Probing the Limits: Ultraslow Diffusion and Heterogeneous Electron Transfers in Redox Polyether Hybrid Cobalt Bipyridine Molten Salts

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This paper describes microelectrode voltammetry measurements of self-diffusion coefficients and of heterogeneous Co(II/III) electron-transfer rate constants (k^o) in undiluted molten salts of three cobalt tris(bipyridine) perchlorate complexes in which the bipyridine ligands are "tailed" with poly(propylene oxide) and poly(ethylene oxide) oligomers. The self-diffusion coefficients are measured with potential step chronoamperometry and range from 10^{-12} to 10^{-17} cm²/s, while the quasi-reversible reaction rate constants are measured using cyclic voltammetry and small potential steps and range from 10^{-7} to 10^{-12} cm/s. The k° measurements are unusual in that when rate constants become smaller, the reaction remains quasi-reversible, because of concurrently decreasing selfdiffusion rates. The measurements are, furthermore, accomplished in the face of uncompensated resistances that range from mega- to gigaohms, which is made possible by the combination of microelectrode properties and small diffusivities. The melt in which self-diffusion and k° values are smallest is at a temperature below its nominal glassing transition and in the regime of moleculescale diffusion profiles.

This laboratory has designed and synthesized a number of metal bipyridine salts in which either the ligand¹ or the counterion² is are combined ("tailed") with short polyether chains. Labeled "redox polyether hybrids", these highly viscous, semisolid, molten salts are, in electrochemical studies, used mainly in their undiluted states. The central objectives of the electrochemical investigations, among others, are ascertaining the effects of rigidified environments on diffusion dynamics^{1–3} and on heterogeneous⁴ and

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homogeneous $^{\rm 1.2}$ electron-transfer rates and on developing the required electrochemical methodology. 5

This paper describes measurements of diffusion coefficients and of heterogeneous Co(II/III) electron-transfer rate constants (k^{o}) in cobalt tris(bipyridine) perchlorate melts in which the ligands are "tailed" with very short poly(propylene oxide) and poly-(ethylene oxide) oligomers—from one to seven units in length as shown below:



The abbreviations to be used for the three ligands and associated metal complexes are shown. In these materials, the intrinsic viscosity increases, and self-diffusion coefficients and ionic conductivity decrease, with decreasing polyether chain length. We have pointed^{2a} out that this chain length dependence is unusual, being opposite to that seen in conventional polymers.⁶ The explanation is that the volume fraction of the polyether component (and associated free volume content of the melt) decreases with decreasing chain length.

What is exceptional about the k° measurements presented here is that they are of rate constants approaching 10^{-12} cm/s, yet these reactions are quasi-reversible, and are obtained in the face of uncompensated resistances that are very large, ranging from

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mega- to gigaohms. Such uncompensated resistances would normally be considered prohibitively large, especially for quantitative electrochemical kinetics. Several factors help to make k^0 measurements in these media possible. (a) Microdisk and microband electrodes^{5,7} are tolerant of large uncompensated resistances. Microbands especially yield^{5a} more readily measured currents, due to their larger areas relative to microdisks, without corresponding penalty in R_{UNC}; the larger microband currents counter the diminution of current when D_{PHYS} is very small. (b) The physical self-diffusion constant (D_{PHYS}) of the Co complex in neat melts is very small, with values ranging down to $10^{-17}\,\,\text{cm}^2/\text{s}$ for the shortest polyether tails. (c) D_{PHYS} varies with differing polyether chain lengths attached to the complexes, which permits a systematic^{1,4} variation of self-diffusion properties. (d) Detection of small amounts of (impurity) uncoordinated polyether-tailed bipyridine ligand in the Co tailed bipyridine complex has revealed that small percentages of free ligand impurities "plasticize" the melt and enhance D_{PHYS} , giving another avenue to manipulate the melt rigidity. (e) The electrochemical diffusion geometry becomes linear^{1,5} when D_{PHYS} is small, simplifying the analysis of k° from quasi-reversible cyclic voltammetry (ΔE_{PEAK} values) and from small potential step current-time curves, the methods employed in the report. (f) Last, a previous study⁴ ascertained that the Co-(II/III) reaction is under "solvent dynamics" control, in which circumstance the value of k° decreases linearly with D_{PHYS} . This proportionality helps prevent k^o from falling under diffusion control when melt rigidity is increased and D_{PHYS} drops. The reaction thus remains quasi-reversible over a very wide range of D_{PHYS} values.

The aim of the present paper is to show how the *k*^o measurements of that previous study^{4a} were carried out, and to validate them. (The Supporting Information of the previous paper only outlined the measurements.) It is also worth noting that, while the previous report⁴ of solvent dynamics control of the Co(II/III) reaction in Co bipyridine complex melts ran counter to what was believed⁸ about the electron-transfer properties of Co bipyridine complexes in dilute aqueous solutions, solvent dynamics control has recently been confirmed to be a characteristic of nonwater solvents for this reaction.9

EXPERIMENTAL SECTION

Synthesis of Co(P₃M) and Co(P₂M). P_NM. The synthesis of 2,2'-bipyridyl-4,4'-bis(tripropylene glycol monomethyl ether carboxylate), P₃M, has been published.^{1b} Briefly, dimethyl bipyridine (Reilly) is oxidized to 4,4'-dicarboxy-2,2'-bipyridine with potassium permanganate under acidic reflux conditions, chlorinated with thionyl chloride (Fisher, used as received), and finally esterified with either the tri- or dipropylene glycol monomethyl ether tail (Aldrich). Chromatographic procedures (silica gel with a 4:1 dichloromethane/acetone solvent) remove monotailed products from the desired bitailed bipyridine ligand. NMR analysis (acetone- d_6 , Aldrich) confirms this via a 3:1 peak area ratio of the bipyridine ring protons to the proton α to the first ester group on the chain.

To prepare the complex $Co(P_NM)$, a slight excess of tailed ligand is reacted with $Co(ClO_4)_2 \cdot (H_2O)_6$ in anhydrous methanol,



Figure 1. Illustrations of microdisk (i), microband (ii), and lithographically defined microband (iii) electrodes where W and R indicate working and reference electrodes, respectively.

removing excess tailed ligand by repeated extraction of a carbon tetrachloride solution with cyclohexane. The extraction is only partly effective; four different batches of Co(P₃M) contained (by NMR analysis, described below) different percentages of free tailed ligand. D_{PHYS} is very sensitive to the amount of excess tailed ligand, as will be shown. A fifth batch of Co(P₃M) contained a 5% (mol/mol) excess of cobalt perchlorate. Two samples of the shorter-tail complex Co(P₂M) were prepared.

Co(E7M). This poly(ethylene glycol)-tailed Co complex (perchlorate), described elsewhere, 1b contains, on average, 7.2 ethylene oxide units per "tail".

Electrochemistry. Pt microelectrodes utilized (Figure 1) were as follows: (i) microdisks, (ii) a microband fashioned by exposing the edge of a thin metal foil, and (iii) a lithographically defined microband¹⁰ (LDM). The microdisks consisted of Pt microwires (Goodfellow) sealed in 1.2-mm-diameter glass capillaries, which were potted in an epoxy tube (EPON 828, Miller-Stephenson) together with a 0.5-mm-diameter Ag wire quasi-reference electrode and a 0.7-mm-diameter Pt wire counter electrode, as described before.^{1,7} The three-electrode cell platform was polished with successively smaller alumina slurries (Buehler) down to 0.05 μ m. The microband electrode has been described previously^{5a} and consists of a nominally 0.7 cm \times 2.7 μ m Pt foil edge (Goodfellow) sandwiched between dual Ag reference electrodes (25 μ m wide) with 2- μ m Mylar spacers, all potted in epoxy together with a 1.0mm-diameter Pt wire tip counter electrode. The LDM electrodes consist of individually addressable 2 mm long \times 3.5 μ m wide, 2 mm long \times 10 μ m wide, and 0.5 mm long \times 10 μ m wide Pt metal

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films, 0.1 μ m in height, deposited atop an insulating Si/SiO₂ substrate, and separated by 1.75 μ m from an adjacent Pt film reference electrode. A 0.5 mm \times 0.3 mm Pt pad counter electrode was nearby on the Si/SiO₂ chip.¹⁰

Electrochemically determined areas of the microdisk and LDM electrodes agreed with their nominal geometric areas. The microband Pt foil, under linear diffusion conditions, exhibited a larger than nominal actual area because the seal between the Pt and the Mylar gap had partially delaminated (like "Type-D-old" of ref 5a). Its area was calibrated as before. (See ref 5a and Supporting Information.)

Films of the cobalt complex were cast from a droplet of an acetone solution directly onto the various microelectrode assemblies. Since the redox polyether hybrids tend to be hygroscopic, dry vacuum conditions are required; cast films were vacuum-dried at \sim 70 °C for at least 12 h and vacuum was maintained throughout the experiments. The LDM electrodes were mounted on a locally built temperature-controlled (Lakeshore 330 autotuning temperature controller) vacuum stage, while experiments with microband and microdisk electrodes were done in a vacuum cell temperature controlled via a circulating bath. The vacuum cells were housed in a Faraday cage. Cyclic voltammetry and chronoamperometry were performed using a locally built, ultrasensitive potentiostat¹¹ having current sensitivity down to a few tens of femtoamps. Experimental control was exercised with a PC interfaced with a Keithley DAS-HRES 16-Bit A/D board, using locally written software.

Ionic Conductivities of Melts. Ionic conductivity (e.g., reciprocal resistivity, ρ^{-1}) was measured for melt films cast and dried on an interdigitated array (IDA) electrode¹⁰ having two opposing sets of 50 Pt fingers (3 µm wide, 2 mm long, 0.1 µm high, 2 μ m gap) and mounted in the same vacuum cell used for LDM measurements. Some resistivity measurements were done with fast linear 100-mV sweeps of a potential bias applied between the IDA finger sets with a Hewlett-Packard 8116A generator, measuring current with a locally built current follower and a Nicolet model 310 oscilloscope. Bulk film resistance (R) was taken as the current-potential slope. Ac impedance measurements were done with a Solartron model SI 1260 impedance analyzer and 1267 electrochemical interface, scanning the 10-100 mV amplitude ac voltage frequency from about 1 MHz to 0.5 Hz, at 0 V dc. Specific resistance (ρ) was calculated as $\rho = (R)/(\text{cell constant})$, with the IDA cell constant 0.0848 cm⁻¹ determined as previously.^{1b,d} Values of uncompensated resistance in voltammetric experiments, R_{UNC}, were calculated from $R_{\rm UNC} = \rho/4\pi r$ for microdisks⁶ and from

$$R_{\rm unc} = \frac{\rho}{\rho L} \ln \left(\frac{2d + w}{w} \right) \tag{1}$$

for microbands,^{5a} where r is microdisk radius and w and L are microband width and length, respectively, and d is the gap between working and reference electrodes.

NMR Determination of Free Tailed Ligand. Proton NMR spectra were taken of dry Co complex samples dissolved in chloroform-*d* and under N₂, observing in particular the ratio of bipyridine ring protons of free ligand (i.e., not complexed to Co,



Figure 2. Chronoamperometric Cottrell analysis of the current– time transient (60 s < time < 600 s) for a 500-mV electrolysis step to the plateau of the Co(II/III) wave in melt example C, Co(P₃M) with 5% excess Co at 76 °C. Microband electrode ($A = 3.1 \times 10^{-3}$ cm²). Slope is 9.4 × 10⁻⁸ and intercept is 4.2 × 10⁻¹⁰ A; $D_{PHYS} = 1.1 \times 10^{-12}$ cm²/s. Top inset shows Co(II/III) and background current–time transients for first 300 s; bottom inset shows 0.5 mV/s cyclic voltammogram in which $\Delta E_{PEAK} = 179$ mV, from which $k^{o} = 9 \times 10^{-8}$ cm/s.

excess ligand) to those on the α -carbon on the polyether tails of Co-bound ligand. These ratios were observed in standard addition analyses in which incremental volumes of degassed 0.020 M P_NM ligand in chloroform-*d* were added to the sample in the NMR tube.

RESULTS AND DISCUSSION

Measurements of diffusion coefficients were conducted with potential step chronoamperometry, those of heterogeneous electrontransfer coefficients (mostly) from ΔE_{PEAK} values of cyclic voltammetry. Figure 2 gives some illustrative results for both experiments. Analysis of the chronoamperometric current-time data for diffusion coefficients will be presented first.

Self-Diffusion Results. The Figure 2 inset shows a typical current–time response for a 500-mV potential step, from -0.2 to 0.3 V vs Ag quasi-reference and across the Co(II/III) voltammetric wave to the diffusion-limited regime. Since the microelectrode dimensions (*r* and *w*) are smaller than $[D_{PHYS}t]^{1/2}$, even at long electrolysis times (owing to the very small D_{PHYS} values), linear diffusion conditions prevail and the current–time curve can be analyzed using the Cottrell relation¹²

$$i(t) = nFACD^{1/2}/\pi^{1/2} t^{1/2}$$
(2)

where *A* is electrode area and *C* the concentration of the Co complex in the melt. Density measurements give C = 0.57, 0.71, and 0.44 M in the neat Co(P₃M), Co(P₂M), and Co(E₇M) melts, respectively. The dilution effect of excess free ligand or cobalt is minor and was ignored. Cottrell plots of current–time curves (see Figure 2 inset example) were satisfactorily linear with negligible intercepts. Table 1 lists values of D_{PHYS} determined in this manner for the various melts, which are discussed further below.

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Table 1. Self-Diffusion Coefficients in Polyether-Tailed Cobalt Bipyridine Complex Melts as a Function	n of Tail
Length, Excess Free Ligand and Metal, and Temperature	

$D_{\rm PHYS}$, cm ² /s	<i>T</i> , °C	% free ligand ^a	microelectrode, comments
$1.0(\pm 0.5) imes 10^{-16}$	25	<1	microband ^b
2.6×10^{-16}	25	1.9	microband ^b
$6.0(\pm4.3) imes10^{-15}$	25	3.1	microband, ^b disk ^{c,e}
$3.1(\pm 2.3) imes 10^{-14}$	25	5.1	microband, ^c disk ^{c,d-g}
$2.4 imes10^{-13}$	25	9.0^{b}	disk ^{c,e}
$6.1 imes10^{-12}$	25	36 ^b	disk ^{<i>c,e</i>}
$9.7 imes10^{-12}$	25	100 ^b	disk ^{<i>c,f</i>}
$2.2 imes10^{-14}$	25	5% xs Co	microband, ^b Table 2
$2.6 imes10^{-13}$	46	5% xs Co	microband, Table 2
$1.1 imes10^{-12}$	76	5% xs Co	microband, ^b Tables 2, 4
$1.5 imes10^{-16}$	25	1	microband ^b
$9.0 imes10^{-16}$	25	8	microband ^b
$3.1 imes10^{-17}$	19	1	microband. ^b Table 4
$2.4 imes10^{-15}$	60	1	LDM2, ^{<i>i</i>} Table 4
$1 imes 10^{-16}$	30	1	LDM3, Table S-I
$5 imes 10^{-12}$	25	Nil	disk, ^{c,d-g} Table S-I
	$\begin{array}{c} D_{\rm PHYS},{\rm cm}^2/{\rm s}\\ 1.0(\pm0.5)\times10^{-16}\\ 2.6\times10^{-16}\\ 6.0(\pm4.3)\times10^{-15}\\ 3.1(\pm2.3)\times10^{-15}\\ 3.1(\pm2.3)\times10^{-14}\\ 2.4\times10^{-13}\\ 6.1\times10^{-12}\\ 9.7\times10^{-12}\\ 2.2\times10^{-14}\\ 2.6\times10^{-13}\\ 1.1\times10^{-12}\\ 1.5\times10^{-16}\\ 9.0\times10^{-16}\\ 3.1\times10^{-15}\\ 1\times10^{-16}\\ 5\times10^{-12} \end{array}$	$\begin{array}{cccc} D_{\rm PHYS},{\rm cm}^2/{\rm s} & T,^{\circ}{\rm C} \\ 1.0(\pm 0.5)\times 10^{-16} & 25 \\ 2.6\times 10^{-16} & 25 \\ 6.0(\pm 4.3)\times 10^{-15} & 25 \\ 3.1(\pm 2.3)\times 10^{-14} & 25 \\ 2.4\times 10^{-13} & 25 \\ 6.1\times 10^{-12} & 25 \\ 9.7\times 10^{-12} & 25 \\ 2.2\times 10^{-14} & 25 \\ 2.6\times 10^{-13} & 46 \\ 1.1\times 10^{-12} & 76 \\ 1.5\times 10^{-16} & 25 \\ 9.0\times 10^{-16} & 25 \\ 3.1\times 10^{-17} & 19 \\ 2.4\times 10^{-15} & 60 \\ 1\times 10^{-16} & 30 \\ 5\times 10^{-12} & 25 \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

^{*a*} % excess ligand, calculated with eq 3 (see text), gives percentage of unbound to bound ligand. ^{*b*} Microband A, 3.1×10^{-3} . ^{*c*} Microdisk electrodes of electrochemical radii $5.0,^{d}$ 12.7, ^{*e*} 49.6, ^{*f*} and 95.0^{g} μ m. ^{*b*} Prepared by standard addition of free ligand to Co(P₃M) 4. ^{*i*} LDM area, 7.0×10^{-5} cm². ^{*j*} LDM area, 2.0×10^{-4} cm².

There are important details associated with the diffusion constant determinations. First, owing to the generally large $iR_{\rm UNC}$, there is a delay in the potential applied at the electrode/melt interface reaching a diffusion-limited value. That is, at short times the current can be observed to gradually rise and then commence to fall. Cottrell plots are made only for times longer than the rollover time and at which no curvature was seen at the shortest times in the plot; a 60-s cutoff of the short-time data was ascertained to suffice. Second, the usual approach of "omitting the redox sample from the solution" to assess the background current correction i_{BG} is inapplicable for these neat materials. After some experimentation, including simulating i_{BG} by potential steps of various sizes in the featureless potential regions between the Co(II/III) and Co(II/I) reactions and in similar potential regions in an Fe(P₃M) analogue melt, current-time curves for 100-mV steps in the former were adopted as an approximate, but best available, i_{BG} correction. The Figure 2 inset shows that, in any case, the i_{BG} is small compared to the current for the Co(II/III) reaction.

There are also important details associated with the interpretation of obtained value of D_{PHYS}. First, many apparent diffusivities observed in redox polyether hybrid melts are enhanced by electron self-exchange reactions in the mixed-valent layer formed around the electrode during electrolysis. This effect has been the source1 of much homogeneous electron self-exchange rate constant data, including data for the Co(II/I) reaction. However, the Co(II/III) homogeneous self-exchange rate constant is quite small⁴ and can be calculated to contribute negligibly to the charge transport. In addition, by analogy to the heterogeneous Co(III/II) reaction, the homogeneous Co(III/II) reaction is solvent dynamics-controlled, so that it decreases as D_{PHYS} decreases. The diffusivity obtained from Cottrell plots like Figure 2 is thus assigned to reflect, over the entire range of complexes studied, solely the physical self-diffusion of tailed Co bipyridine complexes. $D_{\rm PHYS}$ exhibits large thermal activation barriers as has been described.1b

Table 2. Counterion (ClO₄⁻) Diffusion Coefficient and Transference Numbers in the Co(P₃M) That Contains 5% Excess Co

temp, °C	$D_{\rm PHYS}$, ^a cm ² /s	$\sigma_{\rm ION}$, $^b \Omega^{-1}$	D_{ClO_4} , cm ² /s	(ClO ₄)
25	$2.2 imes 10^{-14}$	$1.9 imes10^{-8}$	$4.3 imes10^{-12}$	0.99
46	$2.6 imes10^{-13}$	$1.1 imes 10^{-7}$	$2.6 imes10^{-11}$	0.98
77	$7.7 imes10^{-12}$	$9.4 imes10^{-7}$	$2.4 imes10^{-10}$	0.94

^{*a*} Determined with microband electrode; calibrated area 3.1×10^{-3} cm². ^{*b*} From linear regression of Arrhenius plot of conductivities determined by ac impedance and an IDA (cell constant 0.0848 cm⁻¹).

Second, in regard to interpreting D_{PHYS} , no "supporting electrolyte" is added to the Co complex melts (added electrolyte in fact drastically alters^{1d} the melt properties), so the possibility of ionic migration contribution to D_{PHYS} requires consideration. Ionic migration would depress D_{PHYS} of the cationic Co complex. As before,^{1b} a combination of the D_{PHYS} measurement with the melt ionic conductivity (σ_{ION}) was used to calculate the value of the perchlorate counterion diffusion coefficient D_{CIO4} , using the Nernst–Einstein relation¹³

$$D_{\text{CIO}_{4}} = \frac{\left[\frac{\sigma_{\text{ion}}}{F^{2}/RT} - z_{\text{Co(II)}}^{2} D_{\text{Co(II)}} C_{\text{Co(II)}}\right]}{z_{\text{Co(II)}}^{2} C_{\text{CIO}_{4}}}$$
(3)

where z is the ionic charge. Results for ionic conductivity, D_{ClO_4} , and the associated perchlorate counterion transference number, are given in Table 2, for a Co(P₃M) sample (sample 5 in Table 1, prepared with 5% excess cobalt salt). This sample was studied over a range of temperatures in order to encounter a range of conductivities and D_{PHYS} values. Table 2 shows that the perchlorate

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Figure 3. Proton NMR spectrum for Co(P₃M) with 3.1% Xs ligand (sample 3, Table 1) following addition of an increment of standard tailed ligand P₃M solution. Integrals of (free ligand) tailed bipyridine peaks at about 10.4, 10.0, and 9.2 ppm, 0.037, 0.039, and 0.042, respectively, relative to the integral (1.0) of the α -proton on the polypropylene chain of Co-bound P₃M ligand yield an value of 3.9 \pm 0.3% excess ligand (see eq 4). Inset shows standard addition plots for the 1.9 (**●**) and 3.1% (**▼**) excess ligand samples, with the value for the NMR spectrum (**■**) highlighted.

transference number, i.e., the fraction of current carried by ClO_4^- transport, is near unity in all cases. This analysis shows that ionic migration contribution to D_{PHYS} can be ignored. Also, the analysis ignores ion pairing effects; both the calculated D_{ClO_4} and transference numbers will be lower limits in the presence of ion pairing (which probably occurs^{1f,14}).

Plasticization of Self-Diffusion. It was earlier observed^{4a,15} that values of D_{PHYS} vary widely with differing degrees of purification of Co(P₃M) melt preparations from excess tailed bpy ligand. A more detailed assessment of this effect was undertaken to separate experimental uncertainty in the D_{PHYS} measurement from uncertainties in melt composition. A proton NMR analysis was devised to determine the percentage of excess ligand in Co-(P₃M) melt preparations. The spectrum (Figure 3) of a Co(P₃M) melt containing a small amount of free tailed ligand displays bipyridine ring resonances only for the latter (δ about 10.4, 10.0, and 9.2 ppm). The proton resonances on bpy ligands coordinated to the Co(II) center are severely broadened and contact shifted; the α-proton on the polyether tail can be seen, however, at δ = 8.0 ppm. The ratio of the areas of these peaks allows a calculation of the percentage excess tailed ligand, by

% excess ligand =

$$\frac{\frac{1}{3}\sum(\text{area of free ligand bipyridine protons})}{(\text{area of } \delta = 8 \text{ proton})} \quad (4)$$

Standard addition experiments (Table S-III) were also performed on $Co(P_3M)$ samples 1–4. The proton NMR of one sample displayed no discernible free bpy peaks and was taken to contain less than 1% excess ligand. Standard addition plots were linear; an example is shown in Figure 3, inset. The results for excess bpy ligand in $Co(P_3M)$ melts are given in Table 1 (top four entries).



Figure 4. Effect of excess P_3M ligand on the self-diffusion coefficient of $Co(P_3M)$. Data are found in Table 1.

The chronamperometrically determined self-diffusion coefficients for the above $Co(P_3M)$ melts are given in Table 1, as are those for two melts to which larger amounts of free tailed bpy ligand were deliberately added (samples 4+). The D_{PHYS} results, plotted in Figure 4, show that free ligand has a very strong diffusion-plasticizing effect, provoking a change of nearly 10⁵-fold. The largest changes occur at small percentages of excess ligand and are roughly exponential there as anticipated from free volume theory.^{3,16}

A similar, though not as pronounced, variation in D_{PHYS} with free ligand was also observed in two Co(P₂M) samples (Table 1).

Co(III/II) Heterogeneous Electron-Transfer Coefficients from Cyclic Voltammetry. The above results set the stage for Nicholson–Shain^{12a,17} measurements of heterogeneous electrontransfer rate constants, k^{0} , based on peak potential separations (ΔE_{PEAK}) in the quasi-reversible cyclic voltammetry (Figure 2) of the Co complex melts. The ΔE_{PEAK} values are related to rate constants through the characteristic parameter ψ , which is evaluated by digital simulation of the CV (Digisim 2.1)¹⁸ for the given ΔE_{PEAK} value:

$$\psi = k^{0} (D_{\rm o}/D_{\rm r})^{\alpha/2} / [D_{\rm o}\pi\nu(nF/RT)]^{1/2}$$
(5)

where D_0 and D_r are the self-diffusion coefficients of the Co(III) and Co(II) bpy complexes in the melt, respectively (which are equal, as demonstrated later), α is the transfer coefficient (assumed 0.5), and v is potential sweep rate. The ψ values encountered fall within the $6 \times 10^{-4} \le \psi \le 8.5$ boundaries for quasi-reversibility (where reactions show limitations of electrontransfer kinetics and the reverse reaction has to be considered) described by Matsuda and Ayabe.¹⁹ Cyclic voltammograms were taken at several potential sweep rates to yield an average k^0 value.

Special attention was paid to three examples, to explore a range of $D_{\rm PHYS}$, $k^{\rm o}$, and $R_{\rm UNC}$ values. These were (example A) a Co(P₃M) sample ($D_{\rm PHYS} = 3.1 \times 10^{-17}$ at 19 °C), (example B) a Co(P₂M) sample ($D_{\rm PHYS} = 2.4 \times 10^{-15}$ at 60 °C), and (example C) a Co(P₃M) sample having 5% excess Co ($D_{\rm PHYS} = 1.1 \times 10^{-12}$ at 76

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Table 3. Results for Heterogeneous Electron-Transfer Rate Constants from Cyclic Voltammetry for Examples A-C

A	A, ^a Co(P ₂ M) at 19 °C			B, ^b Co(P ₂ M) at 60 $^{\circ}$ C			C, a Co(P ₃ M) with 5% xs Co at 76 $^\circ$ C			6 °C	
$D_{ m PHYS,} \ { m cm}^2/{ m s}^c$	3.1 × 1	10 ⁻¹⁷		2.4×10^{-15}			1.1 ×	10 ⁻¹²			
scan rate, $\mu V/s$	$\Delta E_{\mathrm{PEAK},}$ mV	ψ	$k^{ m o},{ m cm}/{ m s} imes 10^{12}$	scan rate. mV/s	$\Delta E_{\mathrm{PEAK,}}$ mV	ψ	$k^{ m o},{ m cm}/{ m s} imes10^9$	scan rate, mV/s	$\Delta E_{\mathrm{PEAK}},$ mV	ψ	$k^{ m o},{ m cm}/{ m s} imes 10^8$
15	348	0.025	6.0	5	207	0.14	5.1	200	148	0.32	8.5
25	377	0.019	5.8	10	235	0.11	5.5	300	160	0.27	8.8
30	385	0.017	5.9	20	284	0.066	4.8	400	173	0.23	8.6
40	416	0.013	5.0					500	179	0.21	8.9
50	436	0.011	4.6					600	191	0.18	8.5
60	460	0.0084	4.0					700	201	0.17	8.3
70	484	0.0066	3.4								
80	511	0.0050	2.8								
90	549	0.0034	2.0								
av			4.4 (±1.4)				5.1 (± 0.4)				8.6 (±0.2)

^{*a*} Determined at microband electrode with calibrated area 3.1×10^{-3} cm². ^{*b*} Determined at LDM 2 microband $A = 7.0 \times 10^{-5}$ cm². ^{*c*} Determined with chronoamperometry; see Table 1.

°C). The first and third examples represent extreme and "mild" hostility to rate constant determinations and were studied using the Pt foil-edge microband electrode. Example B was studied using the LDM2 (3.5 μ m width) microband. (The Co(III/II) rate constant measurement was actually done for many other Co bpy complexes; those data will be reported elsewhere.²⁰)

Table 3 gives results for Nicholson–Shain measurement of k° for the three examples (A–C), at varied potential sweep rates (notice their small values). The D_{PHYS} and average k° values in these examples are also quite small, but vary among the examples by ~10⁵-fold. For examples B and C, the determined k° values appear to be potential sweep rate-independent, which is classically taken as indication of freedom from effects of iR_{UNC} effects. For example A, there is a slight trend with potential sweep rate, suggesting that some residual iR_{UNC} effect remains.

 $iR_{\rm UNC}$ in a given voltammogram can be roughly estimated as the product of the Co(II→III) cyclic voltammetric peak current and the value of $R_{\rm UNC}$ obtained from ac impedance measurements (Table 4). For the 90 μ V/s scan in example A, a peak current of 1.4×10^{-11} A and $R_{\rm UNC}$ of $2.7 \times 10^9 \Omega$ ($\rho = 5 \times 10^9$) corresponds to $iR_{\rm UNC} = 38$ mV. This ohmic potential loss is much smaller than the measured 549-mV peak potential separation (Table 3), but nonetheless has a perceptible effect on k^o as calculated from a digital simulation of the cyclic voltammogram, which gives $k^o =$ 5×10^{-12} cm/s when the $iR_{\rm UNC}$ is accounted for, as compared to the 2.0×10^{-12} cm/s result of Table 3. This $iR_{\rm UNC}$ effect is roughly a worst-case error for the examples considered here; analogous estimates of $iR_{\rm UNC}$ for examples B and C at the largest potential sweep rates in Table 3 give 0.4 and 5.4 mV, respectively.

Comparison between experimental peak currents and ΔE_{PEAK} values and digitally simulated¹⁸ ones is an alternative approach to analysis of CV data for heterogeneous electron-transfer rate constants. We measure both D_{PHYS} and k° by fitting the voltammogram to theory; the fitting is done solely for i_{PEAK} and ΔE_{PEAK} , not overall shape. This was done for examples A–C, inserting all

Table 4. Comparison of Experimental and Fitted Values of D_{PHYS} and k^{o} for Melt Examples A–C

	A Co(P ₂ M) at 19 °C	B Co(P ₂ M) at 60 °C	C Co(P ₃ M) with 5% xs Co at 76 °C
$D_{\rm PHYS}$, cm ² /s ^a	3.1×10^{-17}	2.4×10^{-15}	$1.1 imes 10^{-12}$
k^{0} , CV, cm/s ^{<i>a</i>,<i>b</i>} simulation	4×10^{-12}	5×10^{-9}	8.6 × 10 ⁻⁶
scan rate, V/s	$5.0 imes10^{-5}$	$1.0 imes 10^{-2}$	$7.0 imes10^{-4}$
D_{SIM} , cm ² /s	$9.0 imes10^{-18}$	$5.5 imes10^{-16}$	$2.5 imes10^{-13}$
k⁰ _{SIM} , cm∕s	$6.1 imes10^{-12}$	$2.6 imes10^{-9}$	$2.5 imes10^{-8}$
k⁰ _{STEP} , cm∕s	$5 imes 10^{-11}$	$7 imes10^{-9}$	$5 imes 10^{-8}$
ρ, Ω -cm ^c	$5.1 imes10^9$	$5.3 imes10^6$	$1.1 imes10^6$
$R_{\rm UNC}, \Omega^d$	$2.7 imes10^9$	$5.8 imes10^{6}$	$5.9 imes10^5$
transf no. (ClO ₄)	0.99	0.99	0.98

^{*a*} Chronoamperometry and cyclic voltammetry performed on microband (calibrated area 3.1×10^{-3} cm²) for examples A and C and on LDM 2 microband (7.0×10^{-5} cm²) for melt example B. ^{*b*} k^o is average of values at several scan rates; see Table 3. ^{*c*} Specific resistance determined with ac impedance for melt examples A and B and with fast linear potential sweeps on melt example C. ^{*d*} Uncompensated resistance, $R_{\rm UNC}$, calculated from $R_{\rm UNC} = \rho^{-1}\pi I \ln[(2d + w)/w]$, as discussed in text.

experimental parameters (electrode area, Co(II) concentration, temperature, potential sweep rate, electrode double-layer capacitance, transfer coefficient (assumed to be 0.5), and ac-impedancedetermined $R_{\rm UNC}$) into the simulation. Such fitting was done for potential sweep rates of 40 μ V/s, 10 mV/s, and 700 μ V/s for examples A, B, and C, respectively, with results shown ($D_{\rm SIM}$ and $k^{o}_{\rm SIM}$) in Table 4 and Figure 5. The $D_{\rm SIM}$ and $k^{o}_{\rm SIM}$ values are in generally good agreement with experimental $D_{\rm PHYS}$ and k^{o} results from the simpler Nicholson–Shain method (especially considering the range of magnitudes).

The simulated voltammetric shapes are also in good agreement with experiment, except for the most slowly self-diffusing $Co(P_2M)$ melt (example A, Figure 5), whose experimental current peak is more "spread-out" than predicted. This discrepancy is all the more interesting because example A, besides having extremely slow self-diffusion and electron-transfer dynamics, falls into an exceptional category on two other accounts. First, according to dif-

⁽²⁰⁾ Crooker, J. C., unpublished results, University of North Carolina, Chapel Hill, NC, 1997.



Figure 5. Experimental (--) and simulated (···) cyclic voltammograms for melt examples A–C, at potential scan rates of 0.05, 10, and 0.7 mV/s, respectively (Table 4). Current bar: 1×10^{-11} , 2.5 × 10^{-11} , and 4.8 × 10^{-9} A, respectively. See Table 4 for electrode areas and parameters used in the simulation.

ferential scanning calorimetry results,²¹ example A exhibits a thermal transition interpreted as a "glassing transition" at 25 °C. This temperature is higher than the 19 °C at which example A was studied, so that it is in a glassy state. We interpret the glassy state as referring to quenching of thermal motions of the short polyether chains attached to the bpy ligands and to a lack of quenching of overall self-diffusion of "hard" Co complex segments. A detailed study of this unusual situation will be reported elsewhere.²¹ Second, the physical self-diffusion rate in example A is so slow that it falls into the "molecule-scale" diffusion regime,²² in which the electrolytic diffusion layer has a dimension $[2D_{PHYS}t]^{1/2}$ comparable to the dimension of the redox substance studied. Thus, in example A ($D_{PHYS} = 3.1 \times 10^{-17} \text{ cm}^2 \text{ s}^{-1}$), the diffusion layer thickness 300 s after the potential step electrolysis is initiated is 14 Å; the Co complex in contrast has a diameter of \sim 13–14 Å. These two notable peculiarities admonish against rationalizing the voltammetric shape of Figure 5 in conventional terms. More information on the molecule-scale diffusion regime will be presented in a future paper.²¹

With regard to double-layer effects, the potential of zero charge (PZC) is unknown for the melt/electrode interface, and the high melt concentrations may hinder ionic space charges forming at



Figure 6. Current time (7 s < *t* < 23 s) transients for potential steps in example B (Co(P₂M) at 60 °C, on LDM2 electrode, plotted according to eq 6. Regression lines (dashed) for 7 s < *t* < 23 s, produce ($i_{t=0}$) 9.8 × 10⁻¹², 1.8 × 10⁻¹², and 2.8.0 × 10⁻¹¹ A intercepts, for steps to E° -60 mV, E° -30 mV, and E° .

the usual depths. Also, the planes of closest approach of the metal complex and of its counterion to the electrode surface probably differ, complicating the interfacial potential profile. For these reasons, no attempt is made to introduce double-layer corrections (Frumkin correction)¹³ on the rate constants.

Co(III/II) Heterogeneous Electron-Transfer Coefficients from Potential Step Current Transients. Another approach to measuring heterogeneous electron-transfer rate constants^{12a} is based on transient currents resulting from potential steps onto the leading edge of the Co(II/III) voltammetric wave. At short times for quasi-reversible charge-transfer kinetics, a plot of current vs $t^{4/2}$ should be linear according¹³ to

$$i = nFAk_{\rm f}C_{\rm o}(1 - 2 Ht^{1/2}/\pi^{1/2})$$
(6)

where the $(i_{t=0})$ intercept yields k_{f} :

$$k_{\rm f} = i_{t=0} / nFAC_{\rm o} \tag{7}$$

and

$$k_{\rm f} = k^{\rm o} \exp[-\alpha n (F/RT) (E - E^{\rm o})]$$
(8)

These relations indicate that a plot of $\ln(k_{\rm f})$ vs $(E - E^{\circ})$ for a series of potential steps gives an intercept of k° , the heterogeneous electron-transfer coefficient. Figure 6 shows several accordingly plotted experimental current—time results for example B, for times 10-20 s, for potential steps onto the Co(II/III) reaction wave. (The E° used was determined from the average of several CV scans.) Figure 7 shows the potential dependence of the rate constants obtained, according to eq 8. Figure 7 is reasonably linear at potential steps to E° and more positive than that. We believe that the curvature results from $iR_{\rm UNC}$ effects, since the currents are larger when the potential step is larger. The key result from Figure 7 is that extrapolation of the points below E° yields a $k_{\rm OSTEP}$ value of 7×10^{-9} cm/s, which agrees with that obtained by cyclic voltammetry, 5×10^{-9} cm/s (Table 4).

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Figure 7. Plots of eq 8 for various overpotential steps (-0.1 to +0.12 V vs E°) in melt example B [Co(P₂M) at 60 °C on the LDM2 electrode]. $k_{\rm f}$ was determined from ($i_{t=0}$) intercepts in plots such as Figure 6.

Similar experiments were performed for melt examples A and C, plotting current vs $t^{1/2}$ for various potential steps over time scales of 300–500 s for example A and 2–5 s for example C. (The different times used are related to the differences in D_{PHYS} and thus time scales of breakdown¹³ of the linearization that led to eq 6, as well as ohmic drop at short times.) The experiments in the example C melt produced $k^{0}_{STEP} = 5 \times 10^{-8}$ cm/s, close to the Table 3 results from cyclic voltammetry. Example A showed a larger difference between the potential step and voltammetric k^{0} values: 5×10^{-11} and 5×10^{-12} cm/s, respectively. This latter observation serves to further illustrate the level of uncertainty in results for the peculiar example A, keeping in mind its molecule-scale diffusion characteristic and that eqs 6–8 presume that transport occurs by conventional diffusion.

The slopes of plots such as Figure 7 give transfer coefficient values (α) of 0.35, 0.60, and 0.41 for examples A–C, respectively.

Self-Diffusion of the Co(III) Complex. Double potential step chronoamperometry was employed to examine the relative self-diffusivities of the Co(II) and Co(III) bipyridine melt complexes. In this experiment, the potential is first stepped to a positive value, remaining there for a time τ , and then stepped back to the initial value (at which time the electrode/melt interface is returned to a Co(II) state). The time dependencies of the oxidative and subsequent reductive current—time transients are analyzed, the former by eq 2 and the latter^{12a} by

$$-i_{\rm r}(t) = \frac{nFACD_r^{1/2}}{\pi^{1/2}} \left[\frac{1}{(t-\tau)^{1/2}} - \frac{1}{t^{1/2}} \right] \tag{9}$$

The results of four such experiments on two melts, the purest

Table 5. Diffusion Coefficients *D*_{PHYS} Determined in Co(P₃M) Melt with Double Potential Step Chronoamperometry

melt sample	electrode	$D_{\rm PHYS(OX)}$	D _{PHYS(RED)}	$D_{\rm OX}/D_{\rm RED}$
3.1% excess	disk ^c	$1.3 imes 10^{-14}$	$9.0 imes 10^{-15}$	1.4
	disk ^c	$6.4 imes10^{-15}$	$5.7 imes10^{-15}$ b	1.1
	microband ^{d}	$1.5 imes10^{-15}$	$1.8 imes 10^{-15}$	0.8
	microband ^d	$3.2 imes 10^{-15}$	$1.8 imes 10^{-15}$	1.8
neat(<1% excess)	microband ^{d}	$1.5 imes 10^{-16}$	5.8×10^{-17}	2.6
^a Switching tim	$e \tau = 4000 s.$	^b Switching ti	ime $\tau = 12$ h.	Microdisk
radius 12.7 <i>u</i> m. ^a N	/licroband ele	ctrode. calibi	ated area A =	$3.1 imes 10^{-3}$

Co(P₃M) melt, and the sample with 3.1% excess ligand sample are given in Table 5. It can be seen, even for extremely large values of τ , that the self-diffusion coefficient obtained from the reverse, Co(II \rightarrow III) oxidation, reaction is essentially identical to that obtained from the Co(III \rightarrow II) reduction. When τ is very large, on the reverse potential step, the electrode is effectively bathed in a sea of the Co(III) complex. That D_{PHYS} is the same in that circumstance is strong evidence that the self-diffusion coefficients for the Co(II) and Co(III) complexes are reasonably the same.

CONCLUDING OBSERVATIONS

cm².

As noted earlier, one objective of this study was validation of the heterogeneous Co(II/III) rate constant determinations that were central to our demonstration^{4a} that this reaction is under solvent dynamics control over an astounding range of 10¹¹-fold in D_{PHYS} and k° , in which these two parameters are proportional to one another. It is useful to note the rough k° –D proportionality is sustained in the three examples presented (Table 3); the ratio k°/D^{-1} is 1 × 10⁵, 2 × 10⁶, and 0.8 × 10⁶ for examples A, B, and C, respectively.

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SUPPORTING INFORMATION AVAILABLE

Information concerning details and table of electrode area determinations, NMR analysis data, Cottrell data, and figure. This material is available free of charge via the Internet at http://pubs.acs.org.

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