J. Am. Chem. Soc. **1996,** *118,* 1743−1749

Solvent Dynamics Effects on Heterogeneous Electron Transfer Rate Constants of Cobalt Tris(bipyridine)

Radha Pyati and Royce W. Murray*

Contribution from the Kenan Laboratories of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599-3290

Received August 23, 1995. Revised Manuscript Received December 18, 1995[⊗]

Abstract: This paper presents microelectrode voltammetry-derived heterogeneous electron transfer kinetic rates k_{ET} for the redox couple $[Co(bpy)_3]^{2+/3+}$ in a series of solvents for which (τ_L) longitudinal relaxation values are known (four polar monomeric solvents and four oligomeric polyether solvents, $CH_3O-(CH_2CH_2O)_n-CH_3$ where $n = 1$, 2, 3, and 4) and one, a higher oligomer ($n = 8$, MPEG-400), for which τ_L is estimated. τ_L ranges from 0.2 to 38 ps. The results show that k_{ET} varies inversely with τ_L, and according to other modes of analysis, as predicted for control of the energy barrier-crossing rate by the dynamics of solvent dipolar relaxation. Additionally, the observed k_{ET} is proportional to the diffusion coefficient D_{Co} of $[Co(bpy)_3]^{2+}$, which is rationalized by the mutual connection of D_{Co} and k_{ET} to the solvent viscosity. D_{Co}, k_{ET}, and viscosity were also measured as a function of electrolyte concentration in MPEG-400 which allowed extension of the overall solvent viscosity range. The $[Co(bpy)_3]^{2+/3+}$ rate constant in these media was also proportional to D_{Co}, indicating solvent dynamics control over a time scale range of ca. 500-fold, larger than any previously reported. Experiments at constant viscosity but varied electrolyte concentration demonstrated the absence of strong double layer or ion pairing influences on the reaction rate.

This paper presents experiments showing that the heterogeneous electron transfer rate constant for the metal complex $[Co(bpy)_3]^{2+/3+}$ is inversely proportional to the solvent longitudinal relaxation time τ_L and viscosity and directly proportional to the diffusion coefficient of the metal complex for a series of nine monomer and homologous oligomeric solvents. These results are interpreted as reflecting solvent dynamics rate control over a $>10^2$ range of values. The range is even larger for variations in electrolyte concentration.

The solvent dependence of electron transfer processes has experienced substantial research attention,[1] for both homogeneous and heterogeneous reactions. A number of experimental examples have been reported in which solvent properties affect both the activation barrier to electron transfer and the barrier-crossing frequency[2] either qualitatively or quantitatively as predicted by theory. Useful reviews of the now extensive literature have been prepared by Weaver[3] and Fawcett.[4] Treatment of rate constants usually involves the relation[5]

$$k_{ET} = K_P \kappa_{EL} \nu_N \exp\left(\frac{-\Delta G^*}{RT}\right) \quad (1)$$

in which K_P is the precursor formation constant, κ_{EL} is the adiabaticity parameter, ν_N is the electron-transfer barrier-crossing frequency, and ΔG^* is the sum of outer- and inner-sphere reorganizational energy barriers. The connection of rate constants to the dynamics of solvent dipolar relaxation (longitudinal relaxation time constant, τ_L) for an adiabatic, outer-sphere energy barrier-controlled reaction is[1a−c,5] through the barrier-crossing frequency

$$\nu_N = \tau_L^{-1}\left(\frac{\Delta G_{OS}^*}{4\pi RT}\right)^{1/2} \quad (2)$$

where ΔG_{OS}^* is the outer-sphere reorganizational barrier energy. Thus, rate constants should scale with τ_L^{-1} after accounting for other solvent-dependent factors such as the solvent dielectric properties contained in ΔG_{OS}^*. In the case of a lower reaction adiabaticity, the inverse $k_{ET} - \tau_L^{-1}$ relation is weakened, which has been seen.[3,4] Large inner-sphere reorganizational barriers are also expected to weaken the solvent dynamical dependency of electron transfer rate although theory does predict[3b,6] that a substantial dependence of k_{ET} on τ_L can persist even when $\Delta G_{IS}^* \sim \Delta G_{OS}^*$, and there are experimental examples of this.[7]

Most solvent dynamics investigations reported to date have relied on relatively simple, polar, solvent systems in which the

---

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1996.

(1) (a) Zusman, L. D. *Chem. Phys.* **1980**, *49*, 295. (b) Calef, D. F.; Wolynes, P. G. *J. Phys. Chem.* **1983**, *87*, 3387. (c) Wolynes, P. G. *J. Chem. Phys.* **1987**, *86*, 5133. (d) Maroncelli, M.; MacInnis, J.; Fleming, G. R. *Science* **1989**, *243*, 1674. (e) Kang, T. J.; Kahlow, M. A.; Giser, D.; Swallen, S.; Nagarajan, V.; Jarzeba, W.; Barbara, P. F. *J. Phys. Chem.* **1988**, *92*, 6800. (f) Hynes, J. T. *J. Phys. Chem.* **1986**, *90*, 3701.

(2) (a) Kapturkiewicz, A.; Behr, B. *J. Electroanal. Chem.* **1984**, *179*, 187. (b) Kapturkiewicz, A.; Opallo, M. *J. Electroanal. Chem.* **1985**, *185*, 15. (c) McManis, G. E.; Nielson, R. M.; Gochev, A.; Weaver, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 5533. (d) Fawcett, W. R.; Foss, C. A. *J. Electroanal. Chem.* **1989**, *270*, 103. (e) Fawcett, W. R.; Foss, C. A. *Electrochim. Acta* **1991**, *36*, 1767. (f) Sahami, S.; Weaver, M. J. *J. Electroanal. Chem.* **1981**, *124*, 35. (g) Nielson, R. M.; Weaver, M. J. *J. Electroanal. Chem.* **1989**, *260*, 15. (h) Weaver, M. J.; Phelps, D. K.; Nielson, R. M.; Golovin, M. N.; McManis, G. E. *J. Phys. Chem.* **1990**, *94*, 2949. (i) McManis, G. E.; Golovin, M. N.; Weaver, M. J. *J. Phys. Chem.* **1986**, *90*, 6563. (j) Grampp, G.; Harrer, W.; Jaenicke, W. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 161. (k) Opallo, M. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 339. (l) Jarrer. W.; Grampp, G.; Jaenicke, W. *J. Electroanal. Chem.* **1986**, *209*, 223. (m) Gennett, T.; Milner, D. F.; Weaver, M. J. *J. Phys. Chem.* **1985**, *89*, 2787. (n) Nielson, R. M.; McManis, G. E.; Golovin, M. N.; Weaver, M. J. *J. Phys. Chem.* **1988**, *92*, 3441. (o) Hupp, J. T.; Weaver, M. J. *J. Phys. Chem.* **1984**, *88*, 1463. (p) Harrer, W.; Grammp, G. *Chem. Phys. Lett.* **1984**, *112*, 263. (q) Grampp, G.; Harrer, W.; Hetz, G. *Ber. Bunsen-Ges. Phys. Chem.* **1990**, *94*, 1343. (r) Grampp, G.; Kapturkiewicz, A.; Jaenicke, W. *Ber. Bunsen-Ges. Phys. Chem.* **1990**, *94*, 439. (s) Grampp, G.; Jaenicke, W. *Ber. Bunsen-Ges. Phys. Chem.* **1991**, *95*, 904.

(3) (a) Weaver, M. J.; McManis, G. E. *Acc. Chem. Res.* **1990**, *23*, 294. (b) Weaver, M. J. *Chem. Rev.* **1992**, *92*, 463.

(4) Fawcett, W. R.; Opallo, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2131.

(5) (a) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155. (b) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679.

(6) (a) Sumi, H.; Marcus, R. A. *J. Chem. Phys.* **1986**, *84*, 4894. (b) Nadler, W.; Marcus, R. A. *J. Chem. Phys.* **1987**, *86*, 3906.

(7) (a) Mu, X. H.; Schultz, F. A. *J. Electroanal. Chem.* **1993**, *353*, 349. (b) Nielson, R. M.; Weaver, M. J. *J. Electroanal. Chem.* **1987**, *260*, 15.

0002-7863/96/1518-1743$12.00/0

longitudinal relaxation time constant (τ_L) of the solvent is known. While this approach favors an in-depth dissection of the details of the reaction dynamics,[3] it also restrains the range of values of electron transfer kinetics that can be compared to solvent dynamical properties. It is of interest to know whether solvent dipolar relaxation control can extend over very wide ranges of τ_L values and especially to much slower time scales of motion since little is known about the larger τ_L domain. Exploration of current boundaries of understanding is aided by recourse to solvents less well defined in dynamical terms than those typically studied. One tactic has been to employ[2a,i,l,p,8] variations in solution viscosity through additives or solvent mixtures; our own laboratory has explored polymeric solvents.[9] Electron self-exchange rate constants in mixed-valent solids appear to be generally slowed[10] relative to fluid solutions; whether this reflects local dynamics to any extent is unknown. More extensive variation of solvent dynamics, even when less is known in detail about their dynamical parameters, is thus worth exploring.

This paper presents microelectrode voltammetry-derived heterogeneous electron transfer kinetic results for the redox couple $[Co(bpy)_3]^{2+/3+}$ in a series of solvents for which τ_L relaxation values are known (four monomeric solvents and four oligomeric polyether solvents, $CH_3O-(CH_2CH_2O)_n-CH_3$ where $n = 1$, 2, 3, and 4) and one, a higher oligomer ($n = 8$, MPEG-400), for which τ_L is estimated. This series of solvents allowed exploration of the response of the $[Co(bpy)_3]^{2+/3+}$ reaction rate constant to changes in the solvent τ_L values, using solvents ranging from small and polar (i.e., CH_3CN) to oligomeric and relatively nonpolar (MPEG-400).

Additionally, the $[Co(bpy)_3]^{2+/3+}$ reaction rate was measured in several of the solvents as a function of electrolyte concentration and temperature. Electrolyte concentration changes in MPEG-400 cause large alterations in its macroscopic viscosity. The estimated $\tau_L = 38$ ps solvent dipolar relaxation time for the polymer solvent MPEG-400 is *ca*. 200-fold larger than that for the shortest τ_L solvent (0.2 ps, CH_3CN), and could be increased (judging by viscosity) by another 5-fold through additions of electrolyte. To estimate the effects of varying solvent dipole dynamics, or more properly, of varying the collective diffusive motions of the ion−solvent ensemble, caused by added electrolyte and by temperature and in solvent mixtures, we reckon the changes in solvent dynamics properties indirectly, through (a) measurements of the solution viscosity, η, which is made to vary by a factor >200-fold, and through (b) measurements of the diffusion coefficient, D_{Co}, of the $[Co(bpy)_3]^{2+/3+}$ metal complex, based on the relations[11]

$$\tau_L = \left(\frac{\epsilon_\infty}{\epsilon_s}\right)\tau_D; \qquad \tau_D = \frac{4\pi\alpha^3\eta}{k_B T} \tag{3}$$

and the Stokes−Einstein equation

$$D = \frac{k_B T}{6\pi r_H \eta} \tag{4}$$

where τ_D is the Debye relaxation time and ϵ_∞ and ϵ_s are the high-frequency and static dielectric constants, respectively. Let us state assumptions involved in the use of eqs 3 and 4. They assume Debye and Newtonian solvents, respectively. If there are multiple modes of dipolar relaxation in the oligomeric polyethers, the relaxation most influential on ν_N is assumed to be the same throughout the oligomeric series. The dielectric constants of the five structurally related ether solvents are similar,[11] which is a simplifying aspect of their use; we further assume that the dielectric constants are not significantly changed by added electrolyte. Equation 3 also assumes that the mass transport diffusivity of the complex $[Co(bpy)_3]^{2+/3+}$ (D_{Co}) and the collective diffusivity of solvent dipoles (D_{SOLV}) respond in the same manner to viscosity changes, and when used at varied temperatures, that the solvent relaxations and D_{Co} have similar thermal activation barriers. The merits of these various assumptions will be part of the data analysis.

In first order terms, eqs 2−4 anticipate an inverse relationship of the heterogeneous electron transfer rate constant k_{ET} to viscosity and a proportional relationship to D_{Co}. The experimental observations display these relationships. In the nine solvents for which the τ_L parameter is known, at fixed electrolyte concentration and temperature, the electrode kinetics for the redox couple $[Co(bpy)_3]^{2+/3+}$ not only vary in a nearly inverse proportionality with τ_L but also vary proportionally with D_{Co}. Further, among experiments including variation of electrolyte concentrations and temperatures (to elicit a larger range of solvent dynamical characteristics), the first-order relationships between k_{ET}, η, and τ_L are also unmistakably present. Either the eqs 2−4 first order approximation has some validity for the $[Co(bpy)_3]^{2+/3+}$ reaction, or some other—as yet undefined—kinetic phenomenon not involving solvent dipolar relaxations has properties that lead to the observed proportionalities. While there have been a number of studies of Co(II)/(III) electrode kinetics, that by Crawford and Schultz being an instructive recent one,[12] we are unable to find previous studies that examine the sensitivity of the $[Co(bpy)_3]^{2+/3+}$ redox couple to solvent dynamics.

Experimental Section

Chemicals. $[Co(bpy)_3](PF_6)_2$ was synthesized according to the literature.[13] Cobalt(II) chloride hydrate (Alfa Aesar), dichloromethane and acetone (Fisher), and propylene carbonate, 2,2′-dipyridyl, glyme, diglyme, triglyme, and tetraglyme (Aldrich) were used as received. The latter are isostructural oligomers of formula $CH_3O-(CH_2CH_2O)_n-CH_3$ where $n = 1$, 2, 3, and 4, respectively. Polyethylene glycol dimethyl ether (MPEG-400, $n = 8$, PolySciences, Warrington, PA) was stored under vacuum. $LiClO_4$, Et_4NClO_4, and Bu_4NClO_4 were recrystallized and dried under vacuum at 50 °C. $LiCF_3SO_3$ and *N*-methylpyridinium perchlorate were dried overnight under vacuum at elevated temperatures. Acetonitrile was distilled over calcium hydride.

All solutions were degassed, were 1 mM in $[Co(bpy)_3](PF_6)_2$ and 0.1 M in electrolyte, and were at 23 ± 1 °C unless otherwise specified.

---

[8] (a) Zhang, X.; Yang, H.; Bard, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 1916. (b) Zhang, X.; Leddy, J.; Bard, A. J. *J. Am. Chem. Soc.* **1985**, *107*, 3719. (c) Karpinski, Z. J.; Song, S.; Osteryoung, R. A. *Inorg. Chim. Acta* **1994**, *225*, 9.

[9] (a) Zhang, H.; Murray, R. W. *J. Am. Chem. Soc.* **1991**, *113*, 5183. (b) Zhang, H.; Murray, R. W. *J. Am. Chem. Soc.* **1993**, *115*, 2335.

[10] (a) Sullivan, M. G.; Murray, R. W. *J. Phys. Chem.* **1994**, *98*, 4343. (b) Surridge, N. A.; Sosnoff, C.; Schmehl, R.; Facci, J. S.; Murray, R. W. *J. Phys. Chem.* **1994**, *98*(3), 917. (c) Sosnoff, C. S.; Sullivan, M. G.; Murray, R. W. *J. Phys. Chem.* **1994**, *98*(51), 13643. (d) Surridge, N. A.; Zvanut, M. E.; Keene, R. F.; Sosnoff, C. S.; Silver, M.; Murray, R. W. *J. Phys. Chem.* **1992**, *96*, 962. (e) Dalton, E. F.; Surridge, N. A.; Jernigan, J. C.; Wilbourn, K. O.; Facci, J. S.; Murray, R. W. *Chem. Phys.* **1990**, *141*, 143. (f) Rosseinsky, D. R.; Tonge, J. S.; Bertheolot, J.; Cassidy, J. F. *J. Chem. Soc., Faraday Trans.* **1987**, *83*(2), 231. (g) Facci, J. S.; Abkowitz, M.; Linburg, W.; Knier, F. *J. Phys. Chem.* **1992**, *95*(120), 7908. (h) Facci, J. S.; Abkowitz, M. A.; Limburg, W. W.; Renfer, D. S.; Yanus, J. F. *Mol. Cryst. Liq. Cryst.* **1991**, *194*, 55. (i) Deiss, E.; Sullivan, M.; Haas, O. *J. Electroanal. Chem.* **1994**, *378*(1−2), 93. (j) Ren, X.; Pickup, P. G. *J. Electranal. Chem.* **1994**, 365(1−2), 289. (k) Mathias, M. F.; Haas, O. *J. Phys. Chem.* **1993**, *97*(36), 9217. (l) Velazquez, C. S.; Hutchison, J. E.; Murray, R. W. *J. Am. Chem. Soc.* **1993**, *115*, 7896.

[11] Frolich, H. *Theory of Dielectrics*; Oxford University Press: New York, 1949.

[12] Crawford, P. W.; Schultz, F. A. *Inorg. Chem.* **1994**, *33*, 4344.

[13] Burstall, F. H.; Nyholm, R. S. *J. Chem. Soc.* **1952**, 3570.

Temperature control in activation studies was with a Brookfield circulating bath. The MPEG-400 solution in the activation study contained 1 mM 2,2′-dipyridyl in order to inhibit ligand loss by Co^{2+} that has been observed earlier at elevated temperatures in MPEG-400 solutions.[14] Background voltammetry of 2,2′-dipyridyl/$LiClO_4$/MPEG-400 indicated no faradaic activity in the potential region of $[Co(bpy)_3]^{2+/3+}$.

Viscosity Measurements. Viscosities of solutions were measured using a Cannon-Fenske viscometer. Densities required to calculate absolute viscosity were obtained by weighing a known solution volume in a tared vial. Viscosities of solutions containing MPEG-400 were measured using a Brookfield Digital Viscometer, calibrated with prior data on MPEG-400 viscosity.[9]

Isoviscous solutions were made by mixing appropriate amounts of MPEG-400, tetraglyme and $LiClO_4$ to achieve the desired viscosity. In the 1.54 M solution, tetraglyme and triglyme were used instead of tetraglyme, and MPEG-400 because neat tetraglyme at 1.54 M was too viscous to match the other solutions.

Electrochemical Measurements. Electrochemistry was performed using a locally-built low-current potentiostat and locally-written data acquisition software. Experiments were controlled by an IBM-compatible personal computer interfaced to the potentiostat via an analog-to-digital conversion board.

Microelectrodes were used in order to minimize problems from uncompensated resistance and capacitive distortion.[15] The working electrodes were either 25 or 50 μm diameter platinum microdisks sealed into glass capillaries and cleaned by initial polishing (on microcloth with 0.05 μm alumina powder (Buehler) suspended in Nanopure water, 18.1 MΩ·cm), sonicating in methanol, and drying in a stream of argon. In the interest of reproducibility, the electrodes were polished, rinsed, and sonicated in (only) methanol between series of kinetic measurements. A silver quasireference wire was employed in all solutions except in $LiClO_4/CH_3CN$, where a Ag/0.1 M $AgNO_3$ reference was used. A platinum mesh at the bottom of the electrochemical cell served as the auxiliary electrode.

Uncompensated solution resistance was compensated electronically (positive feedback IR) in many of the rate constant measurements. Rather than relying on circuit instability criteria, the uncompensated solution resistance was measured directly using alternating-current impedance spectroscopy, with a Solartron 1286 Electrochemical Interface and 1255 Frequency Response Analyser (Schlumberger, Houston, TX), both controlled by ZPlot, a commercially available impedance software package (Scribner Associates, Charlottesville, VA). Poising the electrode potential in a double layer region, Nyquist plots over frequencies from 100−1 kHz were obtained. A typical (microelectrode) uncompensated resistance value for 0.01 M $LiClO_4/CH_3CN$ is 75 kΩ, corresponding (using $R_{UNC} = \rho/4r$ where ρ is bulk resistance and r is microelectrode radius) to a bulk solution resistivity of 396 $\Omega^{-1}\cdot cm^{-1}$. The positive feedback IR compensation corresponded typically to 80−90% of the measured resistance. (Since the $[Co(bpy)_3]^{2+/3+}$ rate constants are not very fast, the remaining uncompensated resistance constitutes a minor effect.) In experiments when, for the highest potential scan rate in a series of voltammograms, the product of the uncompensated resistance and four times the peak current equaled less than 3 mV, positive feedback IR compensation was deemed not necessary.

Results and Discussion

Microelectrode Voltammetry: Diffusion Coefficients and Rate Constants. The diffusion coefficient (D) of $[Co(bpy)_3]^{2+}$ was measured from the radial-diffusion-limited plateau currents[15a] ($i_{LIM} = 4nFrDC$, where r is microelectrode radius and C is $[Co(bpy)_3]^{2+}$ concentration) of cyclic voltammograms taken at slow potential scan rates, like those in Figures 1a and 1c in monomer ($LiClO_4/CH_3CN$) and oligomeric polyether ($LiClO_4$/MPEG-400) solvent, respectively. The heterogeneous electron transfer rate constants k_{ET} of the $[Co(bpy)_3]^{2+/3+}$ couple were measured using[16] cyclic voltammetric peak potential separations taken typically in a mixed diffusion geometry regime (includes both linear and partially radial diffusion, as in Figures 1b and 1d). This method, based upon describing the space around a microdisk electrode with a conformal map, was used to avoid capacitative distortions associated with high potential scan rates required to achieve linear diffusion conditions[15a] at the microelectrodes and in the oligomeric polyether solvent. Kinetic analysis based upon achieving purely radial diffusion was precluded by the reproducibility requirements for half-wave potential measurements[17] which are difficult to achieve with the quasireference electrodes employed in the polyether electrolytes. The appropriate theory being available, use of a mixed linear-radial diffusion regime was possible. Each rate constant was measured using two different microelectrode sizes at seven scan rates each to improve statistics. For example, in CH_3CN solvent, over a scan rate range[18] of 3.46 to 13.84 V/s, ΔE_P varied between 105 and 135 mV, and the obtained k_{ET} was constant ($\sigma = \pm 44\%$) with no trend, and in the MPEG solvent, over a scan rate range[19] of 12 to 68 mV/s, ΔE_P varied between 99 and 113 mV, and the obtained k_{ET} was constant ($\sigma = \pm 20\%$) again with no trend. In contrast to historical difficulties experienced in measurements of ferrocene$^{+/0}$ electrode kinetics,[3,4] the electrode kinetics of the $[Co(bpy)_3]^{2+/3+}$ redox couple are moderately slow; this and the use of microelectrodes alleviates the potential for measurement artifacts in electrode kinetics discussed recently by Weaver.[3]

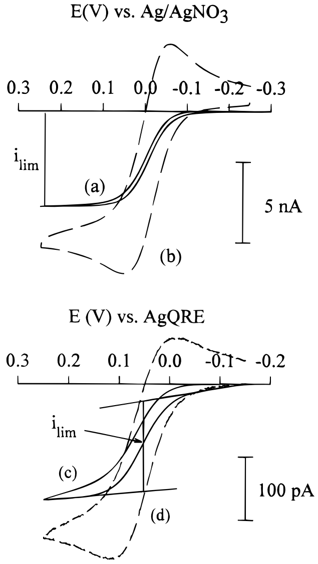

Figure 1. (a, b) 1.01 mM $[Co(bpy)_3](PF_6)_2$ in 1.0 M $LiClO_4/CH_3CN$, r = 27.1 μm: scan rate = 10 mV/s; (b) Scan rate = 308 mV/s. (c, d) 5mM $[Co(bpy)_3](PF_6)_2$ in 1 M $LiClO_4$/MPEG-400, r = 13.5 μm: (a) scan rate = 1 mV/s, (d) scan rate = 30 mV/s.

---

[14] Wooster, T. T.; Murray, R. W. Unpublished results.

[15] (a) Wightman, R. M.; Wipf, D. O. In *Electroanalytical Chemistry: A Series of Advances*; Bard, A. J., Ed.; Marcel Dekker: New York, 1989; Vol. 15, pp 267−353. (b) Howell, J. O.; Wightman, R. M. *Anal. Chem.* **1984**, *56*, 524. (c) Dayton, M. A.; Brown, J. C.; Stutts, K. J.; Wightman, R. M. *Anal. Chem.* **1980**, *137*, 946.

[16] (a) Lavagnini, I.; Pastore, P.; Magno, F. *J. Electroanal. Chem.* **1992**, *333*, 1. (b) Lavagnini, I.; Pastore, P.; Magno, F.; Amatore, C. A. *J. Electroanal. Chem.* **1991**, *316*, 37. (c) Michael, A. C.; Wightman, R. M.; Amatore, C. A. *J. Electroanal. Chem.* **1987**, *267*, 33.

[17] Oldham, K. B.; Myland, J. C.; Zoski, C. G.; Bond, A. M. *J. Electroanal. Chem.* **1989**, *270*, 79.

[18] The following data in 0.1 M Et_4NClO_4/CH_3CN exemplify the independence of k and scan rate: at 3.46 V/s, k = 0.105; 4.99 V/s, k = 0.135; 6.78 V/s, k = 0.105; 8.86 V/s, k = 0.090; 11.21 V/s, k = 0.085; 13.84 V/s, k = 0.105.

[19] The following data in 1.54 M $LiCF_3SO_3$/MPEG-400 exemplify the independence of k and scan rate: at 12 mV/s, $k = 1.5 \times 10^{-4}$; 18 mV/s, $k = 2.2 \times 10^{-4}$; 25 mV/s, $k = 2.9 \times 10^{-4}$; 34 mV/s, $k = 2.0 \times 10^{-4}$; 44 mV/s, $k = 2.4 \times 10^{-4}$; 55 mV/s, $k = 2.1 \times 10^{-4}$; 68 mV/s, $k = 1.9 \times 10^{-4}$.

Table 1. Solvent Parameters, Diffusion Coefficients, and Heterogeneous Electron Transfer Rate Constants for $[Co(bpy)_3]^{2+/3+}$ in Nine Solvents

solvent	ϵ_s[e]	ϵ_{op}[g]	$1/e_s - 1/\epsilon_{op}$	τ_L (ps)[h]	D (cm^2/s)[i]	k (cm/s)[j]	EO's[k]	η (Cp)[l]
CH_2Cl_2[a]	8.93	2.02	0.383	0.4	$7.3 (\pm 0.3) \times 10^{-6}$	$1.0 (\pm 0.4) \times 10^{-1}$		
CH_3CN[b]	35.94	1.800	0.528	0.2	$9.9 (\pm 0.04) \times 10^{-6}$	$8.6 (\pm 0.4) \times 10^{-2}$		
acetone[b]	20.56	1.839	0.495	0.3	$8.8 (\pm 0.5) \times 10^{-6}$	$7.3 (\pm 1.4) \times 10^{-2}$		
PC[c]	64.92	2.016	0.481	2.7	$1.3 (\pm 0.2) \times 10^{-6}$	$3.2 (\pm 2.4) \times 10^{-3}$		
glyme ($n = 1$)[d]	7.20	1.903	0.388	1.7	$2.3 (\pm 0.1) \times 10^{-6}$	$2.4 (\pm 1.3) \times 10^{-2}$	1	0.48
diglyme ($n = 2$)[d]	5.79	1.982	0.332	6.1	$2.5 (\pm 0.2) \times 10^{-6}$	$3.0 (\pm 1.0) \times 10^{-2}$	2	1.07
triglyme ($n = 3$)[d]	5.79f	2.024	0.321	6.8	$6.0 (\pm 0.1) \times 10^{-7}$	$5.7 (\pm 1.5) \times 10^{-3}$	3	2.45
tetraglyme ($n = 4$)[d]	9.16	2.051	0.378	7.8	$3.4 (\pm 0.02) \times 10^{-7}$	$3.0 (\pm 1.5) \times 10^{-3}$	4	3.53
MPEG-400[d]	9.16[f]	2.128	0.361	(38)	$1.1 (\pm 0.1) \times 10^{-7}$	$8.4 (\pm 2.9) \times 10^{-4}$	8	15.7

[a] 0.1 M Bu_4NClO_4. [b] 0.1 M Et_4NClO_4. [c] PC = propylene carbonate, 0.1 M Et_4NClO_4. [d] 0.1 M $LiClO_4$, $CH_3(OCH_2CH_2)_nOCH_3$. [e] Static dielectric constant from ref 32. [f] Estimated to equal that of diglyme and tetraglyme, respectively. [g] Optical dielectric constant from ref 2n and measurements made in 1f. [h] Longitudinal relaxation time, from ref 2m, except the value in parentheses which is extrapolated (eq 3) from the relationship between τ_L and η. An experimental estimate of $\tau_L = 22$ ps for MPEG-400 was made in ref 9b. [i] Diffusion coefficient of $Co(bpy)_3^{2+}$, from two measurements. [j] Electron transfer rate constant of $[Co(bpy)_3]^{2+/3+}$, 7 measurements each at two different microelectrodes. [k] Number of ethylene oxide units. [l] Viscosity, from three measurements.

Table 2. Solution Viscosity, Diffusion Coefficient of $[Co(bpy)_3]^{2+}$, and Electron Transfer Rate Constant of $[Co(bpy)_3]^{2+/3+}$ in CH_3CN and CH_2Cl_2 with Variable Electrolyte Concentration and in MPEG-400/CH_3CN Mixtures

solution	η (Cp)[a]	D (cm^2/s)[b]	k (cm/s)[c]
$LiClO_4/CH_3CN$			
0.01M	0.37	$1.1 (\pm 0.01) \times 10^{-5}$	0.11 (±0.019)
0.05 M	0.38	$1.1 (\pm 0.02) \times 10^{-5}$	0.14 (±0.029)
0.1 M	0.39	$1.1 (\pm 0.01) \times 10^{-5}$	0.099 (±0.029)
0.5 M	0.47	$8.2 (\pm 0.3) \times 10^{-6}$	0.16 (±0.060)
1.0 M	0.66	$5.6 (\pm 0.1) \times 10^{-6}$	0.052 (±0.003)
1.5 M	0.93	$4.2 (\pm 0.1) \times 10^{-6}$	0.12 (±0.063)
Bu_4NClO_4/CH_2Cl_2			
0.1 M	0.53	$7.3 (\pm 0.3) \times 10^{-6}$	0.10 (±0.042)
0.5 M	0.76	$5.1 (\pm 0.4) \times 10^{-6}$	0.058 (±0.022)
1.0 M	1.60	$2.1 (\pm 0.3) \times 10^{-6}$	0.047 (±0.029)
MPEG/%CH_3CN[d]			
0%	45.9	$6.2 (\pm 0.1) \times 10^{-8}$	$2.3 (\pm 0.7) \times 10^{-4}$
10%	33.3	$1.1 (\pm 0.1) \times 10^{-7}$	$1.5 (\pm 0.17) \times 10^{-3}$
20%	24.0	$1.4 (\pm 0.2) \times 10^{-7}$	$2.2 (\pm 0.69) \times 10^{-3}$
30%	19.6	$3.2 (\pm 0.2) \times 10^{-7}$	$5.6 (\pm 3.3) \times 10^{-3}$

[a] Viscosity, from three measurements. [b] Diffusion coefficient of [Co(bpy)32+], two measurements. [c] Electron transfer rate constant of $[Co(bpy)_3]^{2+/3+}$, 7 measurements each at two different microelectrodes. [d] 1.0 M $LiClO_4$ electrolyte.

Table 3. Solution Viscosity, $[Co(bpy)_3^{2+}]$ Diffusion Coefficient and $[Co(bpy)_3]^{2+}$ Electron Transfer Rate Constant in MPEG-400 Solutions with Varied Electrolyte Concentrations

electrolyte (M)	η (Cp)[a]	D (cm^2/s)[b]	k (cm/s)[c]
$LiClO_4$			
0.02 M	14.4	$1.6 (\pm 0.2) \times 10^{-7}$	$1.2 (\pm 0.9) \times 10^{-3}$
0.1 M	15.7	$1.1 (\pm 0.1) \times 10^{-7}$	$8.4 (\pm 2.9) \times 10^{-4}$
0.2 M	18.6	$1.5 (\pm 0.3) \times 10^{-7}$	$5.5 (\pm 1.1) \times 10^{-4}$
1.0 M	45.9	$6.2 (\pm 0.5) \times 10^{-8}$	$2.3 (\pm 0.7) \times 10^{-4}$
1.5 M	66.4	$3.3 (\pm 0.2) \times 10^{-8}$	$2.1 (\pm 0.9) \times 10^{-4}$
N- $MePyClO_4$			
0.02 M	13.9	$2.1 (\pm 0.2) \times 10^{-7}$	$2.4 (\pm 1.4) \times 10^{-3}$
0.2 M	17.2	$1.7 (\pm 0.2) \times 10^{-7}$	$2.7 (\pm 1.4) \times 10^{-3}$
1.0 M	27.7	$9.4 (\pm 0.9) \times 10^{-8}$	$1.1 (\pm 0.6) \times 10^{-3}$
1.5 M	36.1	$4.7 (\pm 1.2) \times 10^{-8}$	$5.9 (\pm 3.5) \times 10^{-4}$
$LiCF_3SO_3$			
0.03 M	14.5	$2.0 (\pm 0.04) \times 10^{-7}$	$1.2 (\pm 0.2) \times 10^{-3}$
0.1 M	15.6	$1.8 (\pm 0.1) \times 10^{-7}$	$1.3 (\pm 0.3) \times 10^{-3}$
0.2 M	17.8	$1.6 (\pm 0.04) \times 10^{-7}$	$1.1 (\pm 0.4) \times 10^{-3}$
1.0 M	40.4	$8.6 (\pm 0.2) \times 10^{-8}$	$6.9 (\pm 0.8) \times 10^{-4}$
1.6 M	74.3	$3.5 (\pm 0.6) \times 10^{-8}$	$3.2 (\pm 1.6) \times 10^{-4}$
$LiClO_4$ isoviscous			
0.02 M[d]	14.4	$1.6 (\pm 0.2) \times 10^{-7}$	$1.2 (\pm 0.9) \times 10^{-3}$
0.1 M[e]	14.5	$1.2 (\pm 0.1) \times 10^{-7}$	$1.5 (\pm 0.2) \times 10^{-3}$
0.2 M[e]	14.3	$1.2 (\pm 0.01) \times 10^{-7}$	$1.3 (\pm 0.3) \times 10^{-3}$
1.0 M[e]	14.3	$1.3 (\pm 0.1) \times 10^{-7}$	$1.3 (\pm 0.1) \times 10^{-3}$
1.5 M[f]	12.9	$6.6 (\pm 3.9) \times 10^{-8}$	$5.1 (\pm 1.9) \times 10^{-4}$

[a] Viscosity, three measurements. [b] Diffusion coefficient of $[Co(bpy)_3]^{2+}$, two measurements. [c] Rate constant of $[Co(bpy)_3]^{2+/3+}$, 14 measurements. [d] MPEG-400 only. [e] Tetraglyme:MPEG-400 mixtures: 0.1 M, 1:19 (v/v); 0.2 M, 1:5.25 (v/v); 1.0 M, 7:3 (v/v). [f] Triglyme: tetraglyme mixture, 1:4 (v/v).

Results of these measurements are shown in Tables 1−3 and in Figures 2 and 3. The (fixed electrolyte concentration) rate constant, diffusion coefficient, and dielectric property data in Table 1 are taken in solvents for which τ_L is known or (in the case of MPEG-400) is estimated (see footnote *h*). These solvents comprise a span of *ca*. 200-fold in τ_L values. Table 2 gives rate constant, diffusion coefficient, and viscosity data for a series of electrolyte concentrations in two of these solvents (CH_2Cl_2 and CH_3CN) and for mixtures of CH_3CN with MPEG-400. Table 3 shows results in MPEG-400 at varied electrolyte and in isoviscous experiments (see Experimental Section). Figure 2 shows activation plots for diffusion coefficient and for electron transfer rate constants obtained in propylene carbonate and in MPEG-400; the obtained activation barriers are indicated on the figure. Figure 3 compares rate constants and diffusion coefficients.

We now proceed to the analysis of these results.

Correlation of Rate Constant with Diffusion Coefficient. Proceeding directly to the first-order analysis anticipated by eqs 2−4, Figure 3 plots values of D_{Co} against $[Co(bpy)_3]^{2+/3+}$ heterogeneous electron transfer rate constants, and shows a remarkable result. The upper panel, a plot for only those nine solvents listed in Table 1, for which τ_L is *known*, has a slope of 1.07 ± 0.11, i.e., rate constant varies proportionately to the diffusion coefficient D_{Co}. The out-lier data point is for propylene carbonate, which exhibits a higher frequency relaxation dispersion.[4] Figure 3, upper panel, demonstrates that the $[Co(bpy)_3]^{2+/3+}$ reaction kinetics respond in a sensitive way to diffusive characteristics of the solvent medium, and insofar as the dynamics of solvent dipolar relaxations influencing the barrier crossing frequency (i.e., ν_N) vary in a parallel manner to solute diffusive characteristics, solvent dynamics control of the $[Co(bpy)_3]^{2+/3+}$ electrode reaction is indicated by these results. This will be confirmed later in this paper, through a comparison of τ_L and k_{ET} values.

The lower panel of Figure 3 extends the comparison to all of the rate constant and D_{Co} data from Tables 1−3. Again, the slope is unity. The combination of the upper and lower panels of Figure 3, is a strong indication that variation of electrolyte and temperature are effective ways to manipulate the collective diffusive motions of the ion−solvent ensemble that solvent dipolar relaxation represents. If the results in Figure 3, lower panel, are examined by subsets of the data (see sets of symbols in figure), a correlation can still be seen but the substantial

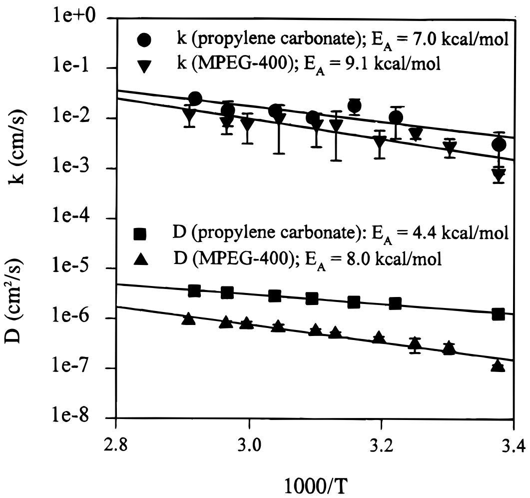

Figure 2. Activation plot of rate constants in 0.1 M Et_4NClO_4/propylene carbonate (●) and 0.1 M $LiClO_4$/MPEG-400 (▼) and diffusion coefficients in propylene carbonate (☐) and MPEG (▲) of $[Co(bpy)_3]^{2+/3+}$.

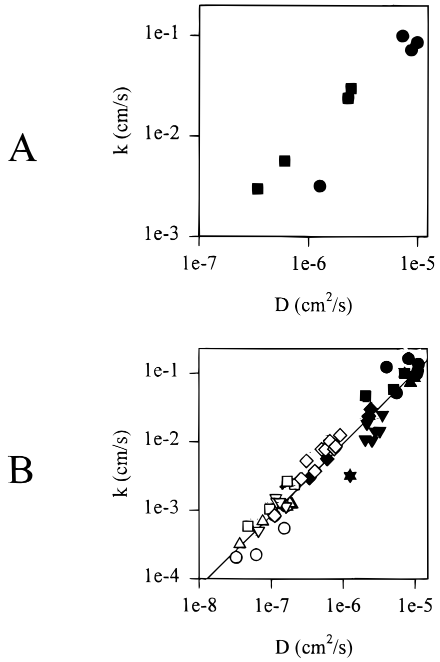

Figure 3. (A) Rate constant of $[Co(bpy)_3]^{2+/3+}$ vs diffusion coefficient in solvents of known τ_L. (●) five solvents of widely varying dielectric constants, (■) glymes. (B) Rate constant vs. diffusion coefficient for all data sets, Tables 1−3: (●) $LiClO_4/CH_3CN$, (■) Bu_4NClO_4/CH_2Cl_2, (▲) five monomer solvents, (▼) Et_4NClO_4/propylene carbonate at several temperatures, (◆) glymes, (+) CH_3CN/MPEG-400 mixtures, (○) $LiClO_4$/MPEG-400, (☐) $NMPyClO_4$/MPEG-400, (△) $LiCF_3SO_3$,/MPEG-400, (▽) isoviscous $LiClO_4$/MPEG-400, (◇) 0.1 M $LiClO_4$/MPEG-400 at variable temperature.

scatter in the data makes it not cleanly convincing. In at least one sub-set of data (the temperature variation in propylene carbonate solvent, ▼), the data seem to indicate a different slope; this is understandable by activation parameters (*vide infra*). However, by provoking solvent variations over a *large* span with different solvents, electrolyte concentrations, and temperatures, as done in Tables 1−3, the data scatter and secondary influences on k_{ET} (and on D_{Co}) are overpowered and the obvious *central* dependency comes out.

Different aspects of these data are now examined in order to further probe the diffusive/dipolar relaxation connection, and the associated assumptions.

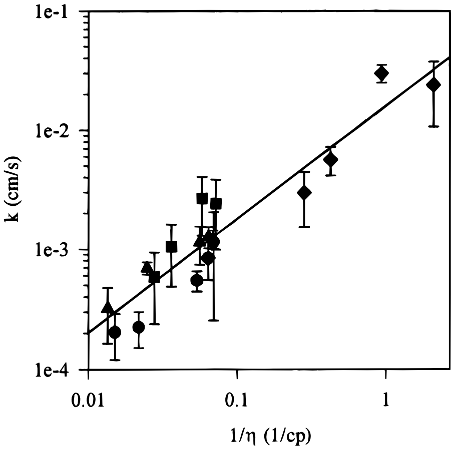

Figure 4. Rate constant of $[Co(bpy)_3]^{2+/3+}$ vs inverse viscosity in MPEG-400: (●) $LiClO_4$, (■) $NMPyClO_4$, (▲) $LiCF_3SO_3$, (◆) glymes.

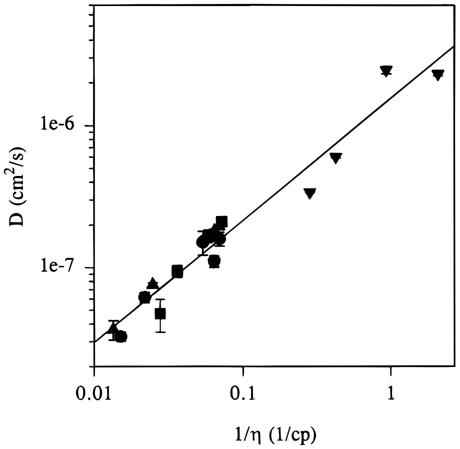

Figure 5. Diffusion coefficient of $[Co(bpy)_3]^{2+/3+}$ vs inverse viscosity: (●) $LiClO_4/CH_3CN$, (■) Bu_4NClO_4/CH_2Cl_2, (+) glymes, (▲) $LiClO_4$, (▼) $NMPyClO_4$, (◆) $LiCF_3SO_3$.

Correlation of Rate Constant and Diffusion Coefficient with Solution Fluidity. Figure 4 examines how rate constants in the oligomeric polyethers vary with changes in viscosity as caused by changes in oligomer polyether chain length (data in Table 1) and in electrolyte concentration (data in Table 3). In this series, the dielectric constants (and other potentially relevant properties like ion-pairing) of the (polyether) solvents should be relatively invariant, and one observes the inverse rate−viscosity correlation anticipated by eqs 2 and 3. Figure 4 shows that manipulating the effective dipolar relaxation behavior of the polyethers by chain length changes and by electrolyte concentration changes are fully equivalent approaches (i.e., data from Tables 1 and 3 fall on the same regression line). The correlation between k_{EX} and η^{-1} is of course the intermediary between the (Figure 3) k_{EX} and D_{Co} correlation if the latter is at all understandable through the connectivity of eqs 2−4. The correlation of Figure 4 is also consistent with previous comparisons[2a,i,l,p,8] of electron transfer rate constants with viscosity that, like here, inferred solvent dynamics origins.

$[Co(bpy)_3]^{2+}$ diffusion coefficients are compared to inverse viscosity (eq 4) in Figure 5, for results obtained at varied electrolyte concentration in monomeric solvents as in Tables 2 (upper) and 3. The macroscopic viscosity changes generated by changes in electrolyte concentration are attributable to electrolyte ion-induced solvent shell formation and resultant solvent ordering and, on average, slowing of solvent dipolar relaxation.[20] The data are presented in a log format to accomodate the wide dynamic range, and there is a clear proportionality as predicted by eq 4. The slope of Figure 5 gives a hydrodynamic radius of 5.3 Å for the $[Co(bpy)_3]^{2+/3+}$ complex that is close to but somewhat smaller than the metal complex radius (∼7 Å).

Double-Layer Effects. Corrections for the influence of the electrical double layer have been made in a number of previous investigations of solvent dynamics effects on heterogeneous electron transfers.[3,4] The relevant relation is the Frumkin equation[21]

$$k_{\mathrm{true}} = k_{\mathrm{app}} \exp\left[\frac{-(\alpha n - z_{\mathrm{Co(bpy)}})F\phi_2}{RT}\right] \qquad (5)$$

where $z_{\mathrm{Co(bpy)}}$ is the charge on the reacting cation, α is the transfer coefficient, and ϕ_2 is the potential at the outer Helmholtz plane. This relation, pertinent to the circumstance of no specifically adsorbed ions, predicts that, in a given solvent, the electrode kinetics should vary with the electrolyte concentration through thus-induced variations in ϕ_2. The direction of the effect depends on the sign of the reactant charge and its formal potential relative to the potential of zero charge on the electrode (*ca.* +0.3 V); these being both positive as in the present case should cause the electron transfer reaction to *accelerate at higher electrolyte concentrations*. (A similar work term prediction can be made for reactions between cations in homogeneous solutions.[22])

Examination of the data in Tables 2 (upper) and 3 (lower, isoviscous data), where electrolyte concentration is varied over a 150-fold range, shows, however, almost no variation of k_{ET} with electrolyte concentration. Table 2 (upper) shows viscosity, diffusion coefficient, and rate constant for a series of electrolyte concentrations in CH_2Cl_2 and CH_3CN solvents. Increasing electrolyte concentration in either solvent causes viscosity to rise moderately with a corresponding small drop in diffusion coefficient. However, in both solvents there is little if any change in rate constant with increasing electrolyte concentration. Table 3 shows viscosity, diffusion, and kinetic results for four experimental series in MPEG-400, varying the supporting electrolyte concentration. These experiments were done in the largest polyether oligomer in order to elicit, in the upper part of the table, a large supporting electrolyte effect[23] on viscosity. Concurrent *decreases* in rate constant are evident in the upper three experiments series in Table 3. Does the change in electrolyte concentration or that in viscosity drive changes in *k*? The data at the bottom of Table 3 (isoviscous experiments) were also taken at widely varied electrolyte concentration but at constant viscosity, as a control to reveal any strong effects exerted by electrolyte-induced changes in double-layer, ion-pairing, or solvent dielectric properties. The results of the isoviscous experiments show *little variation in either rate constants or diffusion coefficient with changing ionic strength*.

The electrolyte concentration results show that the $[Co(bpy)_3]^{2+/3+}$ reaction does not respond to double layer structure in the classical manner. A possible explanation is that a minor population of less highly charged or even neutral ion pairs participates in electron transfers to a sufficient extent as to negate the expected response to electrolyte concentration. In the face of this uncertainty no double-layer corrections to the electrode kinetics are attempted. Others[24] also observed a lack of expected kinetic response to electrolyte concentration changes for solid electrodes in nonaqueous media. Difficulties with double layer corrections in organic solvents at solid electrodes[3,4] are common since the interfacial parameters are not known in any detail.

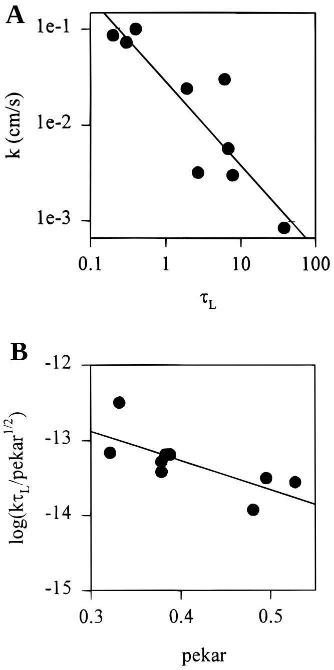

Figure 6. (A) Rate constant of $[Co(bpy)_3]^{2+/3+}$ vs longitudinal relaxation time in log form for nine solvents. (B) $\log\{k_{\mathrm{ET}}\,\tau_{\mathrm{L}}/(\epsilon_{\mathrm{OP}}^{-1} - \epsilon_{\mathrm{s}}^{-1})^{1/2}\}$ *vs* $(\epsilon_{\mathrm{OP}}^{-1} - \epsilon_{\mathrm{s}}^{-1})$ (labeled "Pekar" in the figure).

The important aspect of the results is that the changes in electron transfer rate constants accompanying changes in electrolyte concentration for the other data in Table 3 must be mediated through some other agency than double layer phenomena. We assign that, in a first-order approximation, to the large concurrent changes in solvent viscosity seen for those data that, indirectly, reflect changes in the effective solvent relaxation parameter τ_{L}.

Variation of Rate for Solvents of Known τ_{L}. We next examine the $[Co(bpy)_3]^{2+/3+}$ reaction rate data for solutions of constant electrolyte content, using analyses comparable to previous solvent dynamics studies.[3,4] In particular we test the "Methods I−III" discussed by Weaver.[3] Firstly ("Method I"), a plot of the Table 1 data as log $[k_{\mathrm{ET}}]$ *vs* $[\epsilon_{\infty}^{-1} - \epsilon_{\mathrm{s}}^{-1}]$ has a positive slope (with considerable scatter). It is worth noting in this connection that, in the ether solvents, examination of Table 1 shows that there is no clear correlation between values of τ_{L} and $[\epsilon_{\infty}^{-1} - \epsilon_{\mathrm{s}}^{-1}]$. Secondly ("Method II"), eq 2 predicts that, for constant values of outer-sphere barrier energy, the rate constant should vary inversely with the solvent longitudinal relaxation time τ_{L} . The latter parameter is known for eight of the solvents in Table 1 and was estimated (MPEG-400, see footnote Table 1) for another. Figure 6, upper panel, plots k_{ET} *vs* τ_{L} for these nine cases. The regression slope is -0.87 ± 0.17 which while perhaps a slightly weak dependency on τ_{L} is

---

(20) Gorenbein E. Ya. *Russ. J. Phys. Chem.* **1986**, *35*, 241.

(21) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; John Wiley & Sons: New York, 1980; p 5, 42.

(22) (a) Hirota, N., Carraway, R., Schook, W. *J. Am. Chem. Soc.* **1968**, *90*, 3611. (b) Lewis, N. A.; Obeng, Y. S. *J. Amer. Chem. Soc.* **1988**, *110*, 2306.

(23) MacCallum, J. R.; Vincent, C. A. In *Polymer Electrolyte Reviews*; MacCallum, J. R., Vincent, C. A. Eds.; Elsevier: New York, 1987, pp 23−38.

(24) (a) Phelps, D. K.; Ramm, M. T.; Wang, Y.; Nelsen, S. F.; Weaver, M. J. *J. Phys. Chem.* **1993**, *97*, 181. (b) Gennett, T.; Milner, D. F.; Weaver, *J. Phys. Chem.* **1985**, *89*, 2787.

(25) (a) Szalda, D. J.; Creutz, C.; Mahajan, D.; Sutin, N. *Inorg. Chem.* **1983**, *22*, 2372. (b) Brunschwig, B. S.; Creutz, C.; Macartney, D. H.; Sham, T.-K.; Sutin, N. *J. Chem. Soc., Faraday Discuss.* **1982**, *74*, 113.

within experimental uncertainty the same as the -1.00 slope ideally expected.

Figure 6 neglects, however, the variations in solvent dielectric parameters evident in the Table 1 data. Solvent dielectric constants affect the outer-sphere barrier energy, which appears in eq 1 in the exponential and in 2 as part of the pre-exponential terms, according to the Marcus dielectric continuum model,[5] through the relation

$$\Delta G_{\mathrm{OS}}^* = \frac{Ne^2}{32\pi\epsilon_{\mathrm{o}}}\left(\frac{1}{a} - \frac{1}{R_{\mathrm{h}}}\right)\left(\frac{1}{\epsilon_{\mathrm{op}}} - \frac{1}{\epsilon_{\mathrm{s}}}\right) \qquad (6)$$

where a is the molecule radius (7 Å), and R_{h}, the distance between reactants assuming that reactant-electrode imaging is negligible, is taken as infinity. Inspection of eqs 1 and 2 shows that the dielectric parameter sensitivity can be included ("Method III") by use of plots of log $\{k_{\mathrm{ET}}\,\tau_{\mathrm{L}}/(\epsilon_{\mathrm{OP}}^{-1} - \epsilon_{\mathrm{s}}^{-1})^{1/2}\}$ *vs* $(\epsilon_{\mathrm{OP}}^{-1} - \epsilon_{\mathrm{s}}^{-1})$, which is shown in Figure 6, lower panel. The line shown has a slope of -3.90 and uncertainty indistinguishable from the theoretical one of -4.35 from eqs 2 and 6. Again there is a reasonable correlation with the theory.

This analysis shows that the $[Co(bpy)_3]^{2+/3+}$ reaction, based on conventional analyses, displays to a good approximation the behavior expected for direct control of the barrier-crossing frequency by the solvent dipole relaxation dynamics.

Temperature Effects. Activation results were presented above in the plots of Figure 2. Temperature has the expected effect of increasing diffusion coefficients and rate constants. For the electron transfer, when solvent dynamics help to control the electron transfer rate, the measured barrier energy $\Delta G_{\mathrm{EXP}}^* = \Delta G_{\mathrm{ET}}^* + \Delta G_{\mathrm{DIPOLE}}^*$, i.e., a summation[3,4,26] of the electron transfer (eq 1) and dipolar relaxation thermal barriers. Estimating $\Delta G_{\mathrm{DIPOLE}}^*$ (by subtracting ΔG_{OS}^* calculated using eq 6 from $\Delta G_{\mathrm{EXP}}^*$) gives $\Delta G_{\mathrm{DIPOLE}}^* \approx 1.7$ and 7.0 kcal/mol in propylene carbonate and MPEG-400 solvent, respectively. These estimates of $\Delta G_{\mathrm{DIPOLE}}^*$ (probably *over*estimates owing to neglect of entropic[28] and inner-sphere barrier[25] contributions) can be compared to the 4.4 and 8.0 kcal/mol activation barriers for $[Co(bpy)_3]^{2+}$ diffusion in these two solvents, respectively, and the 6.1 kcal/mol barrier for viscosity[9b] in MPEG-400. This rough comparison shows that the thermal barrier for $[Co(bpy)_3]^{2+}$ diffusion is appreciably larger than that for solvent dipolar relaxation, especially in propylene carbonate, which is not very surprising considering simply the steric size differences of $[Co(bpy)_3]^{2+}$ and the solvent. This conclusion points out the approximation of including the data taken at different temperatures in the diffusivity/electron transfer rate plot of Figure 3, lower panel; there will be a bias in their slope owing to the difference in the thermal barriers. In fact, the subset of data for varied temperatures in propylene carbonate does tend to exhibit a larger slope than the other data, whereas those for varied temperatures in MPEG-400 are not significantly different from the larger data group. One concludes that while, in principle, the varied temperature data should not be mingled in, the discrepancies that result from approximating that $\Delta G_{\mathrm{DIPOLE}}^* \approx \Delta G_{\mathrm{DIFF}}^*$ are not large compared to the overall *central* correlation between rate constant and diffusivity.

Ion Pairing. Insufficient data on ion-pairing of $[Co(bpy)_3]^{2+/3+}$ in the solvents employed prevents thorough examination of its possible effects on rate constants. Previous ion-pairing analyses in heterogeneous electron transfers have looked at double-layer consequences[29] (*vide supra*), effects on formal potential,[30] and the activation barrier to electron transfer.[22] Lewis[22] and Hupp[31] among others have discussed ion-pairing effects in optical electron transfers in solutions. At constant electrolyte concentration, any strong ion-pairing effects should vary with the static dielectric constant and potentially disturb the correlation between rate and τ_{L} in Figure 6, upper panel. Ion-pairing is likely to be present at some level and may contribute to the scatter in the figure, but, if present, it does not destroy the *central* correlation. Likewise, widely varied electrolyte concentrations should change the reservoir of free *vs* ion-paired $[Co(bpy)_3]^{2+}$ and thereby contribute to the slowing of rate with increasing electrolyte concentration. Whether ion-pairing-induced decreases in rate constant could masquerade for viscosity and solvent dynamics-induced ones is an important but unresolved uncertainty in the electrolyte concentration studies represented in Figure 6, lower panel. That ion-pairing is probably not a major factor in rate constant changes for the above reasons is however implied by the relatively constant rate constants observed in the isoviscous experiments of Table 3, lower part.

Acknowledgment. We thank R. H. Terrill for development of the data-acquisition system. R. P. acknowledges a Department of Education Fellowship. This research was supported in part by grants from the National Science Foundation and Department of Energy.

JA952912K

---

[26] The inner-sphere reorganizational energy is calculated to be 2.5 kcal/mol. ν_{is} is a function of molecule vibrational energy and bond distance summed across all the bonds that change length upon change in oxidation state:

$$\Delta G_{\mathrm{is}}^* = 0.5\sum f_{\mathrm{is}}(\Delta a/2)^{1/2}$$

where f_{is} is the reduced force constant of the bond

$$f_{\mathrm{is}} = 2f_{\mathrm{ox}}f_{\mathrm{red}}/(f_{\mathrm{ox}} + f_{\mathrm{red}})$$

and each half of the redox couple has force constant

$$f = 4\pi^2\nu^2\mu_{\mathrm{C-N}}$$

ν_{is} is the symmetric vibrational stretching frequency and $\mu_{\mathrm{C-N}}$ is the reduced mass of the vibrating bond. Other researchers have used the force constants for $[Co(NH_3)_6]^{2+/3+}$ as approximations for $[Co(bpy)_3]^{2+/3+}$.[25] Vibrational frequencies were $\nu_{\mathrm{Co(bpy)3}^{2+}} = 266\ \mathrm{cm}^{-1}$ and $\nu_{\mathrm{Co(bpy)3}^{3+}} = 378\ \mathrm{cm}^{-1}$ from: Saito, Y.; Takemoto, J.; Hutchinson, B.; Nakamoto, K. *Inorg. Chem.* **1972**, *11*, 2003. The symmetric stretching frequency was chosen based upon a similar study of $[Ru(bpy)_3]^{2+}$ stretches: Mallick, P. K.; Danzer, G. D.; Strommen, D. P.; Kincaid, J. R. *J. Phys. Chem.* **1988**, *92*, 5628.

[27] Richardson, J. N.; Harvey, J.; Murray, R. W. *J. Phys. Chem.* **1994**, *89*, 13396.

[28] (a) Richardson, D. E.; Sharpe, P. *Inorg. Chem.* **1991**, *30*, 1412. (b) Sutin, N.; Weaver, M. J.; Yee, E. L. *Inorg. Chem.* **1980**, *19*, 1098. (c) Sahami, S.; Weaver, M. J. *J. Electroanal. Chem.* **1981**, *124*, 35.

[29] It is important to note that conventional consideration of work-term effects in electron transfer are encompassed within double-layer considerations. (a) Bieman, D. J.; Fawcett, W. R. *J. Electroanal. Chem.* **1972**, *34*, 27. (b) Rodgers, R. S.; Anson, F. C. *J. Electroanal. Chem.* **1973**, *42*, 381. (c) Satterberg, T. L.; Weaver, M. J. *J. Phys. Chem.* **1978**, *82*, 1784.

[30] Fawcett, W. R.; Lasia, A. *J. Phys. Chem.* **1978**, *82*, 1114.

[31] Blackbourn, R. L.; Hupp, J. T. *J. Phys. Chem.* **1990**, *94*, 1788.

[32] (a) *Organic Solvents*, 4th ed.; Riddick, J. A., Bunger, W. B., Eds.; Wiley-Interscience: New York, 1986. (b) *Industrial Solvent Handbook*, 3rd ed.; Flick, E. W., Ed.; Noyes Data Corp.: Park Ridge, NJ, 1985.