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Ion Atmosphere Relaxation Controlled Electron Transfers in Cobaltocenium Polyether Molten Salts

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A room-temperature redox molten salt for the study of electron transfers in semisolid media, based on combining bis(cyclopentadienyl)cobalt with oligomeric polyether counterions, [Cp2Co](MePEG350SO3), is reported. The transport properties of the new molten salt can be varied (plasticized) by varying the polyether content. The charge transport rate during voltammetric reduction of the ionically conductive [Cp2Co](MePEG350SO3) molten salt exceeds the actual physical diffusivity of [Cp2Co]+ because of rapid [Cp2Co]1+/0 electron self-exchanges. The measured [Cp2Co]0+/0 electron self-exchange rate constants (kEX) are proportional to the diffusion coefficients (DCON) of the counterions in the melt. The electron-transfer activation barrier energies are also close to those of ion diffusion but are larger than those derived from optical intervalent charge-transfer results. Additionally, the [Cp2Co]+/0 rate constant results are close to those of dissimilar redox moieties in molten salts where DCON values are similar. All of these characteristics are consistent with the rates of electron transfers of [Cp2Co]+/0 (and the other donor–acceptor pairs) being controlled not by the intrinsic electron-transfer rates but by the rate of relaxation of the ion atmosphere around the reacting pair. In the low driving force regime of mixed-valent concentration gradients, the ion atmosphere relaxation is competitive with electron transfer. The results support the generality of the recently proposed model of ion atmosphere relaxation control of electron transfers in ionically conductive, semisolid materials.

Introduction

This paper describes the results of a continuing investigation using model redox semisolids to probe the microscopic effects of semirigid environments on electron-transfer dynamics and physical mass transport rates. The model semisolids are combinations of polyether oligomers with (normally crystalline) redox-active compounds, that produce highly viscous, amorphous, room-temperature, ionically conductive molten salts. The mass transport and electron-transfer properties of these molten salts (e.g., ionic liquids) can be manipulated by varying the polyether chain, chain length, electrolyte, and redox species and by adding small molecules that “plasticize” the melt. In general, the homogeneous electron self-exchange reactions in the semirigid melts, in the mixed-valent layers formed around electrodes, exhibit small rate constants (kEX) and have large thermal activation energy barriers (EAE,EX) relative to those for analogous reactions in dilute, fluid solutions, or to those predicted from classical Marcus theory for an ether-like dielectric environment. Additionally, the thermal barrier energies are approximately 2-fold larger than those derived from optically induced electron-transfer results based on Hush theory.

Our early analysis of the slow electron-transfer dynamics observed in semisolid redox molten salts was based on a solvent dynamics model. This model has been reconsidered recently, and it appears that a more accurate interpretation can be based on the dynamics of the ion atmosphere surrounding the donor–acceptor reaction pair. Specifically, electron transfer is followed by a Coulombically driven redistribution of neighboring ions that, in low free energy gradients characteristic of mixed-valent concentration gradients, competes with the back electron-transfer reaction. Slow ion relaxation allows a high incidence of back electron transfers and overall rate control by the diffusion rates of the ions. The rates and energy barriers for electron transfer thus reflect not the intrinsic electron-transfer barrier but instead the thermal barrier for counterion transport. The new analysis has been supported by results in tris-bipyridine and tris-phenanthrolin cobalt molten salts, where (a) a 1:1 proportionality is found between the counterion diffusion coefficient (DCON) and both heterogeneous Co(III/II) and homogeneous Co(II/0) electron-transfer rates, (b) the electron-transfer barrier energies are close to those of ion diffusion, and (c) electron transfer becomes silent when the counterion is immobile (e.g., DNA). The consistency of the results obtained by varying the fluidity of the melts through polyether chain length differences, temperature, electrolyte addition, or addition of unattached polyether and CO2 plasticizers adds strength to the analysis. In addition, the rates of homogeneous electron transfers in two ruthenium-complex-based melts are in accord with the ion atmosphere relaxation model.

It is important to study semisolid melt redox materials that differ from the Co and Ru poly-pyridine complexes in order to assess how generally applicable the ion atmosphere model is. The cobaltocenium complex was chosen for this study because, as compared to poly-pyridine Co complexes, it is smaller and more diffusive and it is only singly charged. This report describes mass transport and [Cp2Co]+/0 electron-transfer dynamics in molten salts (Figure 1) in which the cobaltocenium...
species is provided with a sulfonate counterion to which a MePEG-tailed counterion (\([\text{FcTMA}]^+\)) having a MePEG 350 oligomer (methyl-terminated poly(ethylene glycol), average MW 350) is covalently bonded, that is, (MePEG 350 SO₃⁻). The fluidity of the \([\text{Cp}_2\text{Co}] (\text{MePEG}_{350}\text{SO}_3)\) molten salt can be manipulated by adding unattached, neutral MePEG₃₅₀ oligomer as a plasticizer. Electron-transfer and mass transport measurements were made in the neat and MePEG-plasticized \([\text{Cp}_2\text{Co}]^+\) melt as a function of temperature. In addition, a structurally similar melt, ferrocenyltrimethylammonium having a MePEG-tailed counterion (\([\text{FcTMA}]^+\)(MePEG₃₅₀SO₃⁻)) in the \([\text{Cp}_2\text{Co}] (\text{MePEG}_{350}\text{SO}_3)\) melt. Charge transport and optically induced Co(III/II) electron-transfer and mass transport measurements are controlled solely by physical diffusion of \([\text{Cp}_2\text{Co}]^+\) (a groundwork of the earlier solvent dynamics interpretation¹ᵃ⁻⁴). These new results add general support for the ion atmosphere relaxation model of electron transfer in ionically conductive, semirigid environments.

**Experimental Section**

**Synthesis of (MePEG₃₅₀SO₃⁻)(Bu₄N⁺).** In a column, ~75 g of Dowex 50WX-2-400 strongly acidic cation exchange resin (Aldrich) (0.33 mol equiv of exchange groups) was treated with ~1 L of 5 M hydrochloric acid, followed by 1 L of Nanopure water. The column was then backwashed with a Bu₄NOH solution and then thoroughly washed with 1 L of distilled water, 500 mL of methanol, and 1 L of Nanopure water. (Thorough washing is essential to remove amines and other contaminants.) A solution containing ~5 mmol of \((\text{MePEG}_{550}\text{SO}_3^-)(\text{Bu}_4\text{N}^+))\) was passed into this column and the \((\text{MePEG}_{550}\text{SO}_3^-)(\text{Bu}_4\text{N}^+))\) product eluted with an excess of 200 mL of water. Complete exchange of Bu₄N⁺ for Na⁺ was confirmed by NMR; 28 aliphatic H’s are seen in the δ = 1.0–1.7 ppm range relative to 28 polymer protons around δ = 3.6 ppm. δ = 1.0 ppm (t 12 H’s), δ = 1.45 ppm (m 8 H’s), δ = 1.65 ppm (m 8 H’s), δ = 2.6 ppm (s 4H’s, impurity eliminated by 100 MWCO dialysis), δ = 3.11 ppm (t 2 H’s), δ = 3.25 ppm (s 8 H’s), δ = 3.35 ppm (s 3 H’s), δ = 3.63 ppm (m 25 H’s), δ = 3.9 ppm (t 2 H’s).

**Synthesis of the Molten Salt [Cp₂Co⁺]([MePEG₃₅₀SO₃]⁻).** Aqueous cobaltocenium hexafluorophosphate (Strem, 98%) and \((\text{MePEG}_{550}\text{SO}_3^-)(\text{Bu}_4\text{N}^+))\) solutions (in 1:1 mol/mol proportions) were mixed, the resulting Bu₄NPFS precipitate was filtered, and the solution was dried in a vacuum. NMR in CDC₁₇ showed complete counterion metathesis: 10 aromatic H’s (singlet δ = 6.5 ppm) relative to 31 polymer H’s (m δ = 3–4 ppm). Additional purification by dialysis in a 100 MWCO bag for 48 h removed excess cobaltocenium, NH₄⁺, and MePEG₃₅₀SO₃⁻. Anal. Calc’d: C, 48.5; H, 6.6; N, 0; S, 5.2; Co, 9.5; F, 0. Found: C, 50.04; H, 7.32; N, <0.02; S, 4.49; Co, 9.33; F, 0.12.

**Synthesis of \([\text{FcTMA}]^+([\text{MePEG}_{350}\text{SO}_3])^⁻\).** Following a published procedure,⁴ an aqueous solution of ~290 mg of \((\text{MePEG}_{350}\text{SO}_3^-)(\text{Na}^+)\) was passed through ~3 g Dowex 50WX-2-200 (Aldrich) strongly acidic cation exchange resin pretreated with 1 L of 4 M hydrochloric acid, producing a solution of \((\text{MePEG}_{350}\text{SO}_3\text{H})\). An aqueous solution containing ~230 mg of ferrocenyltrimethylammonium iodide (FcTMA⁺, Strem, 99%) was passed through ~15 g of Dowex 1X-2-400 (Aldrich) strongly basic anion exchange resin that had been pretreated with 1 L of 4 M sodium hydroxide. The resulting FcTMA⁺OH⁻ solution was immediately titrated to neutrality with the MePEG₃₅₀SO₃⁻ solution and the water removed via vacuum evaporation.

**Plasticization and Dilution of \([\text{Cp}_2\text{Co}]^+([\text{MePEG}_{350}\text{SO}_3])^⁻\).** A 5.2 mg portion of \([\text{Cp}_2\text{Co}]^+([\text{MePEG}_{350}\text{SO}_3])^⁻\) (dried under vacuum for at least 12 h) was added to 4.6 mg of MePEG₃₅₀ (Aldrich, treated with Celite) dissolved in CH₂Cl₂ to make a 1:1.6 mol/mol \([\text{Cp}_2\text{Co}]^+([\text{MePEG}_{350}\text{SO}_3])^⁻/\text{MePEG}_{350}\) mixture. The solvent was removed by rotary evaporation. A 75.2 mg
portion of $[\text{FcTMA}^+][\text{MePEG}_{350}\text{SO}_3^-]$ was combined with 71.4 mg of $[\text{Cp}_2\text{Co}^+][\text{MePEG}_{350}\text{SO}_3^-]$ in the same manner to produce a molten salt containing a 1:1 mole ratio of $[\text{Cp}_2\text{Co}^+][\text{MePEG}_{350}\text{SO}_3^-]/[\text{FcTMA}^+][\text{MePEG}_{350}\text{SO}_3^-]$.

**Electrochemical Measurements.** Potential step chronoamperometry and cyclic voltammetry of the Co(III/II) electrochemical reaction were conducted on a neat film of the redox polyether hybrid resting on a microelectrode assembly, as before.1 See the Supporting Information for further details.

**Digital Simulation.** Simulation of experimental cyclic voltammetry was done with Digisim 3.03.12 A hemispherical microelectrode geometry was used to generate the simulation, taking a hemisphere of the same area as the experimental disk electrode. The concentration was held constant while the diffusion coefficient and uncompensated resistance were varied to fit the peak splitting and peak current of the experimental cyclic voltammograms (CVs) at 25 and 70 °C at 1 mV/s. Then, the scan rate was changed at each temperature to obtain the other simulations.

**Spectroscopic Measurements.** Detection of optically induced electron transfers was sought using an optically transparent thin layer cell consisting of face-to-face indium tin oxide (ITO)-coated (Delta Technologies) 25 mm × 75 mm glass slides, separated by ∼50 μm of MonoKote (TopFlite, Great Plains Model Distributors) and sealed with Torr Seal. The thin layer cavity was filled (before sealing, in a dry, inert atmosphere) with ∼1–2 mg of the 1:1 mixed $[\text{Cp}_2\text{Co}^+][\text{MePEG}_{350}\text{SO}_3^-]/[\text{FcTMA}^+][\text{MePEG}_{350}\text{SO}_3^-]$ melt. The currents resulting from applying potential bias to the two ITO electrodes (Pine Instruments RDE4 potentiostat), so as to oxidize and reduce the two redox constituents at opposing electrodes,13 were monitored on a Yokogawa 3025 X-Y recorder, and near-IR (NIR) spectra of the thin layer sample were monitored with a BioRad FTS 6000 spectrometer fitted with a PbSe detector. Microdisk voltammetry of the melt was used to determine the necessary values of the potential bias. The spectrum of the cell before the potential bias was applied (showing a spectral decay from the IR to visible, presumably from the ITO film) was subtracted from subsequent spectra taken under the potential bias.

**Results and Discussion**

**Mass Transport and Electron-Transfer Rate Measurements.** $D_{\text{PHYS}}$, $D_{\text{APP}}$, and $D_{\text{ION}}$ transport measurements were carried out in three melts: neat $[\text{Cp}_2\text{Co}][\text{MePEG}_{350}\text{SO}_3]$ (solid line), the neat, MePEG 350-plasticized $[\text{Cp}_2\text{Co}][\text{MePEG}_{350}\text{SO}_3]$ melt, and a 1:1 mol/mol $[\text{Cp}_2\text{Co}][\text{MePEG}_{350}\text{SO}_3]/[\text{FcTMA}][\text{MePEG}_{350}\text{SO}_3]$ mixed melt.

The microdisk voltammetry currents observed for the $[\text{Cp}_2\text{Co}][\text{MePEG}_{350}\text{SO}_3]$ (Figure 2A) and MePEG 350-plasticized $[\text{Cp}_2\text{Co}][\text{MePEG}_{350}\text{SO}_3]$ (Figure 2B) melts were large (compared to those in cobalt poly-pyridine melts4) and displayed sigmoidal waveshapes, indicative of radial diffusion conditions resulting from fast charge transport. That the Figure 2A 1 mV/s 70 °C voltammogram is unchanged at 3 mV/s is also consistent with radial diffusion control. The Figure 2 voltammograms are well-fitted by digital simulations15 assuming radial diffusion (Supporting Information Figures S-2, S-3, and S-4), except at lower temperatures in the neat melt (Supporting Information Figure S-1, 25 °C), for reasons associated with adsorption or precipitation of $[\text{Cp}_2\text{Co}]^0$. Regarding the latter, see the discussion at the end of paper.

Voltammograms of the three melts at 38 °C—neat, MePEG 350-plasticized, and mixed—are compared in Figure 3. In the
TABLE 1: Physical Transport and Electron-Transfer Results for [Cp₂Co(MePEG₃₅₀SO₃)] melts (at 25 °C) (Cp₂Co, Neat Melt; Cp₂Co/FcTMA, 1:1 mol/mol [Cp₂Co(MePEG₃₅₀SO₃)][FcTMA][MePEG₃₅₀SO₃] mixed melt; Cp₂Co/MePEG₃₅₀ 1.6:1 mol/mol MePEG₃₅₀plasticized [Cp₂Co(MePEG₃₅₀SO₃)])

<table>
<thead>
<tr>
<th>Melt</th>
<th>Cp₂Co</th>
<th>1:1 Cp₂Co/FcTMA</th>
<th>1:1.6 Cp₂Co/MePEG₃₅₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>C* (M)</td>
<td>1.9</td>
<td>1.0</td>
<td>0.98</td>
</tr>
<tr>
<td>δi (Å)</td>
<td>9.5</td>
<td>11.8</td>
<td>11.9</td>
</tr>
<tr>
<td>DₚHYS (25 °C) (cm²/s)</td>
<td>3.9 × 10⁻¹⁰</td>
<td>3.9 × 10⁻¹⁰</td>
<td>1.1 × 10⁻⁸</td>
</tr>
<tr>
<td>DₚEX (25 °C) (cm²/s)</td>
<td>6.3 × 10⁻⁹</td>
<td>3.5 × 10⁻⁹</td>
<td>1.2 × 10⁻⁸</td>
</tr>
<tr>
<td>DₚE (25 °C) (cm²/s)</td>
<td>3.4 × 10⁻⁹</td>
<td>3.2 × 10⁻⁹</td>
<td>1.2 × 10⁻⁸</td>
</tr>
<tr>
<td>DₚHYS (25 °C) (cm²/s)</td>
<td>1.2 × 10⁻⁸</td>
<td>5.7 × 10⁻⁹</td>
<td>1.3 × 10⁻⁷</td>
</tr>
<tr>
<td>DₚDₚ (25 °C) (M⁻¹ s⁻¹)</td>
<td>10 6</td>
<td>2.3 × 10⁶</td>
<td>5.1 × 10⁷</td>
</tr>
<tr>
<td>EₚPHYS (k/mol)</td>
<td>66</td>
<td>66</td>
<td>25</td>
</tr>
<tr>
<td>EₚEX (k/mol)</td>
<td>32</td>
<td>32</td>
<td>23</td>
</tr>
<tr>
<td>EₚEXₐ (k/mol)</td>
<td>34</td>
<td>43</td>
<td>23</td>
</tr>
<tr>
<td>kₚ(Cional) (25°C) (M⁻¹ s⁻¹)</td>
<td>2.7 × 10⁻¹⁰</td>
<td>1.6 × 10⁻¹⁰</td>
<td>2.4 × 10⁻⁹</td>
</tr>
</tbody>
</table>

Concentrations of the Cp₂Co melt are calculated from density measurements and mass: ρ = 1.2 g/mL for [Cp₂Co(MePEG₃₅₀SO₃)], 1.4 g/mL for [FcTMA][MePEG₃₅₀SO₃], and 1.09 g/mL for MePEG₃₅₀ (as given by Aldrich). δ is the redox center-to-center distance calculated from the concentration assuming cubic packing. From chronoamperometry, of 10 mol % [Cp₂Co][MePEG₃₅₀SO₃] in [FcTMA][MePEG₃₅₀SO₃] or 10 mol % [Cp₂Co][MePEG₃₅₀SO₃] in 1:1 mol/mol MePEG₃₅₀plasticized [FcTMA][MePEG₃₅₀SO₃]: each value is the average of three trials. E calculated from eq 3. Mole-fraction-weighted average of DₚHYS, DₚEX, and where FcTMA is present, DₚHYS,ₐ = 5.5 × 10⁻⁹ cm²/s at 25 °C. From microdisk equation. Calculated via eq 2. From slopes of activation plots in Figure 5. Calculated using Savent’s theory.

Electrode reactant and the Dₚ (and kₚ) value of the [Cp₂Co]⁺⁺ electron-transfer reaction. In the mixed [Cp₂Co(MePEG₃₅₀SO₃)]/[FcTMA][MePEG₃₅₀SO₃] melt, the Co(III/II) currents are smaller than those in the neat melt by more than the 2-fold concentration dilution, probably owing to a percolation effect partially limiting the rate of Co(III/II) electron hopping.

Dₚ was calculated from the limiting currents of 1 mV/s cyclic voltammograms using the radial diffusion microdisk equation. Dₚ results at 25 °C are given in Table 1 and those for other temperatures in Supporting Information Tables S-1, S-2, and S-3. Combining Dₚ with Dₚ (determined as above) using eq 2 gives Dₚ and Co(III/II) electron self-exchange rate constants (kₚ), given for 25 °C in Table 1 and for other temperatures in Supporting Information Tables S-1, S-2, and S-3.

The physical diffusion coefficients of [Cp₂Co]⁺ were measured under conditions where Co(III/II) electron hopping is choked off by diluting it (down to 10 mol %) with structurally similar host matrices [FcTMA][MePEG₃₅₀SO₃] and MePEG₃₅₀plasticized [FcTMA][MePEG₃₅₀SO₃]. The lowered mole fraction of [Cp₂Co][MePEG₃₅₀SO₃] is well below the percolation threshold for electron hopping. Figure 4 shows the cyclic voltammetry of these melt combinations, where the [Cp₂Co]⁺⁺ reduction and [FcTMA]⁺⁺ oxidation are seen at negative and positive potentials, respectively. Potential step chronoamperometry was done on the [Cp₂Co]⁺⁺ wave, stepping the potential from the featureless double layer region to beyond the wave’s diffusion controlled plateau. Currents were measured at times sufficiently short to attain a linear diffusion geometry, and Dₚ was obtained from the slopes of Cottrell plots (current vs t⁻¹/²). Background current corrections were simulated by current-time responses for identical potential steps in a MePEG₃₅₀plasticized [FcTMA][MePEG₃₅₀SO₃] melt (see Supporting Information Figures S-5 and S-6). The results for Dₚ in the neat and plasticized melts are given in Table 1 and Supporting Information Tables S-1 and S-2. Dₚ and ionic conductivity values were assumed to be the same in the structurally similar 1:1 mixed [Cp₂Co][MePEG₃₅₀SO₃]/[FcTMA][MePEG₃₅₀SO₃] and neat [Cp₂Co][MePEG₃₅₀SO₃] melts.

The diffusion coefficients (Dₚ) of the (MePEG₃₅₀SO₃)⁻ counterion were calculated from (ac impedance) measurements of melt ionic conductivities (σ) using the Nernst–Einstein equation.

\[ \sigma = F^2 R T z^2 C D \text{PHYS} C^2 + z_2 C \text{ION} D \text{ION} C \text{ION} \]
Figure 5. Activation plots of $k_{\text{EX}}$ (M$^{-1}$ s$^{-1}$, upper), $D_{\text{PHYS}}$ (cm$^2$ s$^{-1}$, middle), and $\sigma$ (S/cm, lower) of neat [Cp$_2$Co]([MePEG$_{350}$SO$_3$]) (■), MePEG$_{350}$-plasticized [Cp$_2$Co]([MePEG$_{350}$SO$_3$]) (●), and the 1:1 [Cp$_2$Co]([MePEG$_{350}$SO$_3$])/[FCTMA]/[MePEG$_{350}$SO$_3$] mixed melt (▲). See Table 1 for activation barrier energies and Supporting Information Tables S-1, S-2, S-3, and S-5 for complete temperature dependent data sets.

The temperature dependencies of $k_{\text{EX}}$, $D_{\text{PHYS}}$, and $\sigma_{\text{ION}}$ in the three melts (neat, plasticized, and mixed, Supporting Information Tables S-1, S-2, S-3, and S-5) are shown in Figure 5 as activation plots; barrier energies are given in Table 1. The important result in Table 1 is that $E_{\text{A,ION}}$ and $E_{\text{A,EX}}$ are similar and much smaller than $E_{\text{A,PHYS}}$.

In earlier studies,1a,c,d,h,3d,4 in the context of considering a solvent dynamics model to interpret electron transfers in semisolids, the intercepts of $E_{\text{A,EX}}$ activation plots such as those in Figure 5 were discussed in terms of their significance for the electron transfers. In the context of the ion atmosphere model, discussed next, we no longer believe that analysis to be appropriate.

Analysis of Electron-Transfer Rates as Ion Atmosphere Controlled. As noted above, an ionic atmosphere relaxation model has been proposed to explain recent4 electron-transfer rate constant and physical transport rate results in poly-pyridine Co melts. The essential idea of this model, which originated in a theoretical consideration21 of the effect of ion pairing on electron transfers, written in the context of the Co(III/II) reaction of [Cp$_2$Co]$^{+\circ}$, is given by

$$X^{-}[\text{Cp}_2\text{Co}]^{+}[\text{Cp}_2\text{Co}]^{0} \xrightarrow{k_{-1}} X^{-}[\text{Cp}_2\text{Co}]^{0} [\text{Cp}_2\text{Co}]^{+} \xrightarrow{k_{+1}}$$

where ion atmosphere redistribution occurs at rate constant $k_2$ following electron transfer at (forward) rate constant $k_1$. In the reaction intermediate “$X^{-}[\text{Cp}_2\text{Co}]^{+}[\text{Cp}_2\text{Co}]^{0}$”, the back electron transfer (rate constant $k_{-1}$) competes with the ion atmosphere redistribution step. The net electron-transfer rate constant is given by

$$\frac{1}{k_{\text{EX}}} = \frac{1}{k_1} + \frac{k_{-1}}{k_1 k_2} = \frac{1}{k_1} + \frac{1}{K_{\text{EQ}} k_2}$$  \(5\)

The ion atmosphere redistribution refers to a physical relocation of charge compensating ions, which can be modeled21 as diffusion ($D_{\text{CION}}$ or $D_1$) over a distance “$a$” to relieve the Coulombic imbalance created by the electron transfer:

$$k_2 = D_1 \left(\frac{\pi}{2a}\right)^2$$  \(6\)

Clearly, if $k_1 < k_2$, $k_{\text{EX}}$ should reflect the intrinsic electron-transfer dynamics of the [Cp$_2$Co]$^{+\circ}$ couple. On the other hand, if $k_1 > k_2$, $k_{\text{EX}}$ is instead controlled by the movement of the counterion, and in the limit, one anticipates that the measured (via $D_{\text{APP}}$) $k_{\text{EX}}$ value should be proportional to the diffusion coefficient(s) of the surrounding counterions. In the previous cobalt poly-pyridine complex melts,4 since the $D_{\text{PHYS}}$ value of the redox complex was much smaller than $D_{\text{CION}}$, only the latter was needed to examine the correlation with $k_{\text{EX}}$. Here, $D_{\text{PHYS}}$ values are not so negligible and may augment the ion atmosphere relaxation rates, so a mole-fraction-weighted ion diffusion coefficient ($D_1$) (Table 1) is employed in the Figure 6A log−log plots of the $k_{\text{EX}}$ values of the [Cp$_2$Co]$^{+\circ}$ reaction versus $D_1$. The plots for the neat (●), plasticized (○), and mixed (▲) melts are linear with log−log slopes of 1.2, 0.9, and 1.4, respectively. (For contrast, Figure 6A also shows log−log plots of $D_{\text{PHYS}}$ against $k_{\text{EX}}$, according to the previous1,2,22,23 solvent dynamics model; these exhibit less ideal slopes of 0.5, 0.9, and 0.6.) While the $D_1$ plots in Figure 6A are consistent with the ion atmosphere relaxation model, even more impressive is the Figure 6B comparison with a large body of data for cobalt(II/I) poly-pyridine1,d,d and a recent ruthenium(III/II) tris-bipyridine and bis-bipyridine-bis-cyano complex7 melt data. The offset of different data sets from the main body of data may reflect small differences in the term “$a$” (eq 6) or “$K_{\text{EQ}}$” (eq 5). The best-fit line shown in Figure 6B has a slope of 1.0.

The activation barrier energies in Table 1 further support the ion atmosphere relaxation model, in that the energy barriers for electron transfer are similar to those for ionic conductivity but (except the most fluid MePEG-plasticized case, vide infra) much smaller than those for $D_{\text{PHYS}}$.

According to the ion atmosphere relaxation model, the net electron-transfer rate is governed by ionic motions, not the intrinsic electron-transfer rate, which predicts that $k_{\text{EX}}$ results are only apparent rate constants and thus should be independent of the particular redox couple employed. This is perhaps the most impressive aspect of Figure 6B, that different complexes (cobaltoocene, Co poly-pyridine, Ru poly-pyridine) fall into a common framework and exhibit electron-transfer rates in the same (10$^{6}$−10$^{7}$ M$^{-1}$ s$^{-1}$) range. In contrast, in fluid solutions at 25 °C, the electron-transfer rate constant for [Cp$_2$Co]$^{+\circ}$ is 4 × 10$^{7}$ M$^{-1}$ s$^{-1}$,24 while that for [Co(bpy)$_3$]$^{2+\circ}$ is a much faster 1 × 10$^{9}$ M$^{-1}$ s$^{-1}$.25 Clearly, the rate constant for the latter couple in the melts has been suppressed more than the [Cp$_2$Co]$^{+\circ}$ couple.

We establish below an optically induced electron-transfer activation barrier result that predicts a thermal $E_{\text{A,EX}}$ barrier of
The difference is consistent with the Table 1 values of $\Delta k$, which is smaller than the results in Table 1. The intermolecular electron transfers in mixed-valent melts that have been previously successful in observing optically induced reflectings the intrinsic electron-transfer dynamics of the $[\text{Cp}_2\text{Co}]^-$. The results in the MePEG-plasticized $[\text{Cp}_2\text{Co}](\text{MePEG 350 SO}_3)$ melt, which is confined in an ~50 µm layer between transparent, indium tin oxide-coated glass electrodes and an appropriate potential bias is applied, cobaltocenium can be reduced at the cathode to produce a layer of mixed-valent $[\text{Cp}_2\text{Co}]^{1+}$. The currents for the reduction are supported at the anode by ferrocene oxidation, which produces a corresponding mixed-valent $[\text{FcTMA}]^{2+/+}$ layer next to the anode. The minimum necessary potential is judged by the voltammetric spacing between the two electrode reactions, which is ~1.5 V as seen in the voltammogram in Figure 7. Figure 7 shows the optical NIR absorbance result of electrolysis at a 3 V bias; a weak absorbance at 6300 cm$^{-1}$ and a shoulders at ~4700 cm$^{-1}$ grow in as mixed-valent layers of $[\text{Cp}_2\text{Co}]^{1+0}$ and $[\text{FcTMA}]^{2+/+}$ are produced, reaching an apparent steady state after about 75 min. The time dependencies of the optical absorbance at lower potentials are shown in Supporting Information Figures S-8 and S-9. The spectrum in Figure 7 is overlaid with optical interference fringes caused by the thin layer cell. The lower curve shows the Gaussian fits to the average intensities.

No absorbance peaks are seen in the near-IR spectrum at zero potential bias, when only $[\text{Cp}_2\text{Co}]^{1+}$ and $[\text{FcTMA}]^{+}$ are present. Likewise, $[\text{Cp}_2\text{Co}]^{1+}$ and $[\text{Cp}_2\text{Fe}]^{+}$ can be eliminated as causes of the band at 6300 cm$^{-1}$ because dilute solutions of these species have no detectable absorbances in the near-IR wavelength region. Therefore, we infer that the band is caused by electron transfer within one of the two mixed-valent layers produced in the thin layer cell electrolysis. To determine to which mixed-valent couple the 6300 cm$^{-1}$ energy corresponds, we turn to literature data on dilute solutions of mixed-valent bicobaltocene and biferrocene. Bicobaltocene exhibits an optically induced electron-transfer band from 5880 to 6580 cm$^{-1}$, depending on the solvent. The intervalent charge transfer band for biferrocene occurs at lower energies, 5000–5680 cm$^{-1}$. The latter procedure was employed here to generate a melt containing the $[\text{Cp}_2\text{Co}]^{1+0}$ couple.

Figure 7. Steady-state NIR peaks from the 1:1 mol/mol $[\text{Cp}_2\text{Co}](\text{MePEG 350 SO}_3)/[\text{FcTMA}](\text{MePEG 350 SO}_3)$ melt mixture is confined in an ~50 µm layer between transparent, indium tin oxide-coated glass electrodes and an appropriate potential bias is applied, cobaltocenium can be reduced at the cathode to produce a layer of mixed-valent $[\text{Cp}_2\text{Co}]^{1+0}$. The currents for the reduction are supported at the anode by ferrocene, which produces a corresponding mixed-valent $[\text{FcTMA}]^{2+/+}$ layer next to the anode. The minimum necessary potential is judged by the voltammetric spacing between the two electrode reactions, which is ~1.5 V as seen in the voltammogram in Figure 7. Figure 7 shows the optical NIR absorbance result of electrolysis at a 3 V bias; a weak absorbance at 6300 cm$^{-1}$ and a shoulders at ~4700 cm$^{-1}$ grow in as mixed-valent layers of $[\text{Cp}_2\text{Co}]^{1+0}$ and $[\text{FcTMA}]^{2+/+}$ are produced, reaching an apparent steady state after about 75 min. The time dependencies of the optical absorbance at lower potentials are shown in Supporting Information Figures S-8 and S-9. The spectrum in Figure 7 is overlaid with optical interference fringes caused by the thin layer cell. The lower curve shows the Gaussian fits to the average intensities.

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The results in Figure 8 are consistent with the electrode becoming coated with a partially blocking [Cp₂Co]⁺ film. The reductive charge passed before the sudden current drop was estimated from the current–time integrals in experiments such as Figure 8 and converted into equivalent thicknesses of deposited films. The thicknesses, while variable from experiment to experiment (Supporting Information Table S-6), were fractions to several micrometres. These are significant thicknesses when considered as transport-blocking layers. There is generally a reverse peak seen in the voltammetry (Figure 8A), but the charge under it is much less than the forward charge. Either the film is not completely stripped, radial diffusion disperses dissolved film, or the film is continually dissolving and the actual thickness is much less than that estimated in Supporting Information Table S-6. The latter seems to be the most likely, since the currents in Figure 8 do not drop to zero but to small, fairly steady values. If these currents approximate a dissolution rate, conversion of them to thickness/second (Supporting Information Table S-6) shows that it is quite appreciable in comparison to the material reacting prior to the drop in current. Thus, at sufficiently slow potential scan rates, or at higher temperatures, as in Figures 2–4, the [Cp₂Co]⁺ film is either not produced or dissolves too rapidly to hinder diffusional transport.

The data taken at slow scan rates, where blocking is not seen, are considered reliable. (The mismatch between experiment and simulation at lower temperatures in the neat melt, Supporting Information Figure S-1, could reflect a minor degree of film formation.) In the MePEG-plasticized and mixed melts, effects such as Figure 8 were never observed.

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Supporting Information Available: Supplementary information on electrochemical measurements, simulated cyclic voltammetry, Cottrell plots, near-IR spectra, the temperature dependence of \(D_{\text{PHYS, DECAY}}, D_{\text{EX}}, D_{\text{CORR}}\), and migration parameters, and data for reductive cobaltocene film formation. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes


Electron Transfers in Semisolid Ionic Liquids


(6) (a) For symmetric, mixed-valence species, \( E_{DB} = 4\Delta G^{\text{TPH}} \) where \( E_{DB} \) is the barrier energy for optically induced electron transfer and \( \Delta G^{\text{TPH}} \) is the that for thermally induced electron transfer.6b (b) Hush, N. S. J. Am. Chem. Soc. 2003, 125, 3987.


(15) (a) \( i = (nFADP)^{1/2}/0 \), where \( D \) is the diffusion coefficient \( D_{\text{PHYS}} \) and the other symbols have the usual meaning.15b (b) Bard, A. J.; Faulkner, L. R. Electrochemical Methods, 2nd ed.; Wiley: New York, 2001; p 163. (c) Cottrell, F. G. Z. Phys. Chem. 1902, 42, 385. (d) The microelectrode radius was determined by ferrocene voltammetry.

(16) Background currents were measured in 5.4:1 mol/mol MePEG$_{180}$-plasticized [FeTMA][MePEG$_{350}$SO$_3$].


(18) (a) \( \xi_{\text{CION}} = 2\xi_{\text{CION}}C_{\text{D}\text{C}\text{ION}}C_{\text{CION}}/2\xi_{z}^{2}D_{\text{CION}} \). (b) See ref 15b, pp 65 and 140.


(20) The potential effect of ion pairing in the melts, which could depress the apparent \( D_{\text{CION}} \) values, was assessed by assuming that 50% of the [Cp$_2$Co]$^{3+}$ complexes are ion paired to polyether-tailed counterions. The calculated \( D_{\text{CION}} \) values, given in Supporting Information Table S-4, are increased by \( \sim 2-4 \)-fold. We have no direct evidence for strong contact ion pairing; this is simply a test to illustrate that the effect of 50% ion pairing is modest.


(24) (a) In acetonitrile;24b in dimethyl sulfoxide, \( \kappa_{kX} = 2 \times 10^{7} \text{M}^{-1} \text{s}^{-1} \).24b (b) Nielson, R. M.; Golovin, M. N.; McManis, G. E.; Weaver, M. J. Am. Chem. Soc. 1988, 110, 1745.

(25) (a) This rate constant was obtained in aqueous solution.25b (b) Sutin, N.; Brunschweig, B. S.; Creutz, C.; Winkler, J. R. Pure Appl. Chem. 1988, 60, 1817.


(28) The estimate, \( \varepsilon_{\text{max}} \sim 10 \text{ M}^{-1} \text{cm}^{-1} \), is based on the peak absorbance from Figure 7, a 0.5 M concentration of the absorbing mixed-valent species, and a 25 μm path length (one-half of the total thin layer cell thickness). This estimate may be low owing to incomplete development of steady-state concentration profiles in the thin layer cell. Other uncertainties include the implicit assumption that \( D_{\text{APP}} \) is the same for the [Cp$_2$Co]$^{3+}$ and [FeTMA]$^{2+}$ couples.