J. Am. Chem. Soc. **1991**, *113*, 5183–5187

Monomer and Polymer Solvent Dynamic Control of an Electron-Transfer Cross-Reaction Rate at a Redox Polymer/Solution Interface

Honghua Zhang and Royce W. Murray*

Contribution from the Kenan Laboratories of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599-3290. *Received January 7, 1991*

Abstract: The electron-transfer cross-reaction rate constant k_{12} for the thermodynamically disfavored oxidation of the metal complex solute $[Fe(4,7\text{-dimethylphenanthroline})_3]^{2+}$ by a poly($[Os(bpy)_2(vpy)_2]^{3+}$) redox polymer surface has been measured with a microelectrode-based voltammetric method as a function of the solvent in which the iron complex is dissolved. In the monomeric solvents acetonitrile, acetone, methylene chloride, dimethyl sulfoxide, pyridine, dimethoxyethane, and propylene carbonate, variations in k_{12} follow a theoretical model incorporating the monomer solvent relaxation time, dielectric constant, and reaction free energy. The osmium metal complexes at the redox polymer/solvent interface are shown to be well solvated without significant constraints on solvent properties. k_{12} is much smaller when the $[Fe(Me_2phen)_3]^{2+}$ complex is dissolved in the poly(ether) solvent $CH_3O(CH_2CH_2O)_8CH_3$, Me_2PEG-400. In the context of solvent dynamics theory, the results indicate that the relaxation time for the polymer chain segment's dipole reorientation that influences the barrier-crossing frequency is ca. 22 ps. This measurement is a new approach to polymer solvent dynamics and is the first example of an outer sphere electron-transfer cross-reaction rate in a polymeric solvent.

The effects of the solvent on electron-transfer reaction rates have occupied considerable recent research attention.[1] The influence of equilibrium aspects of the solvent medium on the barrier free energy for electron transfer was recognized long ago,[2,3] but the role of nonequilibrium aspects of the solvent in barrier-crossing dynamics has only recently been treated. Current theoretical models predict[4] that both dynamic and dielectric solvent properties exert strong influences on electron-transfer barrier-crossing rates.

Experimental work probing the solvent dynamics aspects of these theories has involved (i) measurements of solvent relaxation times, such as with time-dependent fluorescence Stokes shifts,[1,5] and measurements of the solvent dependence of barrier-crossing rates based (ii) on excited-state initiation of electron-transfer reactions[1,6] and (iii) on ground-state heterogeneous (electrochemical) and homogeneous electron self-exchange processes.[7-10] To our knowledge, there have been no previous investigations of solvent dynamics effects in electron-transfer *cross*-reactions, in electron transfers at electron-transfer-active *polymer surfaces*, or in *polymeric solvents*. We report such studies here.

The solvent effect measurements are based on an electron-transfer cross-reaction at a redox polymer/solution interface:

$$Pt/poly([Os]^{3+}) + [Fe(Me_2phen)_3]^{2+} \xrightarrow{k_{12}} Pt/poly([Os]^{2+}) + [Fe(Me_2phen)_3]^{3+} \quad (1)$$

where poly($[Os]^{3+}$) ($E^\circ_{Os(III/II)} = 0.72$ V vs SSCE) is a thin-film polymer electroreductively deposited on a 10-μm (diameter) Pt microelectrode, from a solution of the monomer $[Os(bpy)_2(vpy)_2]^{2+}$ (bpy = 2,2′-bipyridine, vpy = 4-vinylpyridine), and contacted with a $[Fe(Me_2phen)_3]^{2+}$ solution (Me_2phen = 4,7-dimethylphenanthroline; $E^\circ_{Fe(III/II)} = 0.89$ V vs SSCE). When E_{Pt} is made sufficiently positive of $E^\circ_{Os(III/II)}$, the limiting current flow measures the turnover of poly($[Os]^{3+}$) states and thus the rate of reaction 1. From previous studies[11] of reaction 1 and related reactions in acetonitrile solvent, we know that (a) their rates vary with the reaction free energy $E^\circ_{Fe(III/II)} - E^\circ_{Os(III/II)} = \Delta E^\circ$ in accord with classical theory[2,3] and (b) the redox polymer film is essentially impermeable to the bulky cationic metal complex, so that the energetically simple electron-transfer cross-reaction involves only the outermost layer of poly ($[Os]^{3+}$) sites on the redox polymer film surface.

In this study, k_{12} is measured by using seven monomeric solvents for the $[Fe(Me_2phen)_3]^{2+}$ complex, to establish that reaction 1 responds to the solvent longitudinal relaxation times (τ_L) in the manner expected.[4] k_{12} is additionally measured in a low molecular weight poly(ether) solvent, $CH_3O(CH_2CH_2O)_8CH_3$, under the premise that relaxations of solvent dipoles that are attached to polymeric chains should be much slower than those characteristic of monomeric solvents and accordingly should provoke smaller values of k_{12}. Such a diminution is observed, providing insight into the dynamics of the polymer chain segment dipoles involved in the electron-transfer reaction.

We should note that reaction 1 is the rate-determining step in our scheme because it *occurs in the thermodynamically disfavored direction*. Proof that other steps—electron diffusion of poly($[Os]^{2+}$) states across the redox polymer film or the normally rapid back-reaction of reaction 1—do not interfere is given in the Appendix.

Experimental Section

Chemicals. Acetonitrile, methylene chloride, propylene carbonate (Burdick & Jackson, spectrochemical grade), and dimethoxyethane (Aldrich, anhydrous) were used as received. Acetone, pyridine (Aldrich), and dimethyl sulfoxide (Baker) were purified by standard methods.[12] Poly(ethylene glycol) dimethyl ether (Me_2EG-400; Polyscience; nominal

---

[1] For recent reviews, see: (a) Maroncelli, M.; MacInnis, J.; Fleming, G. R. *Science* **1989**, *243*, 1674. (b) Bagchi, B. *Annu. Rev. Phys. Chem.* **1989**, *40*, 115.

[2] Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

[3] Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679.

[4] (a) Calef, D. F.; Wolynes, P. G. *J. Phys. Chem.* **1983**, *87*, 3387. (b) Zusman, L. D. *Chem. Phys.* **1980**, *49*, 295. (c) Alexandrov, I. V. *Chem. Phys.* **1980**, *51*, 449. (d) Van der Zwan, G.; Hynes, J. T. *J. Chem. Phys.* **1982**, *76*, 2993. (e) Hynes, J. T. *J. Phys. Chem.* **1986**, *90*, 3701.

[5] (a) Simon, J. D. *Acc. Chem. Res.* **1988**, *21*, 128. (b) Barbara, P. F.; Jarzeba, W. *Acc. Chem. Res.* **1988**, *21*, 195.

[6] (a) Jarzeba, W.; Walker, G. C.; Johnson, A. E.; Kahlow, M. A.; Barbara, P. F. *J. Phys. Chem.* **1988**, *92*, 7039. (b) Kang, T. J.; Kahlow, M. A.; Giser, D.; Swallen, S.; Nagarajan, V.; Jarzeba, W.; Barbara, P. F. *J. Phys. Chem.* **1988**, *92*, 6800.

[7] (a) Gennett, T.; Milner, D. F.; Weaver, M. J. *J. Phys. Chem.* **1985**, *89*, 2787. (b) Hupp, J. T.; Weaver, M. J. *J. Phys. Chem.* **1985**, *89*, 2795. (c) McManis, G. E.; Golovin, M. N.; Weaver, M. J. *J. Phys. Chem.* **1986**, *90*, 6563. (d) Nielson, R. M.; McManis, G. E.; Golovin, M. N.; Weaver, M. J. *J. Phys. Chem.* **1988**, *92*, 3441. (e) McManis, G. E.; Weaver, M. J. *Chem. Phys. Lett.* **1988**, *145*, 55.

[8] (a) Opallo, M. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 339. (b) Kapturkiewicz, A.; Behr, B. *J. Electroanal. Chem.* **1984**, *179*, 187. (c) Kapturkiewicz, A.; Opallo, M. *J. Electroanal. Chem.* **1985**, *185*, 15.

[9] (a) Harrer, W.; Grampp, G.; Jaenicke, W. *J. Electroanal. Chem.* **1986**, *209*, 223. (b) Grampp, G.; Harrer, W.; Jaenicke, W. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 161. (c) Harver, W.; Grampp, G.; Jaenicke, W. *Chem. Phys. Lett.* **1984**, *112*, 263.

[10] Zhang, X.; Yang, H.; Bard, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 1916.

[11] Leidner, C. R.; Murray, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 1606.

[12] Mann, C. K. In *Electroanalitical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1969; Vol. 3.

0002-7863/91/1513-5183$02.50/0

Table I. Solvent Properties and Electron-Transfer Kinetic Data for Cross-Reaction 1

solvent	ϵ_s[a]	ϵ_{op}[a]	$1/\epsilon_{op} - 1/\epsilon_s$	η,[a] cp	τ_L,[b] ps	D_s,[c] 10^6 cm^2/s	ΔE^0,[d] V	$k_{12}\Gamma$,[e] cm/s	k_{12},[f] M^{-1} s^{-1}	k_{12}^{corr},[g] M^{-1} s^{-1}
CH_3CN	35.94	1.800	0.528	0.341	0.2	8.3	0.170	1.7×10^{-2}	1.7×10^5	1.7×10^5
acetone	20.56	1.839	0.492	0.3029	0.3	8.7	0.200	7.2×10^{-3}	7.2×10^4	1.3×10^5
CH_2Cl_2	8.93	2.020	0.383	0.4414	0.4	6.1	0.280	1.9×10^{-3}	1.9×10^4	1.6×10^5
py	12.91	2.272	0.363	0.884	1.2	2.5	0.200	3.4×10^{-3}	3.4×10^4	6.1×10^4
DME	7.20	1.899	0.388	0.455	1.9	5.2	0.185	2.7×10^{-3}	2.7×10^4	3.6×10^4
DMSO	46.45	2.183	0.437	1.991	2.35	1.5	0.170	1.7×10^{-3}	1.7×10^4	1.7×10^4
PC	64.92	2.016	0.481	2.53	2.7	1.3	0.145	1.3×10^{-3}	1.3×10^4	8.0×10^3
Me_2PEG-400	9.16[h]	2.128[h]	0.378[h]	14.4	22	0.27	0.220	2.4×10^{-4}	2.4×10^3	6.0×10^3

[a] From *Organic Solvents*, 4th ed.; Wiley-Interscience: New York, 1986. [b] Longitudinal relaxation time, from ref 7a,c and 18. [c] Diffusion coefficient of $[Fe(Me_2phen)_3]^{2+}$. [d] Formal potential difference, $\Delta E^0 = E^{0\prime}_{Fe(III/II)} - E^{0\prime}_{Os(III/II)}$. [e] Effective heterogeneous rate constant, uncorrected for variation in ΔE^0. [f] Calculated with $\Gamma = 1 \times 10^{-10}$ mol/cm^2 (monolayer) from $k_{12}\Gamma$. [g] Electron-transfer rate constant of reaction 1, normalized to ΔE^0 = 170 mV. [h] For ϵ_s, assume the value for tetraglyme (*Industrial Solvent Handbook*; Noyes Data Corporation: Park Ridge, NJ, 1985); ϵ_{op} was obtained from our refractive index measurement (n_D = 1.4587 at 23 °C).

MW 400, av) was dried in vacuo (50 °C). $LiClO_4$, Et_4NClO_4, and Bu_4NClO_4 electrolytes were recrystallized and dried in vacuo (50 °C) and used throughout at 0.1 M concentrations.

Measurements. A 10-μm (diameter) Pt working microelectrode and 26-gauge wire Pt auxiliary and Ag pseudoreference electrodes were sealed in a cylinder of insulating materials and polished so that the wire tips define the electrodes.[13] The 10-μm Pt working electrode was coated with a thin film of poly($[Os(bpy)_2(vpy)_2](PF_6)_2$) by electropolymerization from 0.3–0.5 mM solutions of its monomer, cycling the potential through the ligand reduction waves rapidly (50 V/s) to minimize deposition beyond the microelectrode edge.[14] The quantity of deposited poly[Os] polymer, Γ_T (mol/cm^2), was 1×10^{-8} mol/cm^2 or less, as determined from the charge under the Os(II/III) cyclic voltammetric wave in 0.1 M Et_4NClO_4/CH_3CN. All kinetic measurements were conducted in solvents containing 0.1 M electrolyte, each with a freshly prepared redox film and $[Fe(Me_2phen)_3]^{2+}$ solution. Electrochemical equipment was of standard design.[15] The viscosities of Me_2PEG-400 and its mixtures with CH_3CN, all containing 0.1 M $LiClO_4$, were measured by using Cannon Ubbelohde type viscometers in a temperature bath. All experiments were at 23 ± 1 °C.

Results

Reaction 1. Electron-Transfer Kinetics. Figure 1 presents the essential elements of the k_{12} measurement in 0.1 M Et_4NClO_4/CH_3CN. Curve A is a cyclic voltammogram for the poly($[Os]^{3+/2+}$) couple in the absence of $[Fe(Me_2phen)_3]^{2+}$, from which Γ_T is measured, and curves B and C show the oxidation of $[Fe(Me_2phen)_3]^{2+}$ at Pt microelectrodes coated[16] and not coated with a poly[Os] film. The potential of curve B is slightly more negative than that of curve C, which is more positive than that of curve A, both since the mediation reaction 1 is thermodynamically disfavored.[17] The curve B limiting current is jointly limited by the rate of reaction 1 and $[Fe(Me_2phen)_3]^{2+}$ diffusion to the redox polymer/solution interface,[17] whereas the curve C current is limited only by the latter process and is larger. The curve B limiting current is related to the characteristic currents i_{kin} and i_{MT} for reaction 1 and $[Fe(Me_2phen)_3]^{2+}$ diffusion, respectively, by[17]

$$(i_{lim})^{-1} = (i_{MT})^{-1} + (i_{kin})^{-1} = (4rnFD_sC_s)^{-1} + (nF\pi r^2 k_{12}\Gamma C_s)^{-1} \tag{2}$$

where C_s and D_s are the solution concentration and diffusion coefficient of $[Fe(Me_2phen)_3]^{2+}$, r is the microelectrode radius, k_{12} is the second-order reaction 1 rate constant (cm^3/(mol s)), and Γ is the quantity of osmium complex in the outermost layer of the poly[Os] film. The product $k_{12}\Gamma$ represents the heterogeneous electron-transfer rate constant (cm/s) for $[Fe(Me_2phen)_3]^{2+}$ oxidation at the redox polymer surface. The mass transport current i_{MT} is measured from curve C.

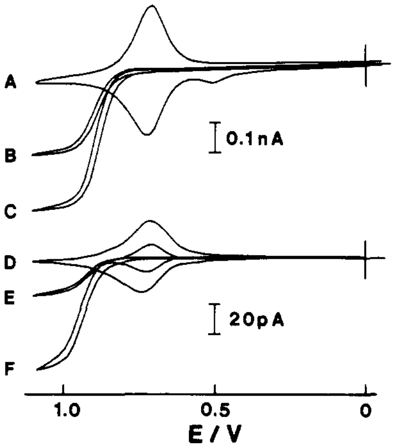

Figure 1. Microelectrode voltammetry of (a) 10-μm Pt disk coated with poly[Os], $\Gamma_T = 5.7 \times 10^{-9}$ mol/cm^2, in 0.1 M Et_4NClO_4/CH_3CN, 50 mV/s; (b) the same electrode in 0.22 mM $[Fe(Me_2phen)_3]^{2+}$, 0.1 M Et_4NClO_4/CH_3CN, 5 mV/s; (c) naked 10-μm Pt disk in 0.22 mM $[Fe(Me_2phen)_3]^{2+}$, 0.1 M Et_4ClO_4/CH_3CN, 5 mV/s; (d) 10-μm Pt disk coated with poly[Os], $\Gamma_T = 4.9 \times 10^{-9}$ mol/cm^2, 0.1 M $LiClO_4/Me_2PEG$-400, 10 mV/s; (e) the same electrode in 1.7 mM $[Fe(Me_2phen)_3]^{2+}$, 0.1 M $LiClO_4/Me_2PEG$-400, 5 mV/s; (f) naked 10-μm Pt disk in 1.7 mM $[Fe(Me_2phen)_3]^{2+}$, 0.1 M $LiClO_4/Me_2PEG$-400, 5 mV/s. Cross represents 0 A and 0 V vs SSCE using Os(III/II) peak as an internal reference (in CH_3CN, $E^\circ_{Os(III/II)}$ = 0.72 V vs SSCE).

Figure 1B and eq 2 yield $k_{12}\Gamma$ = 0.017 cm/s for reaction 1 in acetonitrile solvent, in good agreement with a previous rotated disk electrode measurement[11] in the same solvent ($k_{12}\Gamma$ = 0.019 cm/s). Analogous experiments in pyridine, dimethoxyethane, methylene chloride, acetone, dimethyl sulfoxide, and propylene carbonate solutions of $[Fe(Me_2phen)_3]^{2+}$ reveal completely parallel behavior except that the value of $k_{12}\Gamma$ varies with the solvent as reported in Table I along with some relevant solvent properties and D_s values. Table I also shows k_{12} values calculated by taking Γ as a monolayer, 1×10^{-10} mol/cm^2, and k_{12}^{corr} values after normalizing k_{12} to a common reaction free energy (correcting for ΔE° variation from solvent to solvent, Table I). Values of $k_{12}\Gamma$ for reaction 1 do not vary with the redox polymer coverage Γ_T (from 1 to 8×10^{-9} mol/cm^2) in different solvents, as expected if reaction 1 involves only the outermost monolayer of poly[Os] sites and on the basis of our previous analysis[11] of this aspect of the interfacial reaction.

Me_2PEG-400 is a viscous (η = 14.4 cp for 0.1 M $LiClO_4$ solution) polymer melt that readily dissolves $LiClO_4$ electrolyte and many electroactive monomers. It has a wide potential window and generally low background currents.[19] Using Me_2PEG-400

---

(13) Geng, L.; Reed, R. A.; Kim, M.-H.; Wooster, T. T.; Oliver, B. V.; Egekeze, J.; Kennedy, R. T.; Jorgenson, J. W.; Parcher, J. F.; Murray, R. W. *J. Am. Chem. Soc.* **1989**, *111*, 1614.

(14) Feldman, B. J.; Ewing, A. G.; Murray, R. W. *J. Electroanal. Chem.* **1985**, *194*, 63.

(15) Dayton, M. A.; Wightman, R. M. *Anal. Chem.* **1981**, *53*, 1842.

(16) The poly($[Os]^{3+/2+}$) wave is not noticeable in Figure 1, curve B, because the film represents a limited quantity of charge and its current dies away at slow potential scan rate, whereas $[Fe(Me_2phen)_3]^{2+}$ is replenished by diffusion so its oxidation current is steady state.

(17) (a) Ikeda, T.; Leidner, C. R.; Murray, R. W. *J. Electroanal. Chem.* **1982**, *138*, 343. (b) Andrieux, C. P.; Dumas-Bouchiat, J. M.; Saveant, J. M. *J. Electroanal. Chem.* **1982**, *131*, 1. (c) Andrieux, C. P.; Saveant, J. M. *J. Electroanal. Chem.* **1982**, *142*, 1.

(18) Saar, D.; Brauner, J.; Farber, H.; Petrucci, S. *Adv. Mol. Relax. Processes* **1980**, *16*, 263.

(19) Longmire, M. L.; Wooster, T. T.; Watanabe, M.; Zhang, H.; Murray, R. W. Manuscript in preparation.

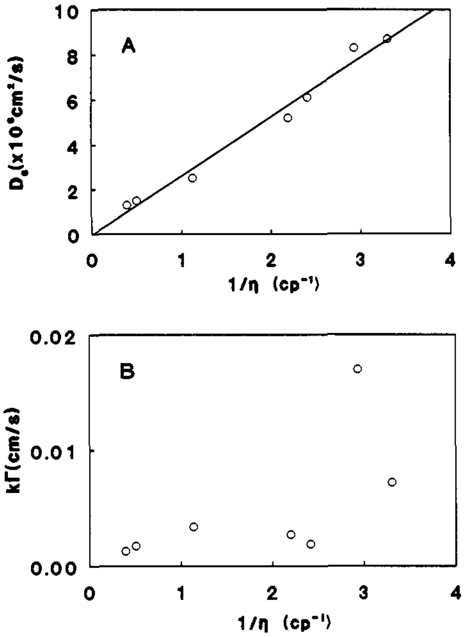

Figure 2. Panel A: $[Fe(Me_2phen)_3]^{2+}$ diffusion coefficient, D_s, vs reciprocal viscosity, eqn. 3, of the monomer solvents. Panel B: $k_{12}\Gamma$ of reaction 1 vs reciprocal monomer solvent viscosity.

polymer as solvent produces voltammetric behavior (Figure 1D–F) like that in the monomeric solvents, except that the limiting currents for $[Fe(Me_2phen)_3]^{2+}$ oxidation are much smaller on both poly[Os]-coated (curve E) and naked (curve F) electrodes. Analysis with eq 2 shows (Table I) that both the $[Fe(Me_2phen)_3]^{2+}$ diffusion coefficient D_s and the reaction 1 $k_{12}\Gamma$ and k_{12}^{corr} values are smaller in the polymer solvent. It is noteworthy that $k_{12}\Gamma$ and k_{12}^{corr} are much smaller in Me_2PEG-400 than in its close chemical relative, DME, which is an explicit illustration of slowed electron-transfer dynamics in a polymeric solvent.

$k_{12}\Gamma$ rate constants were reproducible typically to 30% and 50% in the monomer and polymer solvents, respectively.

Diffusion Coefficients and Viscosity. In the monomer solvents, diffusion coefficients for $[Fe(Me_2phen)_3]^{2+}$ vary (Figure 2A) with viscosity according to the Stokes–Einstein equation

$$D = kT/(6\pi R_h \eta) \qquad (3)$$

where η is viscosity, k the Boltzmann constant, and R_h the hydrodynamic radius of the complex. Figure 2A gives R_h = 8.2 Å for $[Fe(Me_2phen)_3]^{2+}$; this value is needed in the theoretical analysis given below.

Systematic variation in heterogeneous and homogeneous electron-transfer rate constants with solution viscosity has been reported on several occasions;[8b-c,9c,10] Figure 2B shows that no such regular viscosity dependence is found for $k_{12}\Gamma$ in reaction 1. Clearly other factors are involved.

Comparison to Theory for Monomer Solvents. An outer sphere homogeneous electron self-exchange rate constant is classically given by[2,3]

$$k = K_{pre}\kappa_{el}\nu_n \exp[-\Delta G_{Os}^*/RT] = K_{pre}\kappa_{el}\nu_n \exp[-(Ne^2/16\pi\epsilon_0)(1/a - 1/R_h)(1/\epsilon_{opt} - 1/\epsilon_s)/RT] \qquad (4)$$

where ΔG_{Os}^* is activation free energy determined by the outer shell or solvent reorganization energy, a is the equivalent reactant radius, R_h is the reactant internuclear separation (we assume $R_h = 2a$), ϵ_{opt} and ϵ_s are the optical and static dielectric constants for the surrounding solvent, respectively, K_{pre} is the equilibrium constant for forming the precursor (reactant pair) complex prior to electron transfer,[20] κ_{el} is the electronic transmission coefficient,[21] and ν_n describes the net dynamics along the nuclear reaction coordinate in the vicinity of the barrier top.

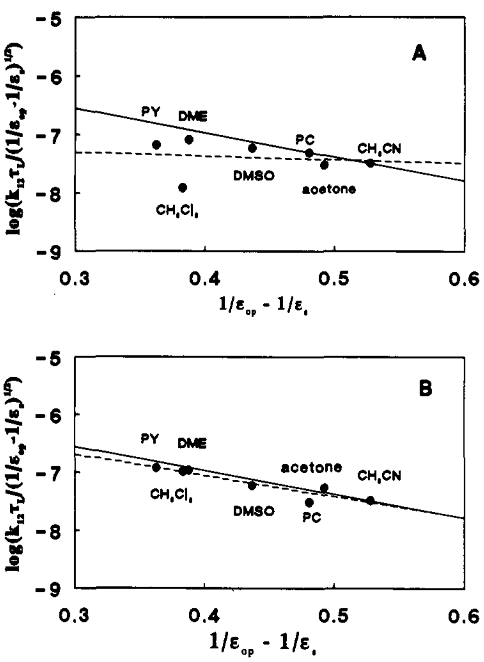

Figure 3. Plots according to eqs 4 and 5 for k_{12} (panel A) and k_{12}^{corr} (panel B). Theoretical line (—) has slope based on $R_h = a_1$ = 8.2 Å for $[Fe(Me_2phen)_3]^{2+}$ and a_2 = 7 Å for[11] poly($[Os]^{3+}$) sites and is forced through the acetonitrile point, for comparison to experimental (- - -).

The classical treatment mainly conveys the solvent influence on electron transfer by the dielectric constant term in ΔG_{Os}^*. However, it is obvious by inspection that the Table I data contain no systematic variation of $(1/\epsilon_{opt} - 1/\epsilon_s)$ with k_{12} and k_{12}^{corr}. That is, while we know[11] that the classical theory satisfactorily describes the free energy dependence of reaction 1, it does not account for the effect of different solvents on its rate.

Recent treatments[4,7] have emphasized that the dynamics of solvent reorganization provide an important contribution to ν_n. At least for a Debye fluid (that having a single relaxation time, τ_D), dielectric continuum treatment of the barrier-crossing dynamics in "over-damped" solvents yields the relation

$$\nu_n = \tau_L^{-1}(\Delta G_{Os}^*/RT)^{1/2} \qquad (5)$$

where τ_L is the solvent longitudinal dielectric relaxation time, related to the Debye relaxation time τ_D by[22]

$$\tau_L = \tau_D(\epsilon_\infty/\epsilon_s) = (\epsilon_\infty/\epsilon_s)4\pi a_s^3\eta/kT \qquad (6)$$

where ϵ_∞ is the high-frequency dielectric constant and a_s the radius of the solvent molecule. These relations introduce a solvent dielectric constant and relaxation time dependence in the preexponential of eq 4.

The rate (k_{12}) of an electron-transfer cross-reaction (i.e., reaction 1) is[2,3] related to the self-exchange rate constants k_{11} and k_{22} of the reactant couples and the reaction free energy (e.g., the equilibrium constant K_{12}) by

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \qquad \log f = (\log K_{12})^2/[4 \log (k_{11}k_{22}/Z^2)] \qquad (7)$$

where Z is the electron-transfer preexponential factor having dimensions of collision frequency, and in the present case, $f \approx 1$.[23]

From these relations and following analogous[9a-b,24] treatments of heterogeneous and homogeneous electron transfers, one predicts that, at constant $\Delta E°$ (i.e., constant K_{12}), $\log [k_{12}\tau_L/(\epsilon_{op}^{-1} - \epsilon_s^{-1})^{1/2}]$

---

(20) (a) Hupp, J. T.; Weaver, M. J. *J. Electroanal. Chem.* **1983**, *152*, 1. (b) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441.

(21) When solvent dynamics become important, κ_{el} tends to unity (i.e., adiabatic or near adiabatic conditions.) See: McManis, G. E.; Nielson, R. M.; Gochev, A.; Weaver, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 5533.

(22) Smyth, C. P. *Dielectric Behavior and Structure*, McGraw-Hill: New York, 1955.

(23) The assumption that f = 1 introduces <10% error in k_{12}; see eq 4, ref 11.

(24) Fawcett, W. R.; Foss, C. A., Jr. *J. Electroanal. Chem.* **1988**, *252*, 221.

should vary linearly with $(\epsilon_{op}^{-1} - \epsilon_s^{-1})$ with slope $(2.303Ne^2/32\pi\epsilon_0RT)(a_1^{-1} + a_2^{-1})$. This analysis is applied to the experimental k_{12} data (Table I) in Figure 3A, where the solid line is forced, with a theoretical slope, through the point for acetonitrile. The experimental–theory comparison is poor; the points are scattered, and the theoretical (—) and experimental (---) slopes differ. However, this comparison neglects the variation in reaction free energy with solvent seen in the $\Delta E°$ values in Table I. Because reaction 1 electron cross-transfers are known[11] to obey the classical free energy relationships, we can normalize the reaction with eq 7 to a rate k_{12}^{corr} at a common free energy $\Delta E° = 0.170$ V, the value in acetonitrile. The k_{12}^{corr} results (Table I) give (Figure 3B) a now impressive linear correlation between $\log [k_{12}^{corr}\tau_L/(\epsilon_{op}^{-1} - \epsilon_s^{-1})^{1/2}]$ and $(\epsilon_{op}^{-1} - \epsilon_s^{-1})$ and a near-theoretical slope (experimental slope −3.61, theoretical −4.01). This agreement rivals that found in previous[7] analysis of solvent effects on electron-transfer reaction rates. (Studies of ionic strength effects by Lewis and Obeng[25] indicate that even better agreement could be sought by extrapolating kinetic data to zero electrolyte concentration, but this was not attempted here.) The result in Figure 3B demonstrates that the solvent dipole reorganization dynamics around the poly($[Os]^{3+}$) sites embedded in the redox polymer/monomer solvent interface are not especially different from those of monomeric solutes. This finding is consistent with the previous[11] observations on reaction 1 free energy effects.

Comparison to Theory for Me_2PEG-400 Polymer Solvent. As noted above, the Figure 1D–F voltammetric measurements in M_2PEG-400 solvent produce a reaction 1 rate constant k_{12}^{corr} that is smaller than observed in any of the monomer solvents (Table I). The Appendix will show that the requirements of eq 2 for measurement of $k_{12}\Gamma$ are satisfactorily met in this medium, so the depressed cross-electron-transfer rate is a real solvent effect on the electron-transfer kinetics. We interpret the solvent effect as being of the same nature as that demonstrated in monomer solvents (i.e., Figure 3B) but in this case governed by motions of dipoles located on linear solvent chains that are sluggish as compared to those in monomeric fluids.

In its melt state, the poly(ether) Me_2PEG-400 is expected to exist as a random coil. The displacements or reorientations of the ether dipoles that are relevant to the electron-transfer barrier crossing in reaction 1 undoubtedly do not involve movement of the entire random coil but instead rearrangements via main-chain bond rotations of one or more segments $-(CH_2CH_2O)-$ or subsegments of the ensemble of coiled molecules comprising the solvation shell of the electron-transfer reactants. Additionally, there may be contributions from the electrolyte dipoles, either directly or more likely through their indirect, coordinative chain cross-linking influence[26] on chain segment mobility. The polymer solvent dynamics are thus considerably more complex than monomeric solvent relaxations.

Since relaxation time data equivalent to those for monomer solvents (Table I) are not known, we chose to employ Figure 3B as a working plot for reaction 1, inquiring what *effective* relaxation "τ_L" value for the polymer solvent would place the experimental k_{12} result in Me_2PEG-400 solvent into agreement with the monomer solvent data. Approximating the static dielectric constant of Me_2PEG-400 with that of tetraglyme (Table I) produces a "τ_L" value of 22 ps (Table I) for Me_2PEG-400. This "τ_L" measures the dynamics for relaxation of ether dipoles located on the poly(ether) chains that are pertinent to the electron-transfer barrier-crossing event in MPEG-400 solvent.

While slower than the relaxation times (Table I) for monomer solvents, the 22-ps "τ_L" for Me_2PEG-400 nonetheless represents a rather fast time scale for polymeric materials. For example, dielectric relaxation loss maxima for poly(propylene oxide), PPO, occur in a much slower (ns) regime[27] and are thought to reflect correlated reorientations of ensembles of dipoles. NMR correlation times for polymer chain motion in poly(ethylene oxide)/$NaClO_4$ are[28] ~400 ps at 69 °C. Polymer dynamics measurements that sense the more rapid structural dipolar relaxations in poly(ethers) appear to be Brillouin scattering data, for which structural relaxation time (τ_s) data has been gathered for poly(propylene oxide) chains.[26a,27,29,30] τ_s values in pure PPO-4000 ($\tau_s \approx 50$ ps) and in solutions containing $NaSO_3CF_3$ ($\tau_s \approx 100$ ps; Na:O = 1:16) all lie substantially above the 10^{-12}-s time range typical of monomer fluid τ_L values (Table I). This is of course a very approximate comparison, but the reaction 1 τ_L time scale is nonetheless encouragingly near known time scales[26a,27,29,30] for local structural motions that lead to dipolar changes.

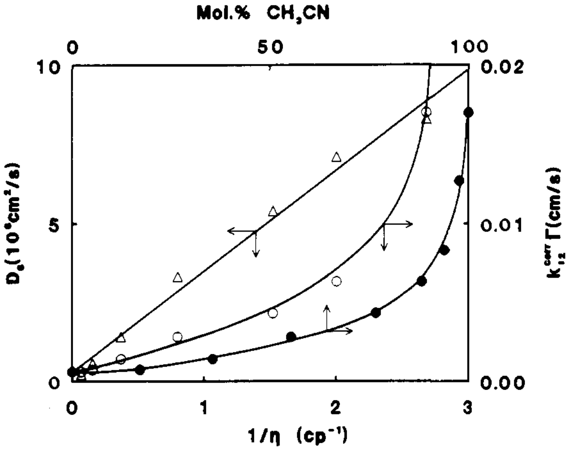

Figure 4. $[Fe(Me_2phen)_3]^{2+}$ diffusion coefficient, D_s, vs reciprocal viscosity, $1/\eta$, of 0.1 M $LiClO_4/CH_3CN/Me_2PEG$-400 mixtures (Δ); $k_{12}^{corr}\Gamma$ vs reciprocal viscosity (○) and mixture mole fraction (moles of CH_3CN vs moles of EO unit) (●).

It is worth emphasizing that the "τ_L" derived for Me_2PEG-400 in reaction 1 is a *microscopic* quantity and bears no correspondence to a time constant estimated by using the *macroscopic* viscosity of the polymer solvent and eq 6. For example, taking a radius of 5 Å (given by root mean square end-to-end distance of polymer chains) for the coiled polymer, we predict via eq 6 a τ_L of ca. 2×10^4 ps, which is far larger than that observed.

Mixtures of Me_2PEG-400 and Acetonitrile. Mixtures of acetonitrile monomer solvent and Me_2PEG-400 polymer solvent were studied to further explore the effects of polymeric media. Acetonitrile is a relatively "fast" solvent with a longitudinal relaxation time ($\tau_L = 0.2$ ps) 100-fold smaller than that for Me_2PEG-400. Of interest was whether a small population of "fast dipoles" in a mixture would negate the slowing of the electron-transfer rate attendant to the sluggish poly(ether) dipoles.

Results in the solvent mixtures are presented in Figure 4. The diffusion coefficient, D_s, of $[Fe(Me_2phen)_3]^{2+}$ continues (Δ) to follow, roughly, solution viscosity according to the macroscopic viscosity law (eq 3). Figure 4 (○) also compares $k_{12}\Gamma$ to reciprocal viscosity; the result is similar to observations by Bard et al.[10] except that the rate constant climbs sharply on the low-viscosity side. Most significantly, the rate constant $k_{12}\Gamma$ of reaction 1 (corrected for change in $\Delta E°$) is responsive (●) to rather small amounts of Me_2PEG-400 in CH_3CN, decreasing sharply and then more gradually as pure Me_2PEG-400 is approached.

Figure 4 (●) clearly shows that dipolar relaxation times for CH_3CN and Me_2PEG-400 do not average together on a simple mole fraction basis, nor does the "fast" CH_3CN dominate the electron-transfer behavior. Inferences possibly drawn from these results are (a) that somehow a relatively small concentration of Me_2PEG-400 chains greatly slows the relaxation dynamics of

---

(25) Lewis, N. A.; Obeng, Y. S. *J. Am. Chem. Soc.* **1988**, *110*, 2306.

(26) (a) Sandahl, J.; Schantz, S.; Borjesson, L.; Torell, L. M.; Stevens, J. R. *J. Chem. Phys.* **1989**, *91*, 655. (b) Ratner, M. A.; Shriver, D. F. *Chem. Rev.* **1988**, *88*, 109.

(27) Yano, S.; Rahalkar, R. R.; Hunter, S. P.; Wang, C. H.; Boyd, R. H. *J. Polym. Sci.* **1976**, *14*, 1877.

(28) (a) Greenbaum, S. G. *Solid State Ionics* **1985**, *15*, 259. (b) Ratner, M. A. *Polym. Electrolyte Rev.* **1987**, *1*, 173.

(29) Torell, L. M.; Schantz, S. In *Polymer Electrolyte Reviews-2*; MacCallum, J. R., Vincent, C. A., Eds.; Elsevier Applied Science: New York, 1989.

(30) Borjesson, L.; Stevens, J. R.; Torell, L. M. *Polymer 28* **1987**, 1803.

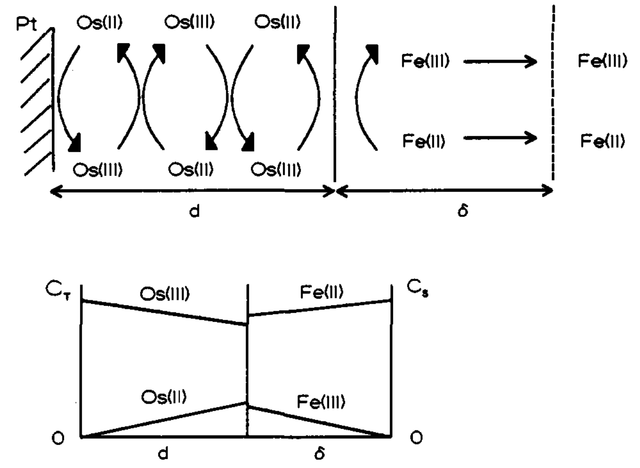

Figure 5. Scheme for reaction 1 and concentration–distance diffusion profiles for poly[Os] sites and metal complex.

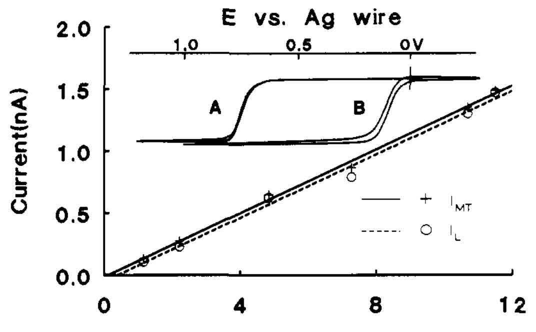

Figure 6. Microelectrode voltammograms (10 mV/s) of 10.7 mM decamethylferrocene, $Cp_2{}^*Fe$, in 0.1 M $LiClO_4/Me_2PEG$-400 at (A) 10-μm Pt disk coated with poly[Os] film, $\Gamma_T = 1.3 \times 10^{-9}$ mol/cm², and (B) not coated, and the ferrocene concentration dependence of the limiting currents.

CH_3CN, (b) the redox polymer surface and the $[Fe(Me_2phen)_3]^{2+}$ reactants are preferentially solvated by coils of Me_2PEG-400 so that the local reaction environment becomes relatively polymer-like, and (c) the rate of dipole relaxations on poly(ether) chains is greatly enhanced in mixtures with CH_3CN. The first of these inferences does not seem very plausible in comparison to the latter two. Indeed, Brillouin scattering results exist that show a relaxation rate increase of poly(propylene oxide) (PPO) upon dilution with methyl cyclohexane.[27] We are unable to carry the analysis further at this point, however.[31]

Acknowledgment. This research was supported in part by grants from the Department of Energy and the National Science Foundation.

Appendix

Justification of Equation 2 for Redox Polymer/Polymer Solvent Interface. We establish here the validity of eq 2 for reaction 1 in a polymer solvent. A crucial issue is whether electron transport in the redox polymer film (D_e) and metal complex diffusion in the polymer solvent (D_s) are sufficiently rapid that poly($[Os]^{2+}$) and $[Fe(Me_2phen)_3]^{3+}$ exit the redox polymer/polymer solvent interface rather than (thermodynamically favored) back-react. The prior evidence is ample[11] that the complex does not penetrate the redox polymer film. Figure 5 shows the concentration–distance diffusion profiles for metal complex and poly[Os] sites set up by the cross-exchange reaction. When E_{Pt} is much more positive than $E°_{Os(III/II)}$

$$i_{lim}/nFA = (D_e/d)C_{Os(II)(x=d)} = (D_e/d)[C_T - C_{Os(III)(x=d)}] \tag{8}$$

$$= (D_s/\delta)C_{Fe(III)(x=d)} = (D_s/\delta)[C_s - C_{Fe(II)(x=d)}] \tag{9}$$

$$= k_{12}C_{Os(III)(x=d)}C_{Fe(II)(x=d)} - k_{21}C_{Os(II)(x=d)}C_{Fe(III)(x=d)} \tag{10}$$

where C_s and C_T are the initial concentrations of $[Fe(Me_2phen)_3]^{2+}$ and poly[Os], $k_{12}/k_{21} = K_{eq} \ll 1$, and d and δ are the thicknesses of the redox polymer film and diffusion layer in the solution. Defining characteristic currents $i_{MT} = nFAD_sC_s/\delta$, $i_{ET} = nFAD_eC_T/d$, and $i_{kin} = nFAk_{12}\Gamma C_s$ gives[17b,c]

$$1 = i_{lim}/i_{kin} + i_{lim}/i_{MT} + i_{lim}/i_{ET} + (i_{lim}/i_{ET})(i_{lim}/i_{MT})[(1/K_{EQ}) - 1]$$

Equation 2 corresponds to the case where the two right-hand terms are negligible. In the present case, in MPEG-400, $D_e = 10^{-8}$ cm²/s[11], $D_s = 3 \times 10^{-7}$ cm²/s, $d \approx 10^{-6}$ cm, $i_{lim} = 10^{-11}$ A, $i_{MT} = 5 \times 10^{-11}$ A, and $i_{ET} \approx 8 \times 10^{-7}$ A, so that $i_{lim}/i_{ET} = 1.2 \times 10^{-5}$, $i_{lim}/i_{MT} = 0.2$, and the fourth right-hand term is 2×10^{-3}, demonstrating that the back-reaction of reaction 1 detracts from the measured rate to a negligible extent.

Since the prior measurement of D_e in poly[Os] was not in MPEG-400 solvent, we explicitly show that $i_{ET} \gg i_{lim}$ by using a substrate with a formal potential *less* positive than that of Os(II/III), making its electron-transfer cross-reaction now fast compared to the transport steps. Figure 6 shows voltammograms and their concentration dependence for decamethylferrocene, $Cp_2{}^*Fe$ ($E°' = 0.13$ V vs Ag wire in Me_2PEG-400/$LiClO_4$), at naked and at poly[Os]-coated electrodes. The currents at the naked electrode, i_{MT}, and those at the coated electrode, i_{lim}, clearly the same, vary linearly with $Cp_2{}^*Fe$ concentration. Were electron diffusion in the redox polymer film current-controlling, the i_{lim} values would become *independent* of $[Cp_2{}^*Fe]$. Since the largest i_{lim} values in Figure 6 are more than 10^2 times larger than i_{lim} values measured for $[Fe(Me_2phen)_3]^{2+}$ in Figure 1E, i_{ET} limitations there can be unambiguously ruled out.

---

[31] (a) We observe, from refractive index measurements of the solvent mixtures, a nonlinear increase in $1/\epsilon_{op}$ with mole percent CH_3CN that parallels (but is smaller than) that in Figure 4. We also attempted to examine differential solvation, following Hupp[31b] and Meyer,[31c] by observing the MLCT transition in the $[Fe(Me_2phen)_3]^{2+}$ complex, but the small change between CH_3CN and Me_2PEG-400 (only 5 nm, blue shift in the latter) prevented any clean inferences. (b) Blackbourn, R. L.; Hupp, J. T. *J. Phys. Chem.* **1988**, *92*, 2817. (c) Kober, E. M.; Sullivan, B. P.; Meyer, T. *J. Inorg. Chem.* **1984**, *23*, 2098.