. в



Singlet ____ Singdoublet

Figure 3. Schematic representation of the excited states formed from the spin coupling of the excited porphyrin and doublet Fe(III) electron configurations. The tripdoublet states are the origin of the calculated "extra" absorptions of CyanoMetMb. State energies are not shown in scale.

states. As a result, four singdoublet states are responsible for the Soret and four singdoublet states for the Q band. The eight tripdoublet states normally do not display absorption intensities. It is the mixing of the charge-transfer transitions, (π, d_{π}) , into four of these tripdoublet states that results in the nonzero oscillator strengths of the four extra bands. In fact, as the contribution of the charge-transfer excitations to the wave function decreases from band I to band IV, the oscillator strength decreases (Table IV). The other four tripdoublet states with zero oscillator strength have only negligible amount of mixing with (π, d_{π}) .

The Q bands were calculated to be near the experimental absorption region and xy polarized. As expected, the wave functions of these states consist mainly of the excitations from $3a_{2u}$, $1a_{1u}$ to $4e_g$. Two weak bands were found at 23 488 and 26 239 cm⁻¹, at higher frequencies than Q but lower than B. These transitions contain significant components of charge-transfer excitation $(d_r, 4e_g)$ and $(1a_{1u}, 2b_{1u})$. Since these two transitions have low intensities and are near the strong Soret band, they are considered to be buried. The wave functions of the Soret bands are significantly mixed with excitations from the lower energy orbitals, $2a_{2u}$ and $2b_{2u}$. The excitation energies of the Soret bands were overestimated by about 6000 cm⁻¹. These results are similar to previous calculations applying ZINDO, indicating the limitations of the method used. The wave functions of these states are strongly mixed with those of the N and L bands, which result from the excitations from the $2a_{2u}$ and the $2b_{2u}$ orbitals to the $4e_g$ orbitals.

Since there is only a small energy difference between the ground state and the ${}^{2}B_{2g}$ state at the RHFSCF level (Table II), S-CI was carried out for the spectrum of the ${}^{2}B_{2g}$ state. The MO energy diagram of this state is also shown in Figure 2. No low-energy charge-transfer states were found for ${}^{2}B_{2g}$, which supports the conclusion that the ground state of CyanoMetMb is ${}^{2}E_{g}$. In general, it can be expected that if the ground state of a doublet ferric heme protein is ${}^{2}B_{2g}$, such extra absorptions should not be observed.

Conclusions

RHFSCF and CI calculations on model CyanoMetMb predict that its ground state is the ${}^{2}E_{g}$ state, the correct description of which requires a symmetric wave function. Although symmetry-broken wave functions of the two components of ${}^{2}E_{g}$ show near degeneracy, they yield incorrect quadrupole splittings in Mossbauer resonance spectra. The four extra absorptions observed in the single-crystal polarized absorption spectra were found to originate predominantly from the excitations from the highest two occupied porphyrin MOs to the two lowest unoccupied MOs with tripdoublet coupling between porphyrin and Fe(III). The nonzero intensities result from the mixing of the $(3a_{2u}, d_{\pi})$ and $(1a_{1u}, d_{\pi})$ charge-transfer excitations into these wave functions. This assignment differs from that proposed by Eaton and co-workers, in which the charge transfer was thought to be the primary nature of these transitions.

Acknowledgment. This work is supported by the National Science Foundation (Grant No. DMB-9096181). We thank Dr. Jack R. Collins for stimulating discussions.

Registry No. Heme, 14875-96-8.

Viologen(2+/1+) and Viologen(1+/0) Electron-Self-Exchange Reactions in a Redox Polymer

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An analysis is given of the electron-self-exchange reactions responsible for the steady-state redox conductivity of thin films of the electropolymerized monomer N,N'-bis(3-pyrrol-1-yl-propyl)-4,4'-bipyridinium tetrafluoroborate, sandwiched between two electrodes. Concentration-gradient-driven electron self-exchange in the liquid-acetonitrile-bathed viologen(2+/1+) mixed-valent state of this polymer, $k_{sx} = 8 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, is much slower than that for the viologen(1+/0) mixed-valent state, $k_{ex} = 1.6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, which has a smaller activation barrier. Neither self-exchange reaction responds to use of alternative counteranions except that both rates decrease in polymer containing tosylate counterions. The rate constant found for the electrical-gradient-driven viologen(1+/0) electron self-exchange, $k_{ex} = 1.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, observed in dry, N₂-bathed polymer where ClO₄⁻ counterion mobility is quenched, is nearly the same as the acetonitrile-bathed value. The rate constants appear to be dominated by characteristics of the polymer phase rather than the bathing environment of the polymer. Estimates are made of the counteranion diffusivity in acetonitrile-bathed films and of how it affects transient electron transport measurements.

This paper presents an analysis of electron and counterion transport in the redox polymer formed by oxidative electropolymerization of the viologen monomer¹ N,N'-bis(3-pyrrol-1-ylpropyl)-4,4'-bipyridinium tetrafluoroborate, 1.

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We abbreviate this polymer in its several viologen-based oxidation states as $poly[V]^{2+}$, $poly[V]^+$, and $poly[V]^0$. According to the ideas of redox conduction,² mixed-valent films of $poly[V]^{2+/+}$ and $poly[V]^{+/0}$ transport electrons by self-exchange reactions between neighboring donor/acceptor pairs, at rates determined by the magnitude of the free energy gradient supplied in the experiment and by the self-exchange rate constants $k_{ex,2/1}$ and $k_{ex,1/0}$, respectively, extant in the polymer phase. Films of this viologen polymer have been examined in electrocatalytic^{1b} and photochemical and spatial charge separation³ schemes, and briefly for their electron transport properties^{3a} as have those of two related viologen polymers.⁴ Other viologens immobilized as polymer membranes have been investigated in photochemical charge separation,⁵ phase-transfer catalysis,⁶ and solid-state microelectrochemical^{4a,7} schemes, and a variety^{1,3-5,7,8} of viologen polymers have been demonstrated as electroactive polymer films on electrode surfaces.

There have not been, however, any detailed transport investigations of the effect of the bathing environment of the viologen, of the source of the free energy gradient, or of the counterion identity and diffusivity, on electron self-exchange reactions between polymer-embedded, diffusively immobile viologen centers. We have been exploring⁹ such effects for metal polypyridine polymers. Following a preliminary study,^{8m} reported here are electron self-exchange rate constants $k_{ex,2/1}$ and $k_{ex/1/0}$ for poly[V]^{2+/+} and poly[V]^{+/0} reactions in mixed-valent films. The reactions are made to occur under the impetus of *steady-state* concentration^{2,12} vs voltage gradients,¹¹ in acetonitrile liquid vs vapor vs dry N₂ bathing environments, and as a function of the anionic counterions present in the polymer films. We also estimate the transient counteranion and electron diffusivities and describe a correction of the transient measurement of electron diffusivity for migration effects.¹⁰

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Figure 1. Schematic of the initial conditions for (A) solvent-wetted, four-electrode, sandwich electrode experiments, (B) solvent-vapor-bathed, two-electrode, sandwich electrode experiments, and (C) dry N₂ bathed, two-electrode, sandwich electrode experiments. The cross-hatched area is a Pt wire tip; the wavy area is an evaporated, porous Au film; the Pt and Au potentials are controlled vs reference electrode in A and vs each other (Δ/E) in B and C. The other areas are viologen polymers (between the electrodes) and solution (A) or gas (B, C) as indicated.

Experimental Section

Chemicals and Equipment. Acetonitrile solvent (Burdick and Jackson) and electrolytes (Fluka) tetraethylammonium tosylate (Et₄NTOS), tetraethylammonium tetrafluoroborate (Et₄NBF₄), tetrabutylammonium perchlorate (Bu₄NClO₄), and tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) were used as received. Tetraethylammonium perchlorate (Et₄NClO₄) was thrice recrystallized from distilled water. Electrochemical experiments were carried out in an inert atmosphere glovebox (Vacuum Atmospheres) using a bipotentiostat (ARDE-4, Pine Instruments). Potentials are reported vs Ag/0.01 M AgNO₃, 0.1 M Et₄NClO₄, CH₃CN, which is approximately +0.3 V vs SSCE. Current transients were recorded with a Nicolet Model 2090 digital oscilloscope.

Monomer Precursor 3-Bromopropylpyrrole, 2. A modification^{13,14} to a previous synthetic procedure for 2-chloroethylpyrrole was used: A mixture of 30 g of 2,5-dimethyltetrahydrofuran (Aldrich), 170 g of 3-bromopropylamine hydrobromide (Aldrich), 112 mL of acetic acid, and 90 g of sodium acetate in a stirred 2-L flask is heated. At ca. 80 °C the mixture melts and the color darkens from beige to brown and to black near 120 °C, where a clear liquid begins to distill. After heating at 120 °C for 30 min the flask contents are cooled and poured into an equal volume of saturated aqueous NaCl which is then extracted with an equal volume of CH₂Cl₂. After washing with saturated aqueous Na₂CO₃, NaCl, and distilled H₂O, the CH₂Cl₂ extract is dried over MgSO4, reduced in volume by vacuum evaporation and eluted with 3:1 hexane/ CH_2Cl_2 from a flash chromatography column (silica gel, J. T. Baker 7024-01). The eluted (clear) product is visualized on silica TLC plates using I₂ vapor and immediately stored in a freezer to avoid its slow room temperature polymerization. NMR (¹H, CDCl₃): δ (ppm) = 2.1 (m, 2 H), 3.2 (t,

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Figure 2. Typical (A) $poly[V]^{2+/+}$ (1 mV/s) and (B) $poly[V]^{+/0}$ (5 mV/s) sandwich electrode steady-state voltammograms in 0.1 M Et₄NClO₄/acetonitrile at 25 °C, showing both Pt (--) and Au (---) electrode currents. A = 0.0033 cm², $\Gamma = 2.1 \times 10^{-7}$ mol/cm².

2 H), 4.0 (t, 2 H), 6.1 (t, 2 H), and 6.6 (t, 2 H).

Monomer 1. The synthesis follows that previously reported.^{1b} Briefly, 0.56 g of 4,4'-bipyridine (Eastman Kodak) is refluxed with 5 g of 2 in 10 mL of absolute EtOH for 36 h, producing a yellow precipitate that is washed with EtOH and EtOEt and dried overnight under vacuum. A 0.06 M aqueous solution of the bromide salt of 1 is passed through a BF₄⁻ Amberlite IRA-93 (Alfa Products) ion-exchange column. The BF₄⁻ salt of 1 is isolated from eluted fractions by freeze-drying and recrystallized from CH₃CN with CH₂Cl₂ precipitant. NMR of BF₄⁻ salt (¹H, D₂O): δ (ppm) = 2.65 (m, 2 H), 4.18 (t, 2 H), 4.75 (t, 2 H), 6.06 (s, 2 H), 6.70 (s, 2 H), 8.30 (d, 2 H), 8.90 (d, 2 H). (Multiple doublets at δ = 8-10 ppm signal partial reaction of 4,4'-bpy with 2.)

Electropolymerization of 1. Submicrometer films of poly-[V](ClO₄)₂ are electropolymerized for 90–120 min onto Pt disks from 0.1 M Et₄NClO₄/CH₃CN with 2 mM 1, at +0.92 V vs Ag⁺/Ag, monitoring the electropolymerization charge, $Q_{\rm ECP}$, with a digital coulometer. The coverage Γ of deposited viologen polymer was typically (1-5) × 10⁻⁷ mol/cm², measured from the charge to reduce the film to the poly[V]⁰ state in a slow potential sweep from 0 to -1.6 V, and converted to thickness d based on an average profilometer-based^{3b} site concentration $C_{\rm T} = \Gamma/d =$ 4.5 M.

Sandwich Electrode Fabrication. Following our established method,^{2,9} electropolymerization of 1 onto one of the polished tips of two 0.32 mm radius Pt wires sealed in soft glass, finishing with the film in the air-stable, pyrrole-oxidized, $poly[V]^{2+}$ state, is followed by evaporation of ca. 300 Å of a porous layer of Au over the film and (for contact) the other electrode tip. $Poly[V]^+$ and $poly[V]^0$ films are not air-stable.¹⁵

Electron Transport in Liquid-Acetonitrile-Wetted Films: "Four-Electrode" Experiments. Figure 1 illustrates the different types of electron transport measurements. In liquid media (Figure 1A) the experiment is akin to that for a twin-electrode thin-layer cell. With the sandwich electrode immersed in 0.1 M Et_4NClO_4/CH_3CN , the potentials of the Pt (cross-hatched area) and Au (wavy area) contacts are manipulated vs reference electrode.^{2,9} To measure $poly[V]^{2+/+}$ electron self-exchange, the Pt potential is held at -0.6 V (all sites at its interface thus in $poly[V]^{2+}$ state) while the Au potential is cyclically scanned (2-20) mV/s) between -0.6 V and ca. -0.9 V (where Au/polymer interface is all poly[V]⁺). A steady-state limiting current flows between the Pt and Au electrodes (Figure 2A). The same procedure is used for $poly[V]^{+/0}$ self-exchange except the Pt potential is -0.9 V (all sites are poly[V]⁺) and the Au electrode potential is scanned between -0.9 V and ca. -1.6 V (poly[V]⁰ state, Figure 2B).



Figure 3. Typical cyclic voltammograms of poly[V] films, wetted by 0.1 M Et₄NClO₄/acetonitrile at 25 °C. (A) Slow potential sweep rate, 5 mV/s, $\Gamma = 2.1 \times 10^{-7}$ mol/cm²; (B) faster potential sweep rate, 20 mV/s, $\Gamma = 4.4 \times 10^{-7}$ mol/cm².

Electron Transport in Gas-Bathed Films: "Two-Electrode" Experiments. Experiments without fluid electrolyte solutions (Figure 1B,C) are done by electrolysis of a sandwich electrode in fluid electrolyte to a 1:1 mixed-valent composition, i.e., poly-[V](ClO₄)_{1,5} or poly[V](ClO₄)_{0.5}. The electrolysis is done by applying potentials that produce limiting currents as in Figure 2, removing the sandwich from solution under potential control, rinsing with pure solvent, removing from potential control to allow the concentration gradients to relax, and drying under N₂. The current-voltage behavior of such dry 1:1 mixed-valent sandwiches under an applied voltage bias is constrained by the internal counterion budget^{9a} and by the gaseous environment's influence on counterion mobility^{9b} (Figure 1B,C).

Results

Electropolymerizations and Cyclic Voltammetry. Voltammetry of the $poly[V](X)_2$ films depends markedly on the potential sweep rate (Figure 3). At slow potential scans, the charge under the $poly[V]^{2+/+}$ and $poly[V]^{+/0}$ waves is nearly the same (Figure 3A). At faster sweep rates the poly[V]2+/+ wave seems markedly smaller and exhibits substantial "tailing". A shoulder or prepeak sometimes appears on the leading edge of the $poly[V]^{+/0}$ reduction wave. These effects are analogous to voltammetry¹⁶ of mixtures of $[Fe(CN)_6]^{3-/4-}$ and $[IrCl_6]^{2-/3-}$ in ion-exchanger films on electrode surfaces and are attributed to a substantially slower charge transport in the $poly[V]^{2+/+}$ mixed-valent state as opposed to the poly $[V]^{+/0}$ state. Additionally, the Figure 3A poly $[V]^{2+/+}$ wave, even at slow sweep rates, exhibits a significantly larger reduction-oxidation peak potential separation (ΔE_{peak}) than does the poly[V]^{+/0} wave; this may reflect a lower counterion diffusivity and thus a larger iR_{uncomp} drop in the poly $[V]^{2+/+}$ state, as compared to poly $[V]^{+/0}$.

The charge passed for $2e^-$ reduction of poly $[V]^{2+}$, $Q_{2/1/0}$, as in Figure 3A, can be compared to that for oxidation of monomer 1, Q_{BCP} , to estimate¹⁷ to what extent oxidation of monomer results in incorporation of an electroactive viologen site in the polymer film. $Q_{2/1/0}/Q_{ECP}$ was typically between 20 and 60% of that ideally expected¹⁷ and was also observed to increase when a given monomer 1 solution was used repeatedly for electropolymerization. Unlike classical pyrrole electropolymerization,¹⁷ where deposition

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TABLE I: Calculated^a Steady-State Limiting Current Correction Factor ω^0 and Corresponding Mole Fractions of Reduced Redox Sites

redox couple	$z_{\rm X} = -1^{b}$		$z_{\rm X} = -2^b$		
	ω	XR	ω	Xr	
A(5/4)	1.037	0.500 40	1.019	0.500 20	
A(4/3)	1.048	0.500 65	1.024	0.500 34	
A(3/2)	1.067	0.501 27	1.034	0.500 66	
A(2/1)	1.114°	0.503 50	1.057	0.501 84	
A(1/0)	1.500°	0.555 56	1.250	0.533 33	

^e Correction factors (ω^0) and mole fractions (χ_R calculated using eqs 12, 14, and 6 in ref 12, n = 1. ^bCharge on the counterion. ^cThese values apply to poly[V]^{2+/+} and poly[V]^{+/0} films (see text).

TABLE II: Electron Diffusion Coefficients Observed in Poly[V]^a **Immersed** in Liquid Acetonitrile

supporting electrolyte, 0.1 M in CH ₃ CN	$D_{\epsilon,2/1},$ $10^{-11} \text{ cm}^2/\text{s}$	$D_{e,1/0},$ $10^{-10} \mathrm{cm}^2/\mathrm{s}$	expt type ^b
Et ₄ NClO ₄	3.2 (±0.8) ^c	6.1 (±1.1) ^d	SS
Et ₄ NClO ₄	1.9 (±0.7)*	15	CA
Bu ₄ NPF ₆	2.0	9.7	SS
Bu ₄ NClO ₄	3.3	9.9	SS
Et ₄ NClO ₄	3.4	10.8	SS
Et ₄ NBF ₄	2.1	8.3	SS
ET ₄ NTOS'	1.1	3.3	SS

"Room temperature; confidence intervals in the first two rows are 68%; data in remaining rows taken on a simple sample ($\Gamma = 2.6 \times 10^{-7}$ mol/cm²) to facilitate comparison. ^bSS is "four-electrode" steady-state experiment; CA is by chronoamperometry. ^cAverage of nine mea-surements. ^dAverage of 10 measurements. ^cAverage of four measurements. TOS is tosylate.

efficiency is typically 100%, the rate of coupling and precipitation of oligomers of 1 onto the electrode appears to be slow, allowing some activated material to diffuse away and accumulate as short-chain oligomers. These soluble oligomers facilitate subsequent electropolymerizations using the same solution, as we have seen in other cases.¹⁸

Electron-Transport Experiments in Liquid-Acetonitrile-Wetted Films. Acetonitrile-wetted sandwich electrode voltammograms are displayed in Figure 2. $E_{1/2}$ of the sigmoidal current-potential curves are coincident with that from cyclic voltammetry (Figure 3), as expected. The poly[V]^{2+/+} limiting current is significantly smaller than that for $poly[V]^{+/0}$ and exhibits more hysteresis between forward and reverse potential sweeps. Consistent with the Figure 3 voltammetry, these observations point to more sluggish charge transport in the $poly[V]^{2+/+}$ films.

At the limiting currents i_{LIM} in Figure 2, steady-state con-centration gradients of poly $[V]^{2+}$ and poly $[V]^+$ sites, and of $poly[V]^+$ and $poly[V]^0$ sites, have been established, down which electrons hop at rates expressed¹⁹ by the "electron diffusion coefficients" $D_{e,2/1}$ and $D_{e,1/0}$, respectively. The current is given by

$$i_{\rm LIM} = \omega^0 n F A D_{\rm e} C_{\rm T} / d \tag{1}$$

where A is electrode area and ω^0 is a correction factor accounting for electrostatic coupling between electron and counterion motion.¹² Values of ω^0 calculated by using the theory¹² for this subject, for various redox polymer compositions (Table I), show that ω^0 = 1.114 for the $poly[V](ClO_4)_{1.5}$ composition and 1.50 for poly- $[V](ClO_4)_{0.5}$. Note that ω^0 depends on the counterion and viologen site charges but not on the counterion or electron diffusivity. As we have explained,^{2,19} values of i_{LIM} should not be affected by macroscopic counterion diffusivity since a steady-state counterion concentration gradient is established in conjunction with those of the viologen sites. Values of $D_{e,2/1}$ and $D_{e,1/0}$ obtained for 0.1

TABLE III: Comparison of Viologen Electron Self-Exchange Data

environment	couple	k _{ex} , M ^{−1} s ^{−1}	E _A , kcal mol ⁻¹	
CH ₃ CN wetted	poly[V]2+/+	8.4×10^{3}	125	
CH ₃ CN wetted	poly[V] ^{+/0}	1.6×10^{5}	98	
CH ₃ CN vapor bathed	poly[V] ^{+/0}	2.7 × 10 ⁵ °		
Dry nitrogen ^d	poly[V] ^{+/0}	1.1 × 10 ⁵ d		
monomer, in solution	poly[V] ^{2+/+}	8.4 × 10 ⁸		
CH ₃ CN/H ₂ O wetted	poly[V] ^{2+/+}	$2.3 \times 10^{3 f}$		
CH ₃ CN/H ₂ O wetted	poly[V] ^{+/0}	2.3×10^{6f}		
CH ₃ CN wetted	poly[V] ^{2+/+}	2.9 × 10 ⁵ *	10 s	
	environment CH ₃ CN wetted CH ₃ CN wetted CH ₃ CN vapor bathed Dry nitrogen ^d monomer, in solution CH ₃ CN/H ₂ O wetted CH ₃ CN/H ₂ O wetted CH ₃ CN wetted	$\begin{array}{c c} environment & couple \\ \hline CH_3CN wetted & poly[V]^{2+/+} \\ CH_3CN wetted & poly[V]^{+/0} \\ Dry nitrogen^d & poly[V]^{+/0} \\ monomer, in solution & poly[V]^{2+/+} \\ CH_3CN/H_2O wetted & poly[V]^{2+/+} \\ CH_3CN/H_2O wetted & poly[V]^{2+/+} \\ CH_3CN wetted & poly[V]^{2+/+} \\ \end{array}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	

^a This work. ^b From Figure 4; see also ΔH^* and ΔS^* there. ^c Calculated by using eqs 1 and 2 from (—) in Figure 5. ^d Calculated by using eq 3 for curve --- in Figure 5. ^c Reference 23. ^f Poly[PQ] is based on N,N'-bis-[3-(trimethoxysilyl)propyl]-4,4'-bipyridinium dibromide. $D_e C_T^2$ in ref 4b converted to k_{ex} by using eq 2 and $C_T = 3.0$ M, $\delta = 8.2$ Å. *Poly[P-V-Me] is based on 1-methyl-1'-(6-(pyrrol-1-yl)hexyl)-4,4'-bipyridinium hexafluorophosphate. $D_{\rm e}$ in ref 4a converted to $k_{\rm ex}$ using eq 2 and $C_{\rm T}$ = 4.5 M, $\delta = 7.2 \text{ Å}.$



Figure 4. (A) $Poly[V]^{+/0}$ (5 mV/s) sandwich electrode steady state voltammograms in 0.1 M Et₄NClO₄/acetonitrile at various temperatures. (B, C) Eyring plot based on rate constants from voltammograms like (A).

M Et_4NClO_4/CH_3CN -wetted films are given in the first row of Table II.

 $D_{\rm e}$ is related to the electron-self-exchange rate constant by^{20,21}

$$D_{\rm e} = k_{\rm ex} \delta^2 C_{\rm T} / 6 \tag{2}$$

where δ is the average viologen site-site distance (taken as 7.2) Å from a cubic site packing calculation, $N_A \delta^3 C_T = 1$). Results for $k_{ex,2/1}$ and $k_{ex,1/0}$ in 0.1 M Et₄NClO₄/CH₃CN-wetted films, given at the top of Table III, show that the poly[V]^{2+/+} self-exchange constant is ca. 20-fold smaller than that for the $poly[V]^{+/0}$ reaction.

Sandwich electrode voltammograms like Figure 2 were obtained over a range of temperatures, to extract activation parameters²² for the two self-exchanges (Figure 4 and Table III). These results indicate that the difference between $k_{ex,2/1}$ and $k_{ex,1/0}$ for solvent-wetted films arises principally from a difference in activation enthalpies, that for $poly[V]^{2+/+}$ self-exchange being larger. The activation entropies for both self-exchanges are somewhat negative (Figure 4B,C), but are similar.

Table III also presents related observations for viologen selfexchange reactions, from previous⁴ measurements that were steady

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state and thus devoid of counterion macroscopic diffusivity effects. Consider first our poly $[V]^{2+/+}$ result. Our observed $k_{ex,2/1}$ (8.4 $\times 10^3$ M⁻¹ s⁻¹) is drastically depressed (by 10⁵) relative to that²³ for methyl viologen^{2+/+} monomer in solution, 8.4×10^8 M⁻¹ s⁻¹. Comparing polymer phase and monomer fluid solution rate constants highlights the extent to which the environment of the polymer phase influences electron self-exchange. For self-exchanges in redox polymers based on porphyrin²⁴ and osmium bipyridyl¹⁹ sites, we have observed some correlation with solution-phase data. Clearly this correlation breaks down for electropolymerized films of 1. Other values of k_{ex} calculated from the literature⁴ for solvent-wetted viologen polymers, Table III, for $poly[V]^{2+/+}$ self-exchange are also smaller than the solution monomer value but are not as small as the present $poly[V]^{2+/+}$ result. These other viologen polymers⁴ use bis(alkoxysilylpropyl) and mono(pyrrolylhexyl) couplings rather than the bis(pyrrolylpropyl) coupling that occurs for 1. These comparisons show that $poly[V]^{2+/+}$ electron self-exchange is not only strongly influenced (decreased) by occurring in a polymeric environment, its rate is additionally quite sensitive to the particular chemical and/or structural details of that environment.

Turning to the poly $[V]^{+/0}$ result, the only available data for comparison, the steady-state $k_{ex,1/0}$ calculated from data by Wrighton et al.,^{4b} is larger than our result by ca. 15-fold which is roughly similar to the difference between the two $k_{ex,2/1}$ results. This again seems to reflect a dominating influence of the particular polymer environment on the self-exchange rate. Wrighton^{4b} also observed that $k_{ex,2/1} > k_{ex,1/0}$, as was also seen in³ transient experiments on a copolymer of 1 with a ruthenium monomer.

The significant features of the above observations are that (i) in the polymer, $k_{ex,2/1} < k_{ex,1/0}$, and (ii) that $k_{ex,2/1}$ is markedly smaller in the polymer environment as compared to a fluid solution of monomer. These features can be explained only in rather general terms. The strong effect (ii) of the polymer environment on the viologen $k_{ex,2/1}$ may reflect polymer lattice-imposed constraints on the nuclear coordinate rearrangements that accompany barrier-crossing; this would amount to a large "inner-sphere' activation barrier term. The E_A for the polymer-phase electron exchange is, indeed, fairly substantial (Table III). Alternatively, the rate change may be associated with weak electronic coupling (overlap) owing to details of the polymer structure, i.e., in which the cross-linked pendant pyrrole chains may enforce some viologen site-site separation.

There are at least two contributions to the difference (i) $k_{ex,2/1}$ $< k_{ex,1/0}$. Firstly, classical electron-transfer theory²⁵ shows that rates are influenced by work terms for electrostatic interactions between charged reactant pairs, and indeed numerous examples exist where the electron-transfer rate for a more highly charged monomeric redox couple is slower than for a related but less charged one. These include the $TMPD^{2+/+}$ vs $TMPD^{+/0}$ couples (20-fold difference) of the monomer N,N,N',N'-tetramethyl-pphenylenediamine,²⁶ the TCNQ^{-/2-} vis TCNQ^{0/-} couples of the monomer tetracyanoquinodimethane,²⁷ and the $Q^{-/2-}$ vs $Q^{0/-}$ couples for various *p*-benzoquinone derivatives,²⁸ among others. We agree with Wrighton et al.^{4b} that such differences can be qualitatively rationalized by charge repulsion (i.e., between $poly[V]^+$ and $poly[V]^{2+}$, but it is also true that work terms may be ameliorated to some extent in the polymer by virtue of the fact that the reactants and products are already constrained into close



Figure 5. Two-electrode poly[V](ClO₄)_{0.5} sandwich experiments in (---) acetonitrile vapor and (--) dry bathing gas, using the same sandwich (32 °C, $\Gamma = 3.2 \times 10^{-7}$ mol/cm²).

proximity by the polymer matrix.

Secondly, the poly $[V]^{2+/+}$ mixed valent polymer has a larger internal counterion content (and possibly a higher solvent content) than does $poly[V]^{+/0}$. Consequently, any ion-pairing²⁹ association effects on the electron exchange would be stronger for the former couple. Thirdly, Wrighton et al.^{4b} observed a thinning of a viologen polymer film as it was reduced, so part of the k_{ex} difference might arise from a difference in viologen site concentration.

Electron Transport Experiments in Gas-Bathed Films. A 1:1 mixed-valent film contacted only by a bathing gas can be manipulated in how the free energy gradient for electron hopping%11 is supplied. In bathing gases where counterion diffusivity in the mixed-valent polymer remains facile, concentration gradients are readily established across the polymer film down which electrons hop; eq 1 again applies. On the other hand, in bathing gases where counterion diffusion is insignificant on the experimental time scale, electroneutrality constraints prevent electrolytic formation of concentration imbalances, so that a stable electrical gradient persists and provides the driving force for electron hopping. In this case, the current rises without limit (in principle) with increased electrical gradients, unlike the concentration gradient case where the magnitude of the attainable gradient (and thus the current) is limited.

Gas-bathed experiments were carried out on $poly[V](ClO_4)_{0.5}$ sandwich electrodes. In a bath of acetonitrile vapor, counterion diffusivity, while slow, does occur and a slow scan of ΔE produces a symmetric sigmoidal wave with limiting current plateaus (Figure 5, —). Application of eqs 1 and 2 gives a self-exchange rate constant $k_{ex,1/0} = 2.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ (Table III) that is close to that obtained in the liquid-acetonitrile-wetted experiment. Such agreement between liquid and vapor-bathed rate constants was also observed for redox polymers derived from osmium bipyridine complexes.30

When a dried $poly[V](ClO_4)_{0.5}$ sandwich electrode is bathed only in N_2 gas, the counterion diffusivity is significantly quenched. Application of a ΔE potential bias now yields a sweep rate independent (20-500 mV/s), apparently Ohmic, current-potential curve (Figure 5, --), the conductivity, σ , from which is related to the electron self-exchange rate constant by^{11,12,31}

$$\sigma = [(nF\delta C_{\rm T})^2/6RT]\chi_{\rm R}(1-\chi_{\rm R})k_{\rm ex}$$
(3)

where $\chi_{\mathbf{R}}$ the mole fraction of reduced viologen sites is 0.5 in the present experiment. Figure 5 (---) yields a rate constant, $k_{ex,1/0} = 1.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, for poly[V]^{+/0} self-exchanges occurring under the impetus of a voltage gradient, that is reasonably close to that obtained from the limiting current measurements discussed above, where electron transfer is driven by a gradient of poly[V]⁺ site concentrations (Table III). Agreement between these two rate constants is ideally expected, based on the idea that the same

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Figure 6. The effect of choice of supporting electrolytes on (top) poly-[V]^{2+/+} and (bottom) poly[V]^{+/0} sandwich electrode steady state voltammograms in acetonitrile at 25 °C; recorded with the same sandwich; (a) Et₄NClO₄, (b) Et₄NTOS, (c) Et₄NBF₄, (d) Bu₄NClO₄, and (e) Bu₄NPF₆. The polymer sandwich ($\Gamma = 2.6 \times 10^{-7}$ mol/cm²) was cycled repeatedly between its poly[V]²⁺ and poly[V]⁺ states in each electrolyte solution to exchange the counterions, prior to recording the sandwich voltammograms.

electron-transfer barrier must be surmounted irrespective of the form in which the free energy to do it is supplied. Comparisons like this are rare^{8m,11} but are useful in that they test the differing principles, theoretical framework, and experimental tactics upon which the two measurements of k_{ex} , by electrical and concentration gradients, are based.

Effects of Charge-Compensating Counterions. In considering the role of the counterion in electron-hopping conductivity, it is important to distinguish macroscopic ion transport from microscopic-level ion motions and ion-site interactions. Macroscopic counterion transport refers to the change in concentration or spatial distribution of counterions in the polymer that accompanies an electrolytically driven change in concentration or distribution of ionic redox sites. The transient electrolysis method, chronoamperometry,³² necessarily involves such changes, and chronoamperometric D_e measurements in redox polymers then necessarily involve the possibility^{10,33} that D_e values may be altered by the values for macroscopic counterion transport. In contrast, under steady-state conditions, no macroscopic counterion transport occurs, and D_e is uncoupled from the counterion diffusivity.

The identity of the counterion used in a steady-state experiment can, nonetheless, potentially affect the electron-hopping rate, in several microscopic-level ways. Bulky counterions may swell the polymer lattice and increase the site-site distance for electron transfer, which may slow electron transfer. Also, specific interactions may exist between counterion and charged redox site that vary with the site's oxidation state, such as strong ion-pairing promoted by the combination of high site concentration and hydrophobic polymer character. Such interactions, and the associated nuclear coordinate changes imposed on accompanying electron transfer, may amount to large inner-sphere activation terms in the electron-transfer barrier height. Ion-site interactions are subtle and difficult to untangle from other aspects of the electron-transfer chemistry, and to date, no direct observations or clear examples of their importance exist. In contrast, recent theory to account for effects of macroscopic counterion transport has been presented.10



Figure 7. (A) Current transient (-O-), normalized to attained steadystate current ($i_{LIM} = 0.8 \text{ mA}$) measured at the Pt electrode of a 0.1 M Et₄NClO₄/acetonitrile-wetted sandwich when its potential stepped from -0.6 to -0.9 V, with the Au electrode held at -0.6 V vs reference ($\Gamma =$ 9.5 × 10⁻⁸ mol/cm², $d = 0.21 \mu$ m). (--) Theoretical curves calculated by using eq 4 for $D_X = 9.0 \times 10^{-12} \text{ cm}^2/\text{s}$ (upper) and 1.6 × 10⁻¹¹ cm²/\text{s} (lower). (B, C) Chronoamperometric current-time Cottrell plots for poly[V]^{2+/+} and poly[V]^{+/0} reductions for films with $\Gamma = 9.1 \times 10^{-8}$ mol/cm² and $\Gamma = 1.2 \times 10^{-7} \text{ mol/cm}^2$, respectively. $D_{e,app}$ values given in Table II, second line.

The following experiments probe the effect of choice of counterion and of its diffusivity on the electron-self-exchange rates in the viologen polymer.

Choice of Counterion. Figure 6 shows steady-state acetonitrile-wetted sandwich electrode voltammograms, using the same electrode specimen in a series of different electrolyte solutions. The results for $D_{e,2/1}$ and $D_{e,1/0}$ (Table II, lower part) show that the electron-hopping rates are not very sensitive to use of alternative counterions ClO_4^- , BF_4^- , and PF_6^- that have similar bulk. This is consistent with the absence of macroscopic counterion transport requirement in the steady-state measurement, as noted above, and with the lack of any variability of inner-sphere barrier contributions present. Electron hopping, on the other hand, is definitely slower in the presence of the bulkier tosylate counterion. A slowing by tosylate has also been observed in other redox polymer films.^{7e,34} This rate retardation is not properly attributable to a slower macroscopic diffusivity; rather it must reflect either a forced increase in the viologen intersite distance, or a specific ion-site (inner-sphere) interaction that contributes to the electron-transfer barrier.

As expected, changing the electrolyte cation has no effect (Table II); cations are charge-excluded from the polycationic polymer.

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Estimation of Counterion Diffusivity. Generally, the diffusivity of the counterion in the redox polymer is unknown. This aggravates the uncertainty about its role in a transient electrolysis experiment. We have suggested³⁵ an *approximate* way to estimate the counterion diffusivity (or its lower limit) that we apply here. Starting with an acetonitrile-wetted sandwich in the poly[V]-(ClO₄)₂ form, and both Pt and Au electrodes at -0.6 V vs reference, the potential of one of the electrodes is stepped to -0.9V vs reference Figure 7A shows the (i_{LIM} -normalized) transient current flowing at that electrode as a gradient of poly[V]⁺ is electrolytically created. The current gradually decays to a steady value, i_{LIM} , which is the same as would be observed in the potential sweep like Figure 2A. An approximate expression for the current transient is

$$i(t)/i_{\text{LIM}} = 1 + 2\sum_{n=1}^{\infty} \exp[-n^2 \pi^2 D_x t/d^2]$$
 (4)

where D_x is the diffusion coefficient of the charge-carrying species (either the hopping electron $D_{e,2/1}$ or the counterion $D_{ion,2/1}$) whose diffusivity limits the approach to steady state. While the theory does not exactly fit the experimental curves, two theoretical curves not differing much in the value of assumed D_X bracket the data, providing an estimate of D_X between 9.0×10^{-12} and 1.6×10^{-11} cm²/s. This value is similar to the $D_{e,2/1}$ obtained from the steady-state current (Table II), and from this we infer that perchlorate ion diffusivity in a poly[V](ClO₄)_{1.5} film, $D_{ion,2/1}$, is equal to or slightly smaller than $D_{e,2/1}$. This result bears on the interpretation of chronoamperometry results given below.

Chronoamperometry. Chronoamperometric current-time transients for the reductions of (non-sandwiched) films initially in the poly $[V]^2$ and poly $[V]^+$ states are analyzed in the classical manner in Figure 7B,C according to the Cottrell relation

$$i(t) = nFAC_{\rm T}(D_{\rm e,app}/\pi t)^{1/2}$$
(5)

 $D_{e,app}$ is the *apparent* electron-hopping diffusion coefficient; i.e., it has potentially been affected by electron/counterion diffusion coupling. For the poly $[V]^{2+/+}$ reaction, the Cottrell analysis is quite linear; that for the poly $[V]^{+/0}$ reaction falls off at longer time owing to the loss of semiinfinite diffusion geometry as is expected and as has been seen by many previous workers.^{8d,36}

The chronoamperometric (CA) value for $D_{e,app,2/1}$ (Table II, top) is smaller than the corresponding steady-state $D_{e,2/1}$, but considering the experimental uncertainty of each, they are not very different. $D_{e,app,1/0}$ is also not very different from the steady-state $D_{e,1/0}$, but in this case the transient measurement exceeds the steady-state value by 2-fold. A difference in this direction is interpretable by a migration effect.¹⁰ Recent theory by Saveant¹⁰ shows that a chronoamperometrically measured apparent electron diffusion coefficient, $D_{e,app}$, is related to the true (steady state) D_e by an expression of the form

$$D_{\rm e,app} = (\pi \Psi^2)(D_{\rm e}) \tag{6}$$

where Ψ is a numerically evaluated¹⁰ function that depends on the ratio $D_{\rm ion}/D_e$ and the counterion and redox site charges. Generally, if $D_{\rm ion}/D_e > 1.0$, $D_{e,app} \approx D_e$ (i.e., chronoamperometry gives a value for the true D_e), but when $D_{\rm ion}/D_e < 1.0$, $D_{e,app} > D_e$ (i.e., chronoamperometry overestimates D_e). The origin of the overestimation, qualitatively, is an acceleration of electron selfexchange by the potential field generated in a poorly ion-conductive (i.e., small $D_{\rm ion}$) film. For the poly[V]^{2+/+} reaction, assuming that $D_{\rm ion,2/1} \leq D_e$ (vide

For the poly $[V]^{2+/+}$ reaction, assuming that $D_{ion,2/1} \leq D_e$ (vide supra), application³⁷ of eq 6 shows that the chronoamperometric $D_{e,app,2/1}$ should overestimate the true electron diffusivity, but only by $\leq 23\%$, a factor which is much smaller than experimental uncertainty (Table II). That is, there is no discernible influence of counterion/electron diffusion coupling in this case.

For the poly[V]^{2+/+} reaction, we were unable to estimate D_x as in the Figure 7A experiment. We instead employ the Saveant theory¹⁰ to ascertain what value of $D_{ion,1/0}$ in a poly[V](ClO₄)_{1.5} film would have caused the observed chronoamperometric $D_{e,app,1/0}$ value (Table II) to be twice the steady-state value. The difference implies that $D_{ion,1/0} < D_{e,1/0}$. Application³⁷ of the theory gives $D_{ion,1/0} \approx 1.5 \times 10^{-10}$ cm²/s, or the ClO₄⁻ diffusion coefficient in the poly[V](ClO₄)_{1.5} film is about 4-fold smaller than the electron diffusion rate measured by the steady-state $D_{e,1/0}$. This estimate illustrates how a chronoamperometric determination of electron diffusion may be inflated by electroneutrality coupling with a counterion that diffuses more slowly.

The above analysis indicates that $\dot{D}_{\rm ion,2/1} \ge {\rm ca.} 1 \times 10^{-11} {\rm cm}^2/{\rm s}$ and that $D_{\rm ion,1/0} \approx 1.5 \times 10^{-10} {\rm cm}^2/{\rm s}$. While this analysis does not exclude the possibility that $D_{\rm ion,2/1} \approx D_{\rm ion,1/0}$, it is more plausible (judging from the difference in $iR_{\rm uncomp}$ and hysteresis effects for the poly[V]^{2+/+} and poly[V]^{+/0} waves in Figures 2 and 3) that $D_{\rm ion,2/1} < D_{\rm ion,1/0}$. A difference of counterion diffusivity in this direction would be consistent with stronger counterion-site ionpairing in a poly[V]^{2+/+} mixed-valent film composition than in a poly[V]^{+/0} composition. Stronger ion-pairing in turn could supply an inner-sphere barrier term to cause the slower electron-self-exchange rate constant that is observed for the poly-[V]^{2+/+} film. Clearly, the issue of the microscopic role of specific counterion-redox site interactions in electron transport is not directly answered by this analysis, but we are able to draw some significant inferences. Further understanding of it should appeal to experiments that more directly detect these ion-site interactions.

Acknowledgment. This research was supported in part by a grant from the National Science Foundation. We thank Dr. A. Deronzier for helpful discussions.

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