

the ratio of the intercept to slope (i/s) in Figure 8 is given by eq 18, where $\alpha = (1 + k_H/k_{30})^{-1} \approx 1$, since $k_H/k_{30} \ll 1$. Then, by

$$\frac{i}{s} = \frac{k_{12}\tau}{1 + (k_{21}/k_{30})((k_{30}/k_{23}) + (k_{32}/k_{23})\alpha)} \quad (18)$$

comparing eq 5 with eq 18, the quenching constant $K_q (=k_q\tau)$ is obtained as 11 from the i/s value in Figure 8. This value agrees well with the K_q value of the fluorescence quenching of 1-Mg²⁺ ion complex by *p*-methylbenzyl alcohol described in the previous section ($K_q = 10$). Such an agreement strongly supports the reaction mechanism (eq 10-14) where the photocatalytic oxidation

of *p*-methylbenzyl alcohol proceeds mainly via the singlet-excited state of a flavin analogue-Mg²⁺ ion complex as the reactive catalyst.

Registry No. 1, 35804-39-8; 2a, 69083-37-0; 2b, 76902-97-1; 2c, 91028-36-3; Mg(ClO₄)₂, 10034-81-8; Zn(ClO₄)₂, 13637-61-1; MeC₆H₅, 108-88-3; *p*-ClMeC₆H₄, 106-43-4; *p*-BrMeC₆H₄, 106-38-7; *m*-(Me)₂C₆H₄, 108-38-3; *o*-(Me)₂C₆H₄, 95-47-6; *p*-(Me)₂C₆H₄, 106-42-3; 1,3,5-(Me)₃C₆H₃, 108-67-8; MeOC₆H₅, 100-66-3; 1,2,3,4-(Me)₄C₆H₂, 488-23-3; (Me)₃C₆H₃, 700-12-9; *m*-Me(MeO)C₆H₄, 100-84-5; *p*-Me(MeO)C₆H₄, 104-93-8; *m*-(MeO)₂C₆H₄, 151-10-0; *p*-(MeO)₂C₆H₄, 150-78-7; *p*-methylbenzyl alcohol, 589-18-4; *p*-methylbenzaldehyde, 104-87-0; hydrogen peroxide, 7722-84-1.

Polymer Films on Electrodes. 17. The Application of Simultaneous Electrochemical and Electron Spin Resonance Techniques for the Study of Two Viologen-Based Chemically Modified Electrodes

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Abstract: Simultaneous electrochemical and electron spin resonance (SEESR) techniques were used to study the environment and rates of electron transfer in two viologen-based chemically modified electrodes. Electrodes derivatized with *N,N'*-bis-[3-(trimethoxysilyl)propyl]-4,4'-bipyridinium, where the redox sites are covalently anchored to the polymer backbone, exhibit broad and featureless spectra upon reduction, suggesting that the spin sites are restrained and immobile. The ESR signal intensity as a function of the extent of film reduction indicates that the rate on electron transfer (self-exchange) is high, $>10^6$ M⁻¹ s⁻¹. Electrodes covered with the perfluorosulfonate polymer Nafion in which MV²⁺ (MV²⁺ = methyl viologen) has been incorporated display ESR spectra upon reduction that are similar to those of MV^{•+} in solution, suggesting that the radicals are free to tumble on the ESR time scale. The rates of electron exchange are smaller in the Nafion modified electrodes ($\leq 8 \times 10^5$ M⁻¹ s⁻¹); this is consistent with physical diffusion of the redox species contributing substantially, if not completely, to charge transport in these films.

This paper concerns the application of electron spin resonance (ESR) spectroscopic techniques to polymer electrodes and a comparison of the behavior of a cation radical (viologen) in two different types of polymer films on an electrode surface: one, where the radical ion is attached to the polymer backbone, and the other, a polyelectrolyte, to which the species is held by electrostatic binding.

Chemically modified electrodes have been characterized by a variety of techniques. Electrochemical methods such as cyclic voltammetry, chronoamperometry, chronopotentiometry, and rotating disk voltammetry have been used to determine the redox, charge transport, and catalytic properties of these electrodes.¹ Spectroscopic techniques, e.g., X-ray photoelectron, Auger, UV-vis, photoacoustic, photothermal, and reflectance spectroscopy, have also provided information about the morphology of the modifying layer.¹ Electron spin resonance spectroscopy has recently been introduced in conjunction with electrochemical techniques to characterize polymer modified electrodes, e.g., in the study tetracyanoquinodimethane (TCNQ)-modified Pt electrodes.² Alberly et al. have developed an electrochemical cell for ESR studies based on convective diffusion and used it to study polymer films of poly(nitrostyrene) and poly(vinylanthraquinone).³

In both previous studies the electrogenerated radical ions were attached to the polymer backbone and the ESR signal was a single line. ESR measurements are particularly attractive for the study of modified electrodes because information concerning the environment and mobility of surface-confined redox couples, as well as some insight into the mechanism of charge transport, can be obtained.

Viologens have been extensively studied in recent years in their role as electron acceptors in photochemical^{4,5} and photoelectrochemical^{6,7} schemes. The reversibility of the 2+/1+ couple and the large visible spectral changes that accompany the oxidation/reduction process have made the viologens especially useful in modified electrode studies as well.⁸⁻¹⁰ Cyclic voltammetric

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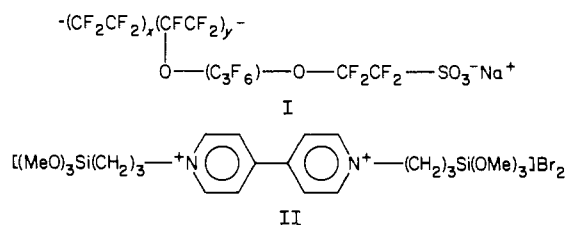
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data for MV^{2+} (MV^{2+} = methyl viologen) incorporated into films of the ion-exchange polymer Nafion (I) cast on carbon electrodes have been reported.⁹ More recently, Bookbinder and Wrighton have described the electrochemical and optical properties of electrodes derivatized by direct anchoring of a viologen to a silicon-oxygen backbone by polymerization of II.^{10b} The existence of two different modification techniques for the same probe molecule allowed us to compare and contrast the environments with these two polymers.



Experimental Section

Chemicals. $\{N,N'$ -Bis[3-(trimethoxysilyl)propyl]-4,4'-bipyridinium} dibromide (II) was synthesized and purified as described by Bookbinder and Wrighton.^{10b} N,N' -Dimethyl-4,4'-bipyridinium dichloride (MV^{2+}) was purchased from Aldrich Chemical Co. and used as received.

Electrode Modification. Electrodes derivatized with II, designated $[(MV^{2+})]_{\text{surf}}$, were prepared by scanning the potential between 0.00 and -0.78 V vs. SCE in an aqueous 0.2 M KCl/0.1 M K_2HPO_4 (pH 8.9) solution containing ~ 3 mM II until the desired coverage was obtained.^{10b} They were then cycled in a 1.0 M KCl solution to check their redox response and to guarantee the exchange of HPO_4^{2-} ions before being placed in the ESR cell. Nafion-modified electrodes, designated $[(MV^{2+})]_{\text{Nafion}}$, were prepared by covering the electrode surface (0.18 cm^2) with 2.5 μL of a 5% ethanolic solution of 1100 equivalent weight Nafion (obtained from C. G. Processing Inc., Rockland, DE) and allowing the solvent to evaporate. After the electrodes were dried at room temperature for 3 h, MV^{2+} was incorporated by soaking the electrode in a 1 mM solution of $MVCl_2$ for 1 h.

Apparatus. ESR measurements (X-band) were made with a Varian E-9 spectrometer (100-kHz field modulation) equipped with a TE₁₀₂ dual-sample cavity. 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). Simultaneous electrochemical and ESR data were recorded on a Soltec Model VP-6432S 2-pen X-YY' recorder (Soltec Corp., Sun Valley, CA). Dry film thicknesses were measured with a Sloan Dektak surface-profile measuring system. Visible absorption measurements were obtained with transparent SnO_2 (PPG Glass) electrodes and a PAR Model 1215-1216 optical multichannel analyzer (Princeton Applied Research Corp., Princeton, NJ) in conjunction with a holographic grating (150 lines/mm) and an attenuated 150-W xenon lamp.

Procedures. Simultaneous electrochemical ESR (SEESR) experiments were performed with a specially designed 1 mm thick flat ESR cell suitable for both electrochemical and ESR studies.¹¹ To exclude the formation of oxygen and to ensure the large uniform current densities needed in these experiments, Ag/AgCl electrodes, placed along the edge of the flat cell, were used as both the counter and reference electrodes. All potentials were referenced to the SCE potential. The working electrode was a ca. 0.3 cm \times 0.6 cm Pt flag. Solutions prepared from triply distilled water were thoroughly purged with prepurified nitrogen before being transferred to the cell. The cell, adapted for Schlenk-line use, was assembled under an atmosphere of nitrogen to ensure the absence of oxygen.

Results

ESR of MV^+ in Solution. The ESR spectrum of an aqueous solution containing 1 mM MV^+ , prepared by exhaustive elec-

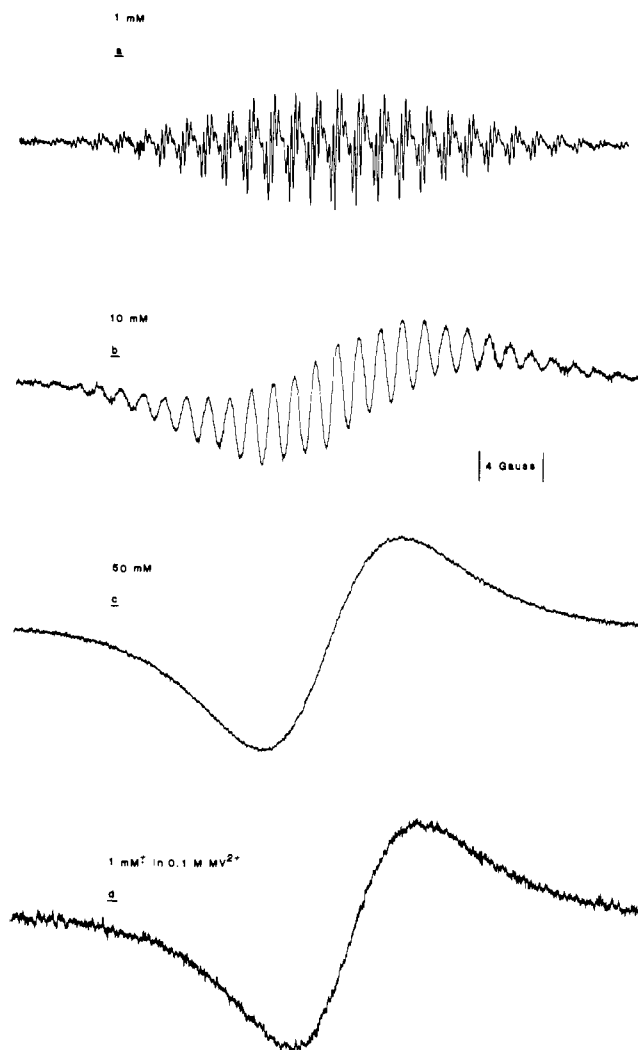


Figure 1. ESR spectra of reduced aqueous MV^{2+} solutions. Concentrations correspond to $(MV^{2+})_2 + MV^+$: (a) 1 mM; (b) 10 mM; (c) 50 mM; (d) 1 mM reduced MV^+ in the presence of 0.1 M MV^{2+} . Modulation ≤ 0.02 G; microwave power ≤ 5 mW.

trochemical reduction of a 1 mM MV^{2+} solution, is shown in Figure 1a. The spectrum is similar to those reported previously.¹² The hyperfine structure is due mainly to coupling of the unpaired electron with two equivalent nitrogens and six equivalent methyl hydrogens. To compare the ESR behavior of the cation radicals in solution and in the films under similar conditions (note that the total viologen concentration in the films is >0.1 M), ESR spectra were recorded for high concentrations of the viologen radicals in solution as well. The spectra were strongly dependent on concentration. Thus, when 1 mM, 10 mM, and 50 mM MV^{2+} solutions were exhaustively reduced, a progressive loss of hyperfine structure and a gradual broadening of the spectrum were observed (Figure 1). In addition to changes in the ESR spectra, noticeable changes were also found in the absorption spectra: the absorption maximum shifted from 603 to 550 nm upon increasing the concentration of the reduced viologen. This spectral change has been attributed to dimer formation $(MV^+)_2$.^{12c} Apart from the dependence of the MV^+ concentration, the ESR spectrum was also dependent on the concentration of MV^{2+} in solution. Thus, the ESR spectrum for 1 mM MV^+ prepared from 1 mM MV^{2+} (Figure 1a) differed substantially from the spectrum of 1 mM MV^+ in the presence of 0.1 M MV^{2+} (Figure 1d), where the spectrum displayed no hyperfine structure. The visible absorption

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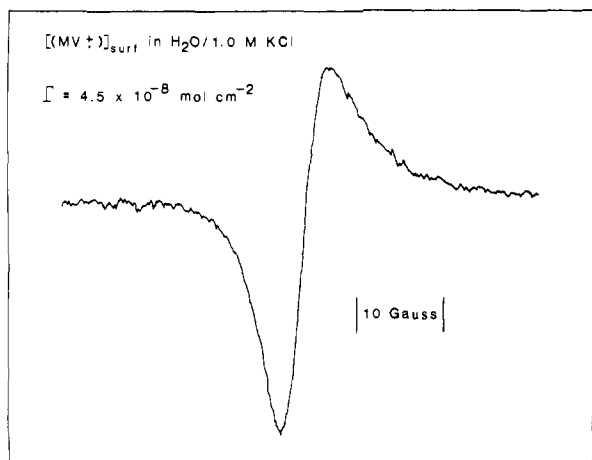


Figure 2. ESR spectrum of fully reduced $4.5 \times 10^{-8} \text{ mol cm}^{-2}$ $[(\text{MV}^{2+})]_{\text{surf}}$ film.

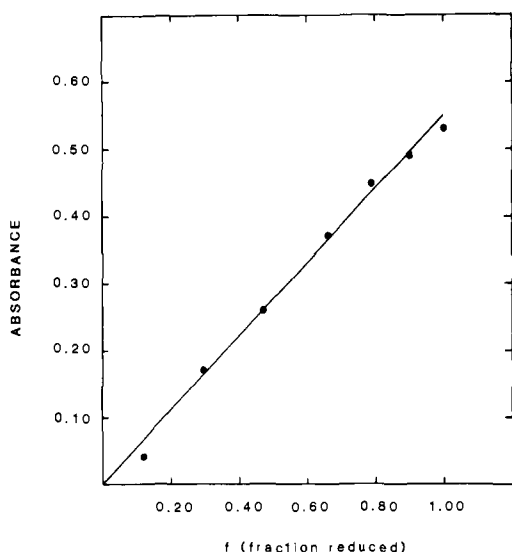


Figure 3. Absorbance at 550 nm vs. f (fraction of film reduced) for $[(\text{MV}^{2+})]_{\text{surf}}$ film.

spectra, however, were similar for the two solutions.

$[(\text{MV}^{2+})]_{\text{surf}}$ Films. In Figure 2 is shown the ESR spectrum of a $0.15\text{-}\mu\text{m}$ film with a surface coverage, Γ^* , of $4.5 \times 10^{-8} \text{ mol cm}^{-2}$ following complete (one-electron) reduction at -0.72 V . The spectrum is broad and featureless (with noticeable asymmetry). The spectral profile was independent of the film thickness and also relatively independent of the fraction of the reduced MV^{2+} in the film. In the latter case, however, a decrease in the peak-to-peak separation was observed as more of the polymer was reduced. The reduced film has an absorbance maximum at 550 nm, indicative of predominantly dimeric species in the film matrix.^{10b} The absorbance at 550 nm was directly proportional to the amount of charge injected into the film (Figure 3), when the fraction of film reduced is greater than 0.1 (see Appendix). The cyclic voltammogram (CV) of the film and the simultaneous ESR response observed are shown in Figure 4. The CV is identical with that observed by Bookbinder and Wrighton^{10b} ($E_{1/2} = -0.55 \text{ V}$), and at a sweep rate of 2 mV s^{-1} the voltammogram approaches behavior characteristic of a surface-confined redox couple.¹ The electrochemical behavior demonstrates, in agreement with the results in ref 10b, that essentially complete reduction of all of the MV^{2+} centers occurs. The relative intensity of the ESR signal is roughly consistent with that number of unpaired spins. The difference in the anodic and cathodic peak potentials (ΔE_p) was 15 mV, and the width at half-height, $\Delta E_{p/2}$, was 105 mV. The position of the peak and the magnitude of $\Delta E_{p/2}$ for a viologen system undergoing Nernstian electron transfer should depend upon the equilibrium constant for dimerization of $\text{MV}^{\cdot+}$, the concen-

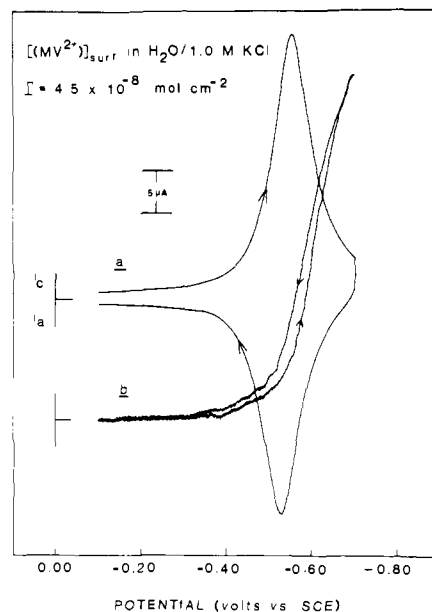


Figure 4. SEESR plot of a $4.5 \times 10^{-8} \text{ mol cm}^{-2}$ $[(\text{MV}^{2+})]_{\text{surf}}$ film: (a) cyclic voltammogram at 2 mV s^{-1} ; (b) corresponding ESR signal intensity.

tration, and interaction parameters of the various species. In this and previous studies of surface-confined viologens^{9,10} finite electron-transfer rates and perhaps small resistive effects cause larger ΔE_p and $\Delta E_{p/2}$ values than expected for a strictly Nernstian system. For example, $\Delta E_{p/2}$ should range from 90.6 mV in the absence of dimerization to 66 mV when dimerization is essentially complete.^{13a}

The interpretation of the SEESR results requires a consideration of dimer formation and electron-transfer effects. If the reaction were an uncomplicated one-electron Nernstian process,^{13b} $\text{O} + ne^- \rightleftharpoons \text{R}$ ($\text{MV}^{2+} + e^- \rightleftharpoons \text{MV}^{\cdot+}$), the following equations would hold:

$$\Gamma_o(t) = \Gamma_o^* \left\{ 1 - \left[1 + \exp \frac{nF}{RT} (E - E^0) \right]^{-1} \right\} \quad (1)$$

and

$$f = \frac{\Gamma_r(t)}{\Gamma_o^*} = \left[1 + \exp \frac{nF}{RT} (E - E^0) \right]^{-1} \quad (2)$$

where $\Gamma_r(t)$ and $\Gamma_o(t)$ are the surface coverage of the reduced and oxidized forms at any time t , respectively, $\Gamma_o^* = \Gamma_o(t) + \Gamma_r(t)$, and f is the fraction of the film that is reduced. The fraction of film reduction would then be directly proportional to the charged passed (Q), i.e.

$$Q = nFA \Gamma_r(t) = nFAf\Gamma_o^* \quad (3a)$$

$$Q = nFA\Gamma_o^* \left[1 + \exp \frac{nF}{RT} (E - E^0) \right]^{-1} \quad (3b)$$

For uncomplicated generation of a radical ion, the relative ESR signal intensity S , where $S = 1$ for a fully reduced film, should be proportional to f (eq 3). However, a plot of S vs. f (Figure 5) is clearly nonlinear. For example, when the film is 50% reduced, the ESR signal height is only 27% of that observed when the film is fully reduced. These values are shown as points in Figure 5.

$[(\text{MV}^{2+})]_{\text{Nafion}}$ Films. The ESR spectrum of a completely reduced $[(\text{MV}^{2+})]_{\text{Nafion}}$ film ($d = 4.2 \mu\text{m}$; $\Gamma_o^* = 3.1 \times 10^{-7} \text{ mol cm}^{-2}$) is shown in Figure 6. In contrast to the spectrum observed for reduced $[(\text{MV}^{2+})]_{\text{surf}}$ the spectrum for the Nafion films exhibits a well-defined hyperfine pattern which is remarkably similar to

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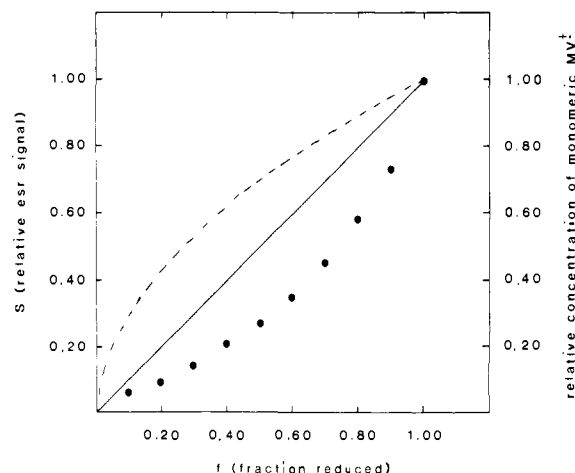


Figure 5. S (relative ESR signal intensity) vs. f (fraction of film reduced) for a $[(MV^{2+})_{\text{surf}}]$ film: (●) experimental results. Also shown is the curve corresponding to the relative concentration of monomeric species (MV^+) as a function of f (---), based on eq A.5 with $K = 380 \text{ M}^{-1}$. The solid line (—) corresponds to the plot that would be obtained if S were directly proportional to f .

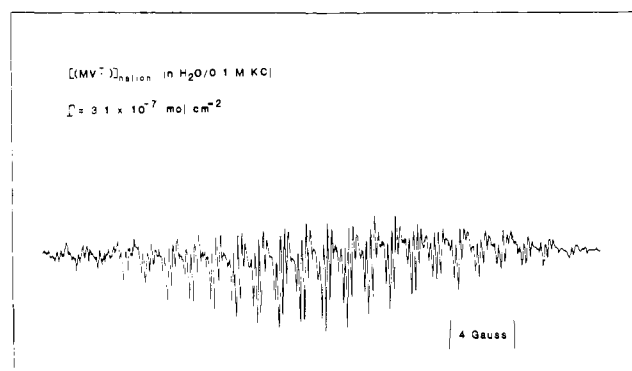


Figure 6. ESR spectrum of fully reduced $3.1 \times 10^{-7} \text{ mol cm}^{-2}$ $[(MV^{2+})_{\text{Nafion}}]$ film.

that of 1 mM MV^+ in solution (Figure 1a). Notice, however, that the bulk concentration of reduced viologen is substantially different in the two cases: 0.74 M in the film compared to 1 mM in solution. For solution concentrations of reduced viologen ≥ 50 mM no hyperfine structure is observed. The spectra of the Nafion films retain their hyperfine structure and narrow line widths, ca. 0.1 G, regardless of the fraction of MV^{2+} which is reduced. This result, therefore, is also very different from that seen for solution systems, where the presence of substantial amounts of MV^{2+} markedly affected the ESR spectral features of MV^+ . That the reduced viologen in the Nafion films exists predominantly in the form of dimers is indicated by the absorption maximum at 550 nm. Moreover, the absorbance at 550 nm is directly proportional to f . These results are, therefore, comparable to those observed for the reduced $[(MV^{2+})_{\text{surf}}]$ films. Shown in Figure 7 is the current and ESR signal observed for a Nafion film when the potential is cycled between -0.15 and -0.80 V at 1 mV s^{-1} . The cyclic voltammogram ($E_{1/2} = -0.66$ V) exhibits diffusional behavior, $\Delta E_p = 60$ mV, and is similar to those observed previously.⁹ One striking difference between the two films is the 150-mV positive shift in the $E_{1/2}$ value with respect to the solution species for $[(MV^{2+})_{\text{surf}}]$ and the lack of any such shift for $[(MV^{2+})_{\text{Nafion}}]$. The shift for $[(MV^{2+})_{\text{surf}}]$ has been attributed to dimer formation.^{10b} The observed shift is a function of the total concentration of reduced species and the equilibrium constant for the dimerizations (reported to be ca. 380 M^{-1} ^{12c} for aqueous solutions based on unpublished electrochemical studies by W. M. Schwarz). This same value is consistent with the shifts reported for $[(MV^{2+})_{\text{surf}}]$ and, in the absence of any other values, we assume this value applies to the polymer films under investigation here. The shape of the ESR profile, as expected, is governed by diffusion,¹¹ with

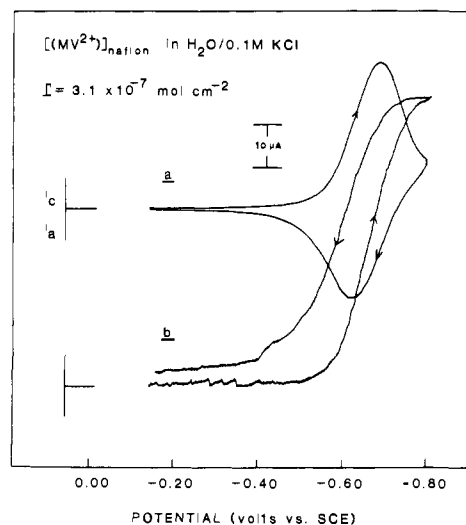


Figure 7. SEESR plot of a $3.1 \times 10^{-7} \text{ mol cm}^{-2}$ $[(MV^{2+})_{\text{Nafion}}]$ film: (a) cyclic voltammogram at 1 mV s^{-1} ; (b) corresponding ESR signal intensity.

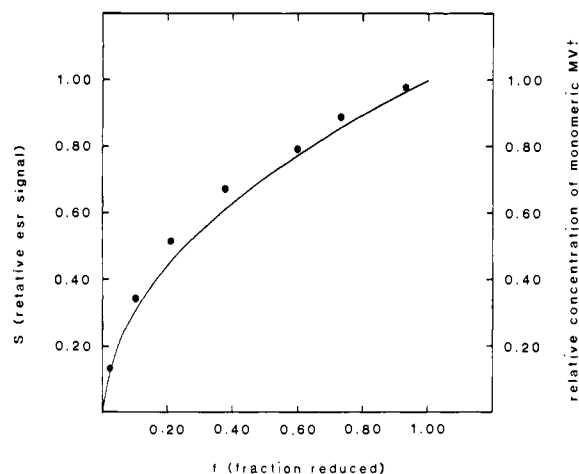


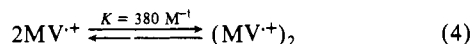
Figure 8. S (relative ESR signal intensity) vs. f (fraction of film reduced) for a $[(MV^{2+})_{\text{Nafion}}]$ film: (●) experimental results; (—) relative concentration of monomeric species (MV^+) from eq A.5 with $K = 380 \text{ M}^{-1}$.

the response showing a large amount of hysteresis. After the film has been reduced, the ESR signal does not decay to zero on the reverse scan, presumably because of diffusion of some radicals away from the electrode surface into the bulk polymer. However, if the potential is held at -0.15 V for 5 min, complete reoxidation of the film occurs and the signal returns to zero. To obtain S as a function of f , the potential was stepped from -0.15 V to specific values along the wave. The potential was then held constant for ca. 30 min to allow any concentration gradients within the film to disappear and S to reach a constant value. The fraction of the film reduced was determined by measuring the number of coulombs required to completely reoxidize the film and comparing this value to that for an initially fully reduced film. These results are shown in Figure 8. As in the case of the $[(MV^{2+})_{\text{surf}}]$ films, f is not directly proportional to S . However, the trend in S vs. f is opposite to that found for $[(MV^{2+})_{\text{surf}}]$; for example, when the Nafion film is 60% reduced the ESR signal is 79% of that observed for the fully reduced film (as compared to a value of 35% for a 60% reduced $[(MV^{2+})_{\text{surf}}]$ film).

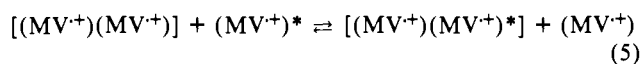
Discussion

A comparison of Figures 2 and 6 indicates that the ESR characteristics of reduced viologen are different in the two films. To interpret these spectra satisfactorily, we must first consider the ESR behavior of reduced viologen in solution. Previous studies^{12,14,15} have shown that the complex behavior of reduced

viologen in aqueous solution can be attributed to the existence of a monomer-dimer equilibrium, with the dimer formation strongly favored for high concentrations of the radical cation.



Apart from the differences in the absorption spectra, the monomer produces an ESR signal while the dimer is diamagnetic; see, for example, Evans et al.,¹⁴ who conducted ESR studies on monomer-dimer equilibria for a number of viologen systems, and Ivanov et al., who studied heptyl viologen films. We assume, therefore, that the ESR spectra in Figure 1a-c are due to the fraction of reduced viologen that exists as monomer in solution. The monomer concentrations corresponding to traces a-c are 0.66, 3.03, and 7.48 mM, respectively. The ESR profiles change drastically upon increasing the concentration of reduced viologen. While increased dipole broadening and spin exchange at high concentrations of MV^+ could account for the loss in spectral resolution and greatly increased line widths, other factors can also contribute to the observed changes. Because of the dynamic nature of the monomer-dimer equilibrium, broadening may also occur by processes analogous to the one shown in eq 5. Hence the dimer, although diamagnetic, may indirectly influence the ESR spectra of the monomeric MV^+ .



The ESR spectrum of MV^+ is also strongly perturbed by the addition of large concentrations (0.1–1.0 M) of MV^{2+} . The hyperfine structure observed in the absence of MV^{2+} (Figure 1a) is completely eliminated upon addition of 0.1 M MV^{2+} (Figure 1d). In addition an asymmetry is evident in the spectrum; the reason for this is unclear at present. The increased line width in the presence of MV^{2+} can be attributed to electron transfer between MV^{2+} and MV^+ ,¹² and the spectral changes are analogous to those observed by Weissman and Ward for the naphthalene-naphthalenide system.¹⁶ In the MV^+ case the electron transfer (exchange) rate constant is estimated to be $\geq 10^8 M^{-1} s^{-1}$, in good agreement with the results of Bock et al.¹⁷

Although the ESR behavior observed at high concentrations of reduced viologen and in the presence of added MV^{2+} in solution is complex, Nafion films exhibit remarkably well-defined ESR spectra (at equivalent high concentrations of MV^+ or MV^{2+}), rich in hyperfine structure, with narrow line widths, and closely resembling the spectrum obtained for 1 mM MV^+ in aqueous solution. Note also that the spectrum remains relatively unchanged regardless of what fraction of the film is reduced. The narrow line widths in the spectrum of Figure 6, ca. 0.1 G, clearly indicate that the ESR-active species is not rigidly held but rather freely tumbles in the film. The experimental results in Figure 8 can be explained by the existence of a monomer/dimer equilibrium in the film. The absence of line broadening in the partially reduced films suggests that the ESR signal intensity should be directly proportional to the concentration of ESR-active species in the film. This concentration is, however, not linearly related to the fraction of reduced viologen in the film, since as already discussed for the solution case, the reduced species equilibrate between monomeric and dimeric forms, and while the monomer is ESR active, the dimer is diamagnetic and consequently, ESR inactive. If we assume a similar situation in the Nafion films (with $K = 380 M^{-1}$), the relative concentrations of the monomeric cation radical as a function of f , the fraction of the reduced viologen that is ESR

active can be calculated from eq A.5 (see Appendix). A plot of these data is shown by the solid line in Figure 8, which closely tracks the experimental results. The results indicate that the monomer-dimer equilibria in the Nafion film and in solution are similar and that only the monomeric species in the film is ESR active.

However, how does one explain the existence of hyperfine structure for the MV^+ in the Nafion films? In solution all of the hyperfine structure is lost as a result of electron-transfer-induced line broadening when 0.1 M MV^{2+} is added to a 1 mM MV^+ solution (Figure 1d), while no line broadening is observed for the Nafion film under similar conditions, e.g., 4.8 mM MV^+ and 0.72 M MV^{2+} . Thus, the electron-transfer rate is apparently much slower in the film than in solution. This may be due to the segregation of the oxidized and reduced forms of viologen in different phases or zones within the Nafion film (note that a multiphase model has previously been proposed for Nafion¹⁸). One other interesting difference is that the ESR spectrum for a solution containing 50 mM reduced viologen ($[MV^+] = 7.48$ mM; $[MV^+]_2 = 21.3$ mM) is broad and featureless while a fully reduced film ($[MV^+] = 31$ mM; $[MV^+]_2 = 0.35$ M) exhibits a well-defined hyperfine pattern, even though the concentrations of both the monomer and dimer are substantially higher in the latter case. Clearly, the influence of dipolar broadening and the processes such as the one in eq 5 are less important in the film. In this case, however, a multiphase model cannot account for the differences from solution behavior, since both reduced species would probably be in the same phase. These apparent anomalies possibly stem from the sizable difference in the diffusion coefficients (D) of the ions in the two media. While D values are typically of the order of 10^{-5} to $10^{-6} cm^2 s^{-1}$ in water, the apparent diffusion coefficients (D_{app}) for MV^{2+} and MV^+ in Nafion, measured by potential step experiments, are $3 \times 10^{-9} cm^2 s^{-1}$. In general, the value of D_{app} includes contributions from actual physical diffusion as well as diffusion via electron transfer between adjacent redox sites (since both processes are possible in Nafion films^{18c,19}), and the relative contribution of each process is given by the Dahms-Ruff equation:²⁰

$$D_{app} = D_0 + \frac{\pi}{4} k_{ex} \delta^2 C \quad (6)$$

where k_{ex} is the second-order electron-transfer rate constant for the redox couple, C is the sum of the concentrations of the reduced and oxidized forms of the couple, δ is the distance between the centers of the reactants when electron transfer occurs, and D_0 is the diffusion coefficient that would be measured in the absence of self-exchange. Since no detectable line broadening was observed in the ESR experiments, the self-exchange rate in the Nafion films is slow on the ESR time scale. If we assume that a 20% increase in the line width would be detectable in our experiments, for an initial line width of 0.1 G, the upper limit of k_{ex} can be calculated from eq 7,

$$\Delta H = \frac{k_{ex}[N]}{1.54 \times 10^7} \quad (7)$$

where ΔH is the increase in line width in gauss and $[N]$ is the molar concentration of MV^{2+} .¹⁶ For $[N] = 0.37$ M, i.e., for a 50% reduced film, $k_{ex} = 8 \times 10^5 M^{-1} s^{-1}$. Substitution into eq 6 of this k_{ex} value, $C = 0.74$ M, and $\delta \approx 8 \text{ \AA}$ yields a value of $\leq 3 \times 10^{-9} cm^2 s^{-1}$ for $(\pi/4)k_{ex}\delta^2 C$. Hence, although the self-

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exchange rate constant is not large enough to broaden the ESR line width, it could, nevertheless, contribute to the value of D_{app} . However, since the value of k_{ex} used in our calculation is only an upper limit, the actual value of k_{ex} may be much smaller, in which case the major contribution to D_{app} would come from the physical diffusion of the ions, i.e., D_0 . The diffusion coefficients are sufficiently different in solution and in the Nafion film to account for the differences in the ESR behavior at the higher concentrations (≥ 50 mM) of reduced viologen, even if D_0 is the sole contributor to D_{app} .

In striking contrast to the well-defined hyperfine structure in the ESR spectrum of $[(MV^+)]_{Nafion}$, $[(MV^+)]_{surf}$ exhibits a broad and featureless spectrum. However, the mode of surface confinement of the viologen radicals is different in the two films. In the $[(MV^{2+})]_{surf}$ films the viologen moieties are constrained by the siloxane backbone and are relatively immobile. Even if the polymer network is sufficiently flexible so as to allow some motion along its chains, the viologens are unlikely to tumble sufficiently rapidly to average out dipole-dipole interactions. This factor alone can cause a broadening of the ESR spectrum (Figure 2); in fact such single line spectra (with noticeable asymmetry) seem to be common features of all radicals which are constrained in a similar fashion in polymers, e.g., those reported by Alberly et al.³ and Chambers et al.²

The monomer-dimer equilibria for the $[(MV^{2+})]_{surf}$ films heavily favor dimer formation because of the high concentrations of MV^+ in these films (3 M). This accounts for the linear increase in the 550-nm absorbance, shown in Figure 3, with the amount of charge injected into the films. Nevertheless, the fact that an ESR signal is detectable indicates that some monomeric MV^+ is present in the film. However, even when the equilibrium constant is taken to be the same in the film as in solution, as was assumed for the Nafion films, the ESR intensity does not track the MV^+ concentration (Figure 5). Since the signal is noticeably smaller in the presence of MV^{2+} , i.e., for partially reduced films, line broadening by electron transfer is probably substantial. Note that the anchored viologens can be rapidly oxidized and reduced and that site-to-site electron transfer is the sole mode of charge transport through these films ($D_{app} = 3 \times 10^{-10}$ cm² s⁻¹).^{10b} Hence, electron transfer between MV^+ and MV^{2+} probably causes the observed attenuation of the ESR signal intensity. Although a quantitative assessment of the self-exchange rate constant is difficult, because of the absence of fine structure in these spectra, a lower limit of 10^6 M⁻¹ s⁻¹ seems reasonable; a smaller rate constant would have a negligible effect on the ESR profile. This value is about an order of magnitude larger than that calculated by Bookbinder and Wrighton based on diffusion coefficient measurements.^{10b} This discrepancy may result from the fact that the local self-exchange rate constant under steady-state conditions may be quite different from the macroscopic self-exchange rate constant measured from potential step experiments. In the latter case counterion diffusion and discontinuities and/or non-uni-

formities in the film also have to be taken into account; note that the values of D_{app} and thus k_{ex} , measured from potential step experiments, depended on the nature and/or concentration of the electrolyte.^{10b}

Conclusions

Simultaneous electrochemical and ESR experiments are useful in providing information concerning the environment and mobility of redox species in chemically modified electrodes and on the electron-transfer rates in these films. For the $[(MV^{2+})]_{surf}$ films, where the redox species are covalently anchored to the polymer chain, the ESR spectrum is broad and featureless, suggesting that they are immobile on the ESR time scale. Data on the ESR signal intensity vs. the concentration of ESR-active radicals suggest that the local electron-transfer (self-exchange) rate in these films is high ($>10^6$ M⁻¹ s⁻¹), although precise values of the rate constant have not been measured. On the other hand, self-exchange rates are smaller in Nafion ($k_{ex} \leq 8 \times 10^5$ M⁻¹ s⁻¹), indicating that actual physical diffusion of ions contributes substantially, if not completely, to the charge transport mechanism within the film. A high local mobility of the ions is suggested by the presence of hyperfine structure in the ESR spectra. Significant differences between the ESR spectra of MV^+ in Nafion and in solution are observed; these are attributed to the differences in the rate of electron exchange for viologen in the film and in solution.

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Appendix

Let $O = [MV^{2+}]$, $M = [MV^+]$, and $D = [(MV^+)_2]$

$$O + M + 2D = C^* \quad (\text{A.1})$$

$$K = D/M^2 \quad (\text{A.2})$$

$$f = (M + 2D)/C^* \quad (\text{A.3})$$

where C^* is the total (analytical) concentration of MV^{2+} and f is the fraction of MV^{2+} reduced. From eq A.2 and A.3

$$2D + (D/K)^{1/2} - fC^* = 0 \quad (\text{A.4})$$

When $fC^* \gg (D/K)^{1/2}$, $D \approx fC^*/2$. For $K = 380$ M⁻¹ and $C^* = 3$ M this holds for $f \geq 0.1$. Hence, the absorbance at 550 nm, attributed to dimer formation in the polymer, will be linear with f for $f \geq 0.1$ (Figure 3). Under these conditions $M \propto (2K/fC^*)^{1/2}$. More rigorously,

$$M = (4K)^{-1}[(1 + 8fC^*K)^{1/2} - 1] \quad (\text{A.5})$$

$$D = KM^2 \quad (\text{A.6})$$

Registry No. I, 39464-59-0; II, 74173-49-2; MV^{2+} , 1910-42-5; MV^+ , 25239-55-8.