anchoring effect by Nafion which had not been observed previously. The ESR spectra of some additional Nafion-confined spin probes such as vanadyl, manganese(II), and the cation radical of *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine (TMPD) were also surveyed. The results indicate that the motion of a given cation within Nafion is determined by the nature of the cation itself.

Introduction

Coating of electrodes with polyelectrolyte polymer films constitutes a versatile modification strategy, since ionic electroactive species can then be incorporated into these films from a contacting solution phase via ion-exchange reactions.[1] This approach was first introduced by Oyama and Anson[2] using poly(4-vinylpyridine) films to incorporate anionic electroactive compounds such as $Fe(CN)_6^{3-}$ and $IrCl_6^{3-}$. Numerous reports[3-5] have described the preparation and behavior of electrodes coated with films of the perfluorinated ion-exchange polymer, Nafion,[6] which can electrostatically bind cationic electroactive species through the sulfonic sites.



$$-(CF_2CF_2)_x-(CFCF_2)_y- \quad | \quad O-(CF_2)_3-O-CF_2CF_2-SO_3^- Na^+$$

Nafion

Our interest in this type of modified electrodes derives not only from the possibility of confining high concentrations of elec-

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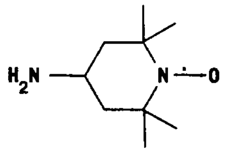
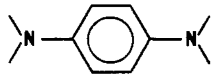
troactive compounds in the vicinity of the electrode surface but also from the remarkable properties of Nafion membranes as catalyst supports.[7]

Several electrochemical methods have been used to investigate the charge-transport mechanisms operating in these electrodes, and their redox properties.[3-5] Morphological details on the structure of modifying polymer films can be obtained by using some spectroscopic techniques.[1] ESR spectroscopy is particularly attractive for these studies because information concerning the motion and chemical environment of surface-confined redox couples, as well as insight into the mechanisms of charge transport, can be obtained. However, ESR spectroscopy has only rarely been utilized for these purposes.[8,9] We have recently described[10] the application of simultaneous electrochemical and electron spin resonance (seesr) techniques for the study of methylviologen incorporated into Nafion-modified electrodes. The cation radical of this compound, electrochemically generated inside the Nafion film, displayed an ESR spectrum similar to the solution spectrum. This surprising experimental fact was interpreted to indicate that the motion of this radical species is about the same in both environments whereas the rate of electron self-exchange is very much decreased inside the polymer film. We have also recently observed[11] an ESR spectrum for Ti(III) ions incorporated into Nafion membranes which closely corresponds to the solution spectra. These results prompted us to continue the use of ESR spectroscopy as a tool to gain an understanding of morphological details inside these polymer films.

Spin labeling is a well-established technique which has found numerous applications in the elucidation of chemical environments, especially in the field of biological chemistry.[12] Moreover, nitroxide compounds (the most widely used type of spin labels) exhibit a well-defined electrochemistry.[13] We thus decided to initiate electrochemical and ESR studies of nitroxide spin-labels incorporated into Nafion. In this work, we report our experimental results obtained with the protonated form of 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (Tempamine, TP). Since the ESR results were quite different from those previously obtained by our group with the cation radical of methylviologen and Ti(III), we expanded the ESR investigation to include other cationic spin probes such as vanadyl (VO^{2+}), manganese(II), and the cation radical of *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine (TMPD).



TP



TMPD

Experimental Section

Materials. Tempamine was purchased from the Aldrich Chemical Co. and used without further purification. Nafion of 1100 equivalent weight was obtained from C.G. Processing Inc. (Rockland, DE) as a 5% (w/v) ethanolic solution. Distilled water was further purified by passage through a Millipore-Q reagent water system. TMPD was recrystallized as described by Michaelis.[14] All other chemicals were of the highest commercially available quality.

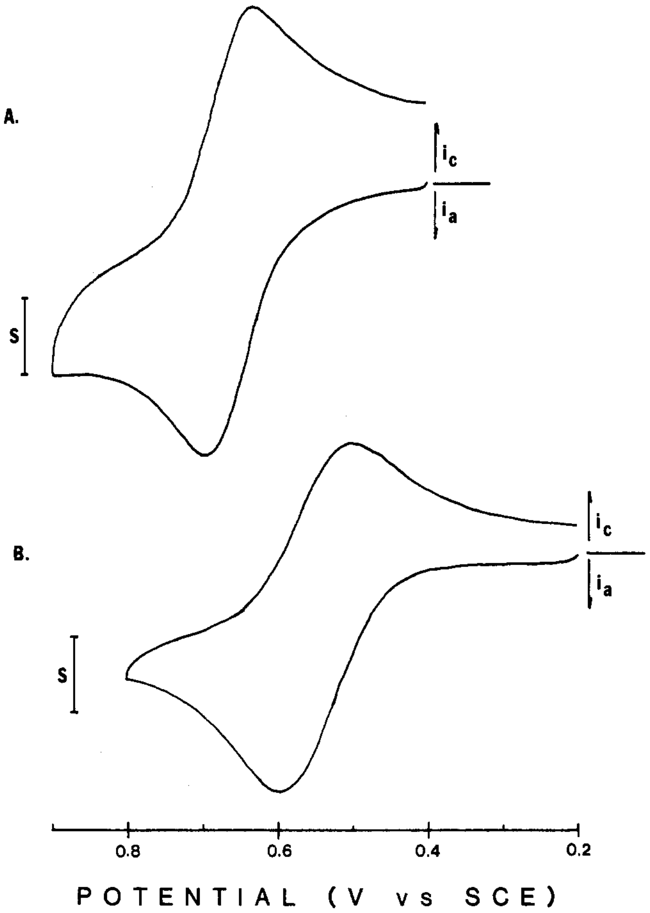


Figure 1. Voltammetric response of a 1.0 mM TP–0.2 M Na_2SO_4 (pH 4) solution (a) at a bare Pt electrode, $S = 2\ \mu A$, and, (b) at a Pt/Nafion (1 μm thickness) electrode, after 30 min of equilibration, $S = 5\ \mu A$. Scan rate = 50 mV/s.

Electrode Modification. Nafion-modified electrodes were prepared by covering the platinum electrode surface (a Pt disk electrode with an area of 0.0533 cm^2 for the electrochemical experiments and a Pt flag electrode with an area of 0.42 cm^2 for the ESR measurements) with a suitable volume of the 5% Nafion ethanolic solution and allowing the solvent to evaporate for 15–30 min. A ratio of 20 $\mu L/cm^2$ of electrode surface was utilized to obtain a film thickness of about 1 μm. Thinner films were obtained by diluting the original Nafion solution. Once the film was cast, the electrode was exposed to a deoxygenated 0.2 M Na_2SO_4 solution for more than 8 h to ensure that the Nafion polymer was in the Na^+ form. Finally, the ESR active cation was incorporated by soaking the electrode into a deoxygenated aqueous solution containing 0.1–5 mM of the corresponding salt (usually the sulfate) and 0.2 M Na_2SO_4. The pH of these solutions was previously adjusted to a suitable value by addition of small volumes of 0.1 M NaOH or 0.05 M H_2SO_4. In the cases where no electrochemical measurements were intended, Nafion membranes (type 125, 1100 equivalent weight, thickness ca. 0.13 mm) were used as exchange matrices. These were pretreated by boiling in concentrated HNO_3 until they became clear and transparent. They were then soaked and stored in 0.2 M Na_2SO_4. The paramagnetic cations were then exchanged from solutions prepared as described above for the modified electrodes. In control experiments, the ESR spectra of a given spin probe incorporated into the Nafion films cast on Pt electrodes and into Nafion membranes were found to be similar.

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TABLE I: Potential Data for the Oxidation of TP in Different Media[a]

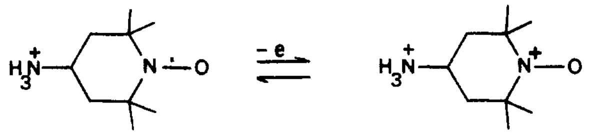
	bare Pt			Pt/Nafion		
pH	$E_{p,a}$	$E_{p,c}$	$E_{1/2}$	$E_{p,a}$	$E_{p,c}$	$E_{1/2}$
1.0	0.705	0.635	0.670	0.630	0.550	0.590
4.0	0.695	0.630	0.663	0.585	0.495	0.540
6.0	0.690	0.625	0.658	0.590	0.500	0.545
8.0	0.695	0.630	0.663	0.600	0.500	0.550

[a] Solutions 1.0 mM TP–0.2 M Na_2SO_4; pH adjusted with 0.1 M NaOH or 0.05 M H_2SO_4. All potentials (error margin ±0.005 V) in V vs. SCE.

Apparatus. ESR spectra (X-band) were recorded with a Varian E-9 spectrometer (100-kHz field modulation) equipped with a TE_{102} dual-sample cavity. Low modulation amplitudes were used to avoid any distortion in line shapes. Microwave powers were low enough to preclude saturation effects. Electrochemical measurements were performed with a PAR Model 175 universal programmer, a Model 173 potentiostat, and a Model 179 digital coulometer (Princeton Applied Research Corp., Princeton, NJ). Cyclic voltammograms were recorded on a Houston Model 2000 x–y recorder (Houston Instruments, Austin, TX). Dry film thicknesses were estimated from previous data obtained by our group with a Sloan Dektak surface-profile measuring system.[10]

Results and Discussion

Electrochemistry of Tempamine Incorporated into Nafion Films. The oxidative electrochemistry of tempamine is characterized by the oxidation of the nitroxide group,[13] according to eq 1. Figure 1A shows the cyclic voltammogram obtained at bare Pt in a 1.0 mM TP/0.2 M Na_2SO_4 solution at pH 4. Figure 1B shows the voltammetric response of the same solution on a Pt/Nafion (1 μm thickness) electrode after equilibration for 30 min. The shapes of these voltammograms confirm that the oxidation of tempamine is a reversible, one-electron process (at bare Pt, ΔE_p = 60–65 mV; at Pt/Nafion, ΔE_p = 90–100 mV). The potential data given in Table I clearly suggests that no protonation steps are coupled to the electron-transfer process, since no trend is detected in the oxidation half-wave potential ($E_{1/2}$) as the pH of the medium varies from 1 to 8. This result agrees with previous reports on the electrochemistry of nitroxide compounds.[13] However, at pH values higher than 9 the oxidation of tempamine becomes chemically irreversible, probably because the oxidized TP reacts with OH^-. In this high pH range, the amount of TP incorporated into the Nafion is very low because most of the TP is in the uncharged, unprotonated form. On the other hand, for TP at the Pt/Nafion electrode, the $E_{1/2}$ at pH 1 is about 50 mV more positive than the values at the higher pH's. The origin of this effect is unclear. To avoid the complications arising at pH values either strongly acidic or basic, we performed the remaining experiments in the pH range 4–8, where the electrochemistry of tempamine is nearly reversible and unperturbed by coupled chemical reactions.



(1)

In this pH range, as can be seen from the data in Table I, the oxidation of tempamine occurs at a potential about 120 mV more positive in aqueous solution than inside Nafion. The magnitude of this shift is remarkable, since it is much larger than that observed with other electroactive cations.[5,10] The relative stabilization of the 2+ oxidized species by the polyelectrolyte matrix is therefore stronger for tempamine than for previously studied cations.

In Nafion films of about 1 μm thick, the peak currents were diffusion controlled, in the range 5 to 200 mV/s, as revealed by the constancy of the ratio anodic peak current/(scan rate)$^{1/2}$. From this ratio an apparent diffusion coefficient (D_0) of 1 × 10^{-10} cm²/s was obtained for protonated TP inside Nafion. At a bare Pt electrode, D_0 was 4.5 × 10^{-6} cm²/s. The voltammogram in Figure 2 shows a shape very close to that of a surface-confined species (ΔE_p = 30 mV) corresponding to a 0.1–0.2-μm film thickness. These results are in agreement with previous reports from this laboratory on other species in Nafion.[5]

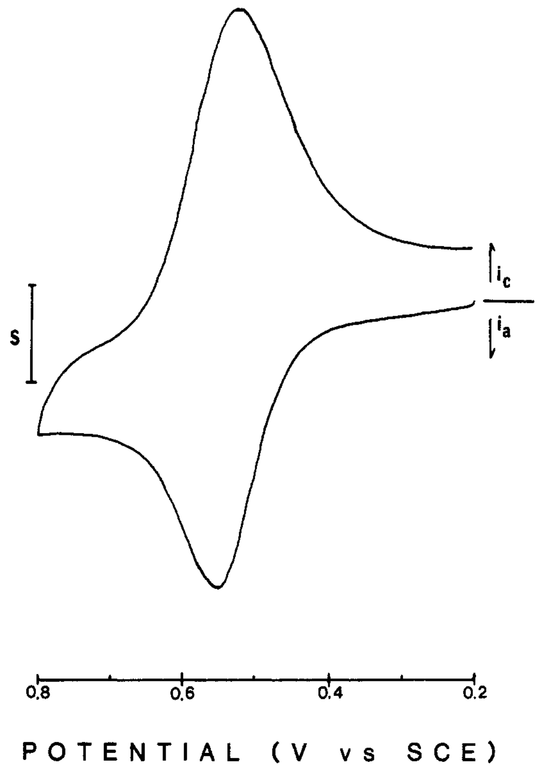


Figure 2. Voltammetric response at a Pt/Nafion (thickness 0.1–0.2 μm) electrode of a 0.5 mM TP–0.2 M Na_2SO_4 (pH 4) solution. *S* = 1 μA. Scan rate = 20 mV/s.

The incorporation of protonated tempamine from a contacting solution into a Nafion film can thus be easily monitored by using cyclic voltammetry (Figure 3). When a film about 1 μm thick and initially in the Na^+ form is immersed in 1 mM TP/0.2 M Na_2SO_4 (pH 7), the cyclic voltammograms grow with immersion time as the electroactive species is incorporated into the film. After about 30 min of cycling, a steady-state voltammogram is obtained. This behavior is similar to that previously observed[5f,g] for other electroactive cations such as $Ru(bpy)_3^{2+}$, $Os(bpy)_3^{2+}$, and Cp_2FeTMA^+ (where Cp_2FeTMA^+ is ((trimethylammonio)-methyl)ferrocene, bpy = 2,2′-bipyridine). However, when the electrode of Figure 3 was removed, rinsed, and cycled in pure supporting electrolyte, the peak currents quickly decreased until only residual waves were observed. The loss of TP from the film is almost complete (more than 90%) and fast (several minutes). This is in contrast to the behavior observed for several other electroactive cations that are retained inside the film at 70% or higher levels after several hours, or even days, of immersion in supporting electrolyte solution.[5f,g] Therefore, the binding of protonated TP to the Nafion film seems to be comparatively more labile than that of $Ru(bpy)_3^{2+}$, $Os(bpy)_3^{2+}$, or Cp_2FeTMA^+. This fact prevented us from determining the extraction coefficient (*K*) of protonated TP into Nafion using the procedure developed for Cp_2FeTMA^+.[5f] However, an upper limit for *K* can be obtained by coulometric determination of the charge consumed in the oxidation of a Nafion film equilibrated with solutions containing different concentrations (C_s) of TP. The charge measured with this approach is consumed not only in oxidizing the protonated TP inside the film, but also in the mediated oxidation of TP in solution by the oxidized TP in the film. Therefore the concentrations in the polymer phase (C_p) determined by this method are overestimated. The logarithmic plot of C_p vs. C_s appears in Figure 4. From the linear segment of the plot an extraction coefficient, $K = C_p/C_s$, of 7.5 × 10^2 was calculated. This value is half that

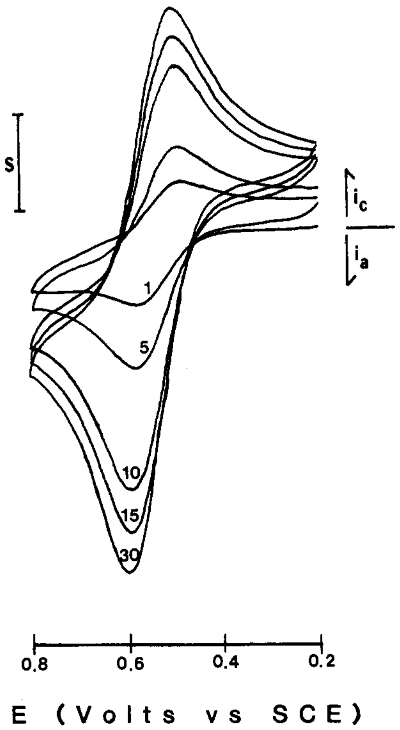


Figure 3. Variation of the voltammetric response with time for a Pt/Nafion (1 μm thickness) electrode, initially in the Na^+ form, after immersion in a 1.0 mM TP–0.2 M Na_2SO_4 (pH 7) solution. $S = 5\ \mu A$. Scan rate = 20 mV/s. The numbers on the figure represent how many scan repetitions had been performed at each time.

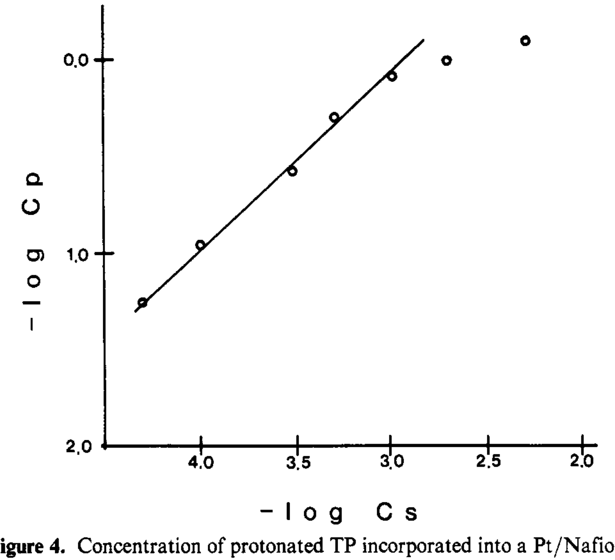


Figure 4. Concentration of protonated TP incorporated into a Pt/Nafion electrode, C_p, as a function of solution concentration, C_s. Data for different 1-μm films.

found for Cp_2FeTMA^+ and similar to those of $Os(bpy)_3^{2+}$ and $Ru(bpy)_3^{2+}$. However, the intrinsic bias in the method implies that the actual K for protonated TP is smaller, although of the same order of magnitude, than those of the above-mentioned cations. This suggests that the high rate of loss of protonated TP from the film cannot be explained by a substantially smaller thermodynamic affinity of this cation for the polyelectrolyte matrix. One possible explanation of the kinetic lability of the electrostatic binding of this cation to the sulfonate sites relates to the protonation equilibrium of the amine group, according to

$$|\text{-}SO_3^-\ TPH^{+\cdot} \rightleftharpoons |\text{-}SO_3^-\ H^+ + TP^\cdot \qquad (2)$$

where $|\text{-}\ SO_3^-$ represents Nafion. The release of tempamine from the polymer matrix, driven by a concentration gradient, could perhaps be notably accelerated by this process in which the replacement cation is already in place in the Nafion film. Another factor, of unknown magnitude, is the rate of interfacial ion transfer at the polymer–solution interface. This rate has been shown to be important for several cases of polymer-modified electrodes,[5i] although not with Nafion films.

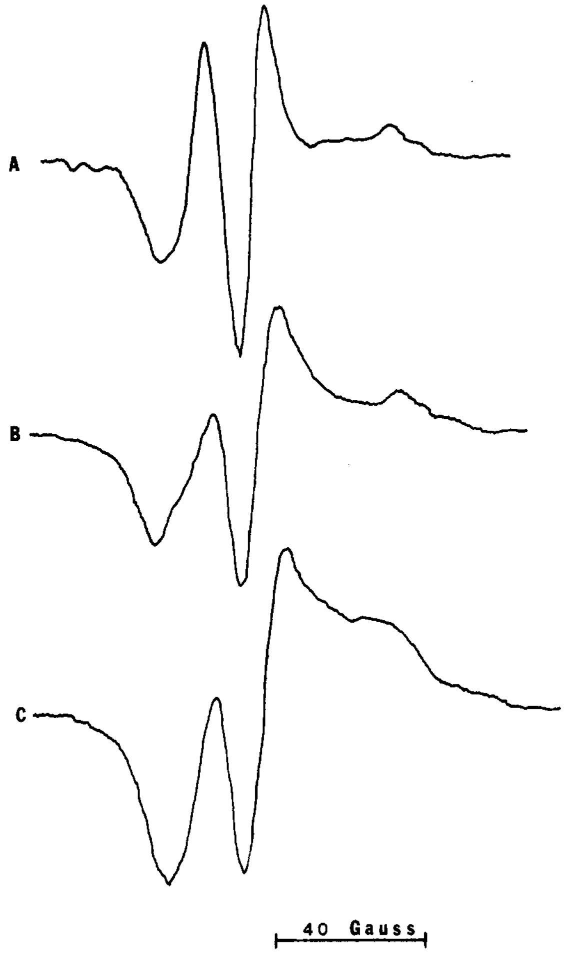


Figure 5. ESR spectra of Nafion films cast onto a Pt flag electrode which had been previously equilibrated with solutions at pH 7 containing 0.2 M Na_2SO_4 and (a) 0.1 mM TP, (b) 0.3 mM TP, and (c) 1.0 mM TP. The films were solvent saturated.

ESR of Tempamine Incorporated into Nafion. The ESR spectra of Nafion films previously equilibrated with solutions containing different concentrations of TP and 0.2 M Na_2SO_4 (pH 7), removed from these solutions, rinsed with distilled water, and placed in a nitrogen-filled, ESR quartz flat cell (1 mm internal thickness) are shown in Figure 5. The films were thus saturated with solvent. In agreement with the electrochemical results, these spectra demonstrate the ability of protonated TP to exchange and incorporate into Nafion matrices. The spectra in Figure 5 differ substantially from the spectrum of tempamine in bulk aqueous solution; at 293 K this spectrum consists of three sharp lines ($A_N = 17$ G) due to the coupling of the unpaired electron with the nuclear spin of the nitrogen atom ($S = 1$).[12] However, the observed spectral features indicate that the motion of the charged probe within the Nafion structure is characterized by a rotational correlation time (T_R) in the slow tumbling region. The spectra in Figure 5 also show some broadening that becomes increasingly evident as the TP solution is made more concentrated. This phenomenon can be explained by dipole–dipole interactions between the spin-label molecules. As the concentration of TP increases inside the film, the average distance between any two tempamine molecules must be shorter, thus enhancing the role of dipole–dipole interactions. We conclude from the electrochemical experiments (see Figure 4) that almost 100% the total exchange capacity of Nafion is used when a film is allowed to equilibrate with a 1.0 mM solution of TP. This is consistent with the noticeably broadened spectrum in Figure 5c. Nonetheless, spectrum 5a shows negligible broadening effects, as expected for

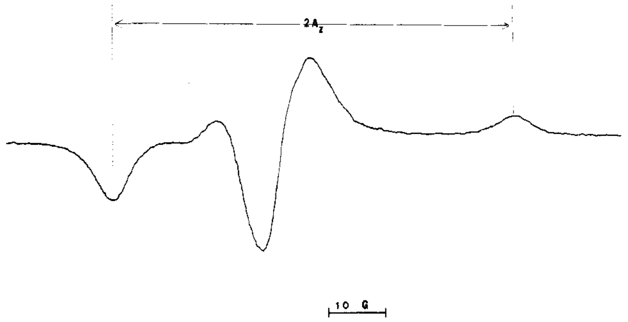


Figure 6. Rigid limit ESR spectrum of a Nafion membrane which had been previously equilibrated with solution A (see description in Figure 5), rinsed, and vacuum dried overnight.

a Nafion matrix in which only about 10% of the exchanging sites are occupied by protonated TP. Nafion membranes, treated exactly like the films coated on Pt flag electrodes, yielded identical ESR spectra. To obtain the rigid limit spectrum a Nafion membrane was loaded in a 0.1 mM TP solution for about 1 h, rinsed, vacuum dried overnight at 80 °C, and placed inside the nitrogen-filled ESR cell. The resulting ESR spectrum is shown in Figure 6.

Freed[12] has shown that the isotropic rotational correlation time for a nitroxide spin probe in the slow motion region (10^{-9} to 10^{-6} s) can be estimated by measurement of the parameter $S = A_{z'}/A_z$ where A_z is one-half the separation of the outer spectral extreme in the rigid limit (see Figure 6) and $A_{z'}$ is that value in the slow tumbling spectrum. Equation 3 relates T_R and S, where a and

$$T_R = a(1 - S)^b \qquad (3)$$

b are parameters related to the motional model chosen and the magnetic characteristics of the probe. From the line width of the rigid limit spectrum and the data from Table II in ref 12, a value of $(1.2 \pm 0.2) \times 10^{-8}$ s was determined (Brownian diffusion) for the correlation time of TP inside Nafion at 298 K.

Similar ESR spectra have recently been found[15] for tempamine probes exchanged into films cast with sodium montmorillonite and poly(vinyl alcohol) (PVA). As is the case with these clay/PVA films, the ESR spectra in Figures 5 and 6 were independent of the Nafion film orientation in the magnetic field. This fact is indicative of probes motionally restricted and ordered on a microscopic scale, but the absence of anisotropy with respect to the magnetic field implies a chaotic collection of microoriented regions. Similar ESR spectra have also been reported recently by Eastman and Gonzalez[16] for protonated TP incorporated into LZ-Y62 zeolite powders.

The restricted motional behavior observed with protonated TP in Nafion films contrasts sharply with that previously reported by this group for the cation radical of methylviologen[10] and Ti(III) ions.[11] In both previous cases, the incorporation of these paramagnetic ions into Nafion did not alter their ESR spectral features, which closely corresponded to those found in solution. Clearly, the tumbling rate of both of these ions was not substantially affected by the polyelectrolyte matrix. Conversely, the rotational correlation time of protonated TP increases by several orders of magnitude when transferred from dilute aqueous solution to a Nafion film and its ESR spectrum changes from the motionally narrowed region (fast tumbling) to the slow motion region. Some unknown specific interactions between Nafion and this nitroxide probe are perhaps responsible for this striking difference. Note that although TP shows motional restrictions within Nafion, it undergoes rapid cation exchange and is readily removed from the Nafion film. Methylviologen shows the opposite behavior: rapid tumbling but strong binding to the Nafion. TP and MV^{2+} have similar D_{app} values. These results suggest that the factors that determine motion in the local environment within the film are different from those that determine longer distance translational motion. However, in an attempt to obtain a better understanding of the factors involved, we performed a series of experiments with several readily available paramagnetic cations. The results are described in the following sections.

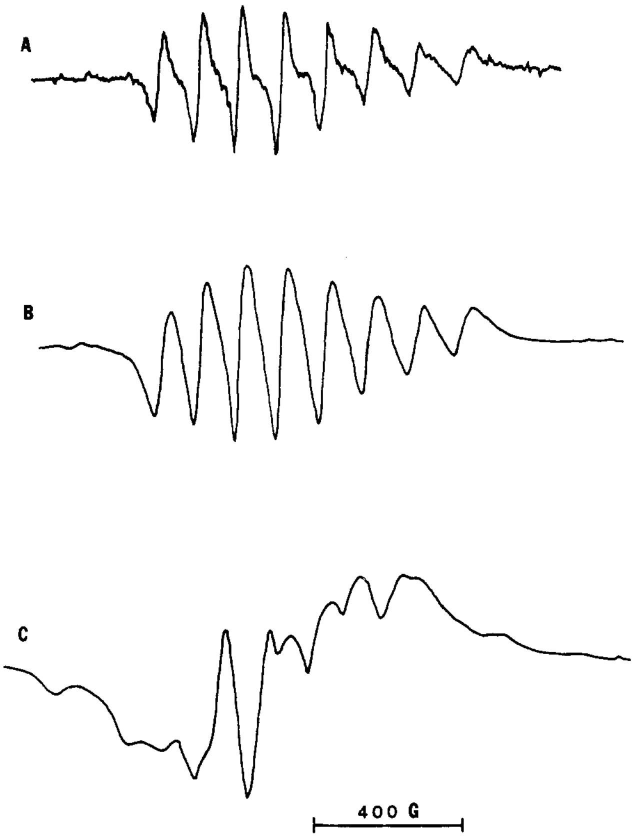


Figure 7. ESR spectra of Nafion membranes which had been previously equilibrated with (a) 1 mM $VOSO_4$–0.2 M Na_2SO_4 (pH 3), (b) 1 mM $VOSO_4$ (pH 3) and, (c) same as in A and then dried under vacuum overnight.

ESR of Vanadyl Ions Incorporated into Nafion. Vanadyl is also a very useful and widely utilized spin probe into the molecular motion of cations in diverse chemical environments. VO^{2+} can be exchanged into Nafion membranes from solutions containing about 1.0 mM VO^{2+} and 0.2 M Na_2SO_4, at pH 3 (see Figure 7A). The amount of incorporated VO^{2+} can be increased by using solutions containing only $VOSO_4$ at similar pH's (see Figure 7B). In both cases, the ESR spectrum consists of eight lines due to the coupling of the $^1/_2$ electronic spin with the nuclear spin of the ^{51}V nucleus ($S = ^7/_2$). The line width results from the modulation of the anisotropic g and A tensors by molecular motions.[17] Even though the observed line widths are much broader than in dilute aqueous solution, these spectra clearly correspond to the fast tumbling region. From comparison with other published vanadyl spectra,[18] its rotational correlation time inside Nafion can be estimated to be about 2×10^{-10} s. However, since the VO^{2+} concentration confined in the polyelectrolyte is probably large, some broadening might arise from dipole–dipole interactions and, hence, this value should be interpreted as an upper limit. When the film of Figure 7A was vacuum dried overnight at 80 °C, an spectrum very close to the rigid limit was obtained (Figure 7C).

ESR of Manganese(II) Ions Incorporated into Nafion. The Mn^{2+} ESR spectrum in dilute aqueous solution consists of six resolved lines owing to the coupling of the electronic spin with the $^5/_2$ nuclear spin of ^{55}Mn. The fine structure due to the $^5/_2$ electronic spin is unresolved and contributes only to the line width.[19] Mn^{2+} ions can also be easily incorporated into Nafion

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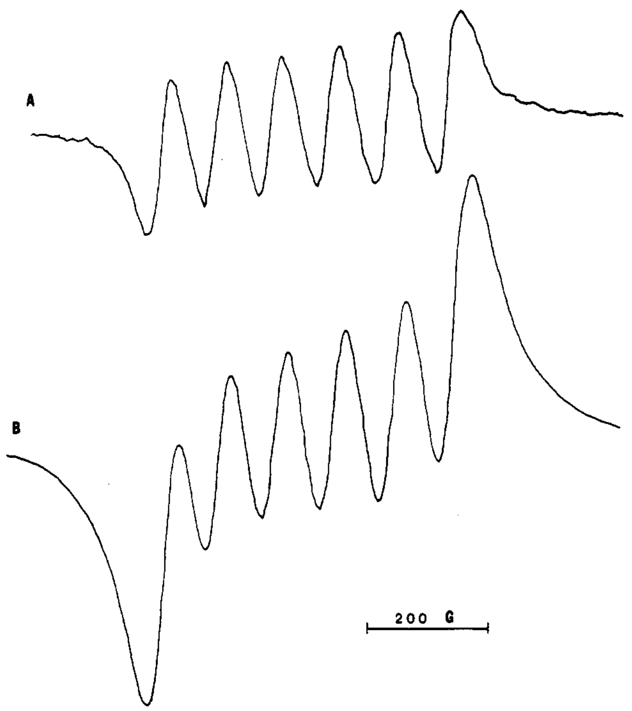

Figure 8. ESR spectra of Nafion membranes after exchange with (a) 1 mM $MnSO_4$–0.2 M Na_2SO_4 (pH 6) and (b) 1 mM $MnSO_4$ (pH 6).

membranes by ion exchange in solutions containing about 1.0 mM $MnSO_4$ and 0.2 M Na_2SO_4 (pH 6). The resulting ESR spectrum appears in Figure 8A. As with vanadyl, the observed spectrum pertains to the fast tumbling region, showing the expected six-line pattern. Broadening of the lines was also detected but no estimates of T_R were attempted, since the line widths of Mn^{2+} are mainly dependent on the frequency of collisions with the solvent which modulates the zero-field splitting tensor.[20]

When the concentration of Mn^{2+} confined into the polyelectrolyte matrix is increased, the ESR spectral features change, although the six-line pattern is still resolved (Figure 8B). This spectrum is similar to that recently reported by Chevalier and Chachaty[21] corresponding to Mn^{2+} ions bound to octyl phosphate micelles. We did not investigate further this phenomenon which, although interesting, is beyond the scope of this work. After drying, the Mn^{2+} containing Nafion membranes showed a featureless and broad, single-line spectrum.

ESR of $TMPD^{+\cdot}$ Incorporated into Nafion. Exhaustive electrochemical oxidation of a 1.0 mM TMPD solution in 0.2 M Na_2SO_4 (pH 3) yields an intense blue solution whose ESR spectrum is very rich in hyperfine structure and corresponds to that reported in the literature for $TMPD^{+\cdot}$.[22] If a Nafion membrane is immersed into this solution for about 30 min, it turns intensely blue, indicating the incorporation of $TMPD^{+\cdot}$. The ESR spectrum obtained for this membrane is shown in Figure 9A. This spectrum is not completely resolved and shows only hints of the complex hyperfine structure found in the solution spectrum. Figure 9B shows that, when this membrane was vacuum dried overnight, most of the residual hyperfine structure disappears in the resulting broad spectrum. Similar spectra were obtained with a Nafion film cast onto a Pt flag electrode when this was used to oxidize the TMPD in solution. The Nafion-confined cation radical of TMPD exhibits then a behavior intermediate between that of fast tumbling cations (vanadyl, manganese(II), titanium(III), and the cation radical of methylviologen) and that of tempamine which, so far, is the only example of a slow tumbling cation upon exchange into Nafion.

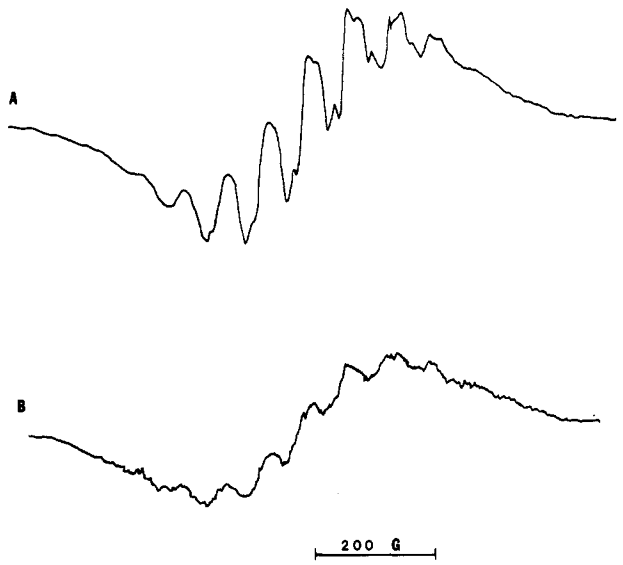

Figure 9. (a) ESR spectrum of a solvent-saturated Nafion membrane after exchange with a 1 mM $TMPD^{+\cdot}$–0.2 M Na_2SO_4 (pH 3). (b) ESR spectrum of the same membrane after overnight vacuum drying.

Comparison of the ESR Results Obtained with Different Spin Probes. The ESR experiments presented in this work along with others previously reported by our group allow some generalizations to be made about the motional behavior and chemical environments of Nafion-confined paramagnetic cations. In the first place, simple inorganic cations retain most of their solution mobility as revealed by the fast tumbling ESR spectra obtained for Nafion-confined VO^{2+} and Mn^{2+}. The same behavior was also observed for Ti^{3+} in a previous report.[11] This suggests that inorganic cations reside in aqueous-like environments within the Nafion matrix.

The behavior of organic paramagnetic cations is more complex. Protonated TP and the cation radical of methylviologen ($MV^{+\cdot}$) exhibit completely opposite behavior. The former seems to be strongly anchored by the polyelectrolyte, whereas the latter tumbles as freely in Nafion as it does in solution.[10] The behavior of $TMPD^{+\cdot}$ can be described as intermediate since its Nafion-confined spectrum shows some hyperfine details but is clearly less resolved than its solution spectrum. All these organic cations are monovalent; however, while protonated TP has a localized charge (on the amine nitrogen), $MV^{+\cdot}$ has its charge delocalized throughout the molecular structure. $TMPD^{+\cdot}$ is also a delocalized cation but its charge is distributed through only one aromatic ring (as opposed to $MV^{+\cdot}$ where the charge is delocalized through two aromatic rings). Thus the type of charge delocalization is apparently important in the extent of anchoring to the polyelectrolyte sulfonate sites and the types of regions in which organic cations are likely to reside within the Nafion films. However, more work is still needed to define further the factors that govern the location and motion of cations within Nafion.

Conclusions

The use of nitroxide spin probes to characterize polyelectrolyte modified electrodes has been exemplified with protonated tempamine incorporated into Nafion. These compounds exhibit a nearly reversible oxidative electrochemistry, as well as ESR activity, which renders them very attractive for further investigations in this field. ESR experiments with additional spin probes have shown that the motional behavior and chemical environment of a given cation within Nafion depend on the nature of the cation itself.

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Registry No. VO^{2+}, 20644-97-7; Mn, 7439-96-5; $TMPD^+$, 34527-55-4; Pt, 7440-06-4; Nafion, 39464-59-0.

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