Electrochemical Reactions and Charge Transport in Undiluted Room-Temperature Melts of Oligo(ethylene glycol)-Based Electron Carriers

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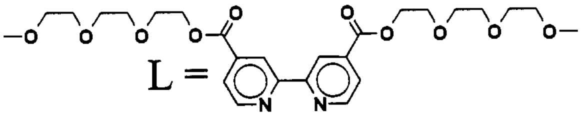
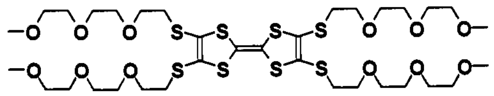
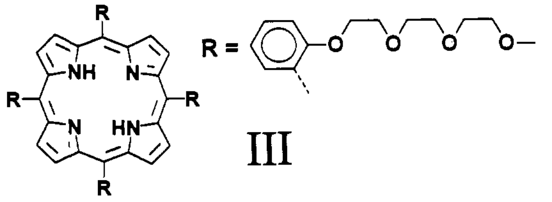
We report how the covalent attachment[1] of short oligo(ethylene glycol) chains to cobalt tris(bipyridine) complexes (**I**), tetrathiafulvalene (**II**), tetraphenylporphyrin (**III**), and ferrocenecarboxylate (**IV**) transforms these normally crystalline materials into room-temperature melts which freely dissolve electrolytes like $LiClO_4$ to yield ionically conductive melts. Compound **I** possesses intrinsic ionic conductivity and is a novel electroactive molten salt. This paper describes a microelectrode-based voltammetric study of diffusion and electron transport phenomena in compounds **I–IV** in *undiluted* forms.[2]



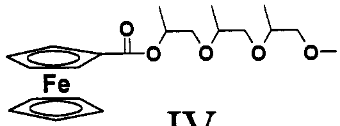
$\mathrm{I} = [\mathrm{CoL_3}]^{+2}(\mathrm{ClO_4^-})_2$



II



III



IV

It is generally impossible to observe electrochemical reactions of crystalline substances, like metal bipyridine complexes, owing to the absence of adequate ionic mobility. Their interfacial electron transfers are known only in dilute fluid solutions, wherein they diffuse rapidly, and in ionically conducting redox polymers[3] in which the complexes do not diffuse (macroscopically) at all. Undiluted small-molecule liquids (4-cyanopyridine, $PhNO_2$) in which diffusion is rapid have been studied by White et al.[4] Transport in **I–IV** is unique, involving sterically bulky and highly concentrated *monomeric* electron carriers *slowly* diffusing among themselves in the electrochemically formed, mixed-valent diffusion layer adjacent to the electrode.

Voltammetric oxidation and reduction of the undiluted (~0.6 M) cobalt(II) complex $\mathbf{I}^{2+}$, an extremely viscous, yellow, room-temperature melt, are shown in Figures 1A and 1B, respectively. The $\mathbf{I}^{2+/3+}$ oxidation wave is linear diffusion-controlled and, at sufficiently slow potential scan rates (50 μV/s),[5] nearly reversible (ΔE_{peak} =.65 mV). The $\mathbf{I}^{2+/1+}$ reduction currents are much larger, and the wave shape indicates radial diffusion control. Chronoamperometry gives apparent self-diffusion coefficients D_{app} for oxidation and reduction of $\mathbf{I}^{2+}$ of 3×10^{-13} and 6×10^{-9} cm^2/s, respectively.

The enormous (10^4-fold) difference in the apparent diffusivity of $\mathbf{I}^{2+}$ during its oxidation and reduction is unusual.[6] Contributing factors include ionic migration and electron self-exchange reactions in the concentrated diffusion layer. While ionic migration[7] (there is no added electrolyte) would depress $D_{\mathrm{app},2/3}$ and enhance $D_{\mathrm{app},2/1}$, these anticipated effects should lead to only small (and certainly $\ll 10^4$-fold) D_{app} differences. Noting that the dilute solution electron self-exchange rate constants k_{ex} of the related complexes $[\mathrm{Co(bipy)_3}]^{2+/3+}$ (~2 M^{-1} s^{-1})[8] and $[\mathrm{Co(bipy)_3}]^{2+/1+}$ (~10^9 M^{-1} s^{-1})[9] are very different, charge transport by fast electron self-exchange of $\mathbf{I}^{2+/1+}$ in the concentrated molten salt is almost certainly the primary reason for the large $D_{\mathrm{app},2/1}$ relative to $D_{\mathrm{app},2/3}$. Coupling of diffusion with electron-transfer reactions is described by the Dahms–Ruff relation,[10] according to which a $\mathbf{I}^{2+/3+}$ k_{ex} of 2 M^{-1} s^{-1} would yield a $\mathbf{I}^{2+/3+}$ self-exchange transport rate negligible[10b] in comparison to the oxidatively observed value, $D_{\mathrm{app},2/3} = 3 \times 10^{-13}$ cm^2/s. Thus, $D_{\mathrm{app},2/3}$ represents the actual physical self-diffusivity D_{phys} of $\mathbf{I}^{2+}$ in a $\mathbf{I}^{2+/3+}$ mixed-valent diffusion layer. In contrast, a $\mathbf{I}^{2+/1+}$ k_{ex} of 10^9 M^{-1} s^{-1} would greatly enhance reductive electron transport, thereby producing the observed $D_{\mathrm{app},2/1} \gg D_{\mathrm{app},2/3}$. The observed enhancement is less than that predicted by $k_{\mathrm{ex}} = 10^9$ M^{-1} s^{-1}; using $D_{\mathrm{app},2/1}$ (6×10^{-9} cm^2/s) and $D_{\mathrm{app},2/3} = D_{\mathrm{phys}}$ (3×10^{-13} cm^2/s), the k_{ex} calculated[10] is 2×10^6 M^{-1} s^{-1}. This calculation is an upper-limit estimate, ignoring acceleration of electron transfer by the migration-generated electrical gradient in the

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[1] (a) These new compounds were prepared using conventional synthetic methods;[1b–f] synthetic details will be reported elsewhere. (b) Otsubo, T.; Ogura, F. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1343–1344. (c) Schultz, R. A.; White, B. D.; Dishong, D. M.; Arnold, K. A.; Gokel, G. W. *J. Am. Chem. Soc.* **1985**, *107*, 6659–6668. (d) Lau, H. H.; Hart, H. *J. Org. Chem.* **1959**, *24*, 280–281. (e) Momenteau, M.; Mispelter, J.; Loock, B.; Bisagni, E. *J. Chem. Soc., Perkin Trans. I* **1983**, 189–196. (f) Evers, R. C.; Moore, G. J. *J. Polym. Sci. A* **1986**, *24*, 1863–1877.

[2] (a) The voltammetry of oligo(ethylene glycol)-tailed redox species described by Gokel et al. was in dilute solutions.[2b–e] (b) Delgado, M.; Gustowski, D. A.; Yoo, H. K.; Gatto, V. J.; Gokel, G. W.; Echegoyen, L. *J. Am. Chem. Soc.* **1988**, *110*, 119–124. (c) Echegoyen, L. E.; Yoo, H. K.; Gatto, V. J.; Gokel, G. W.; Echegoyen, L. *Ibid.* **1989**, *111*, 2440–2443. (d) Gustowski, D. A.; Delgado, M.; Gatto, V. J.; Echegoyen, L.; Gokel, G. W. *Ibid.* **1986**, *108*, 7553–7560. (e) Echeverria, L.; Delgado, M.; Gatto, V. J.; Gokel, G. W.; Echegoyen, L. *Ibid.* **1986**, *108*, 6825–6826.

[3] Oyama, N.; Ohsaka, T. In *Molecular Design of Electrode Surfaces*; Murray, R. W., Ed.; Wiley: New York, 1992; Chapter 8, pp 333–402, and references therein.

[4] (a) Malmsten, R. A.; Smith, C. P.; White, H. S. *J. Electroanal. Chem.* **1986**, *215*, 223–235. (b) Malmsten, R. A.; White, H. S. *J. Electrochem. Soc.* **1986**, *133*, 1067–1068. (c) Morris, R. B.; Fischer, K. F.; White, H. S. *J. Phys. Chem.* **1988**, *92*, 5306–5313. (d) Norton, J. D.; Anderson, S. A.; White, H. S. *Ibid.* **1992**, *96*, 3–6. (e) Norton, J. D.; Benson, W. E.; White, H. S.; Pendley, B. D.; Abruña, H. D. *Anal. Chem.* **1991**, *63*, 1909–1914.

[5] Unconventionally slow (10 μV/s to 1 mV/s) scan rates are (a) possible because natural convection is inhibited by the large viscosity of $\mathbf{I}^{2+}$ and (b) necessary to avoid large ΔE_{p} values and peak broadening brought on by the ionically resistive medium.

[6] (a) Guadalupe, A. R.; Usifer, D. A.; Potts, K. T.; Hurrell, H. C.; Mogstad, A.-E.; Abruña, H. D. *J. Am. Chem. Soc.* **1988**, *110*, 3462–3466. (b) Buttry, D. A.; Anson, F. C. *Ibid.* **1983**, *105*, 685–689.

[7] (a) Amatore, C.; Deakin, M. R.; Wightman, R. M. *J. Electroanal. Chem.* **1987**, *225*, 49–63. (b) Amatore, C.; Fosset, B.; Bartelt, J.; Deakin, M. R.; Wightman, R. M. *Ibid.* **1988**, *256*, 255–268.

[8] Baker, B. R.; Basolo, F.; Neumann, H. M. *J. Phys. Chem.* **1959**, *63*, 371–378.

[9] Brunschwig, B. S.; Creutz, C.; Macartney, D. H.; Sham, T.-K.; Sutin, N. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 113–127.

[10] (a) $D_{\mathrm{app}} = D_{\mathrm{phys}} + k_{\mathrm{ex}}\delta^2 C_{\mathrm{T}}/6$, where D_{phys} is physical diffusivity, k_{ex} the self-exchange rate constant, C_{T} the total site concentration, and δ the average intersite distance (~16 Å for Co–Co in **I**). Assuming that $k_{\mathrm{ex}} = 2$ M^{-1} s^{-1} for $\mathbf{I}^{2+/3+}$, the right-hand term = 5×10^{-15} cm^2/s. (b) Majda, M. In *Molecular Design of Electrode Surfaces*; Murray, R. W., Ed.; Wiley: New York, 1992; Chapter 4, pp 159–206, and references therein.

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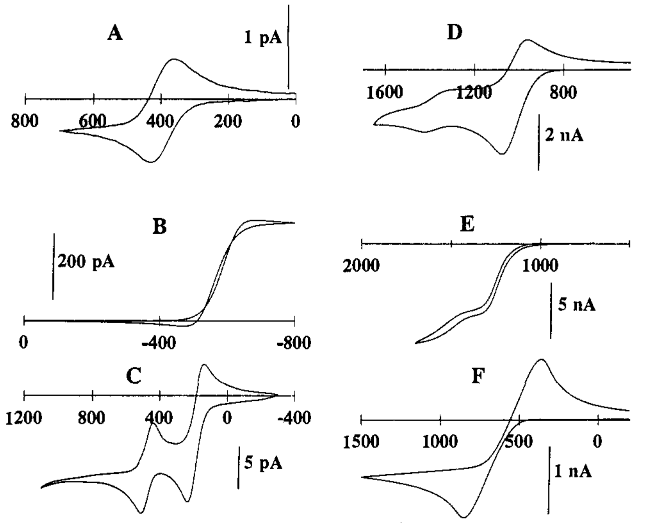

Figure 1. Cyclic voltammetry at 5-μm-radius Pt microdisks in millivolts versus a Ag wire-tip quasi-reference of (A) neat $(I^{2+})(ClO_4^-)_2$ $v = 50$ μV/s, oxidation scan; (B) neat $(I^{2+})(ClO_4^-)_2$ $v = 50$ μV/s, reduction scan (same sample); (C) 1:2 (**II**):($LiClO_4$), $v = 50$ μV/s; (D) 1:1 (**III**):($LiClO_4$), CH_3CN vapor-plasticized, $v = 200$ mV/s; (E) 3.16 mM **III** and 3.27 mM $LiClO_4$ in CH_3CN solution, $v = 500$ mV/s; and (F) 3:1 (**IV**):($LiClO_4$), $v = 10$ mV/s.

diffusion layer.[11] From this preliminary result, it seems that electron self-exchange is much slower in the molten salt **I** than in dilute solutions of $[Co(bpy)_3]^{2+/3+}$.

The extremely slow physical self-diffusivity of I^{2+} (3×10^{-13} cm^2/s) deserves comment. Small diffusion coefficients ($\sim 10^{-12}$ cm^2/s) are observed[12] in network PEO for small diffusants like tetracyanoquinodimethane radical anion only at high concentrations of $LiClO_4$, which depress polyether chain segmental mobility by Li^+-based chain cross-linking. On the other hand, the complex $[Fe(Me_2phen)_3]^{2+}$ diffuses quite rapidly ($\sim 10^{-6}$ cm^2/s)[13] when *diluted* in triglyme (three ethylene glycol units, as in the tails of **I**). The slow self-diffusion of I^{2+} must reflect the difficulty in generating large vacancies for diffusion-hopping of an undiluted bulky diffusant, perhaps augmented by interactions between the oligomeric chains of neighbor diffusants. Further analysis of this new class of monomers exhibiting bulky-site self-diffusion should be interesting.

The tetratailed tetrathiafulvalene **II** freely dissolves $LiClO_4$ electrolyte (at least 2 Li^+/TTF) and remains liquid at room temperature although a substantial viscosity increase occurs. The tetratailed tetraphenylporphyrin **III**, whether pure or containing $LiClO_4$ dissolved at a 1 Li^+/TPP concentration, is a soft, dark, apparently amorphous material. Voltammetry of **II** (at 2 Li^+/TTF, Figure 1C) and of **III** (at 1 Li^+/TPP, Figure 1D)[14] shows two well-defined oxidation steps with unequal currents. The apparent self-diffusivities of **II** and **III** from their first oxidation steps are $D_{app,0/+} = 1.2 \times 10^{-11}$ and 10^{-9} cm^2/s, respectively. The latter value was obtained under plasticization conditions, which typically enhances diffusion.[14]

The disparities of currents in the two oxidation steps of **II** and of **III** (Figures 1C, 1D) are much smaller than those observed for **I** (*vide supra*) and appear to arise mainly from ionic migration[6] and perhaps comproportionation-transport[4d,e] effects. That is, due to the intrinsically high concentrations of undiluted **II** and **III**, it is not possible to add sufficient electrolyte to reduce the transference numbers of the monocations of **II** and **III** to insignificant values. (This was also the case in undiluted small-molecule redox liquids.[4]) In dilute CH_3CN solutions of **II** containing excess electrolyte, the two oxidation currents are equal. At electrolyte concentrations less than 2 Li^+/TTF, the overall self-diffusivity of undiluted **II** increases; at 0.25 Li^+/TTF, the ratio of the two oxidation currents is 12. Completely consistent $LiClO_4$ electrolyte concentration effects are observed using the undiluted monocation salt $(II^+)(ClO_4^-)$, another redox-active molten salt. In dilute CH_3CN solutions of **III** containing 1 Li^+/TPP, the ratio of currents for the two oxidation steps (Figure 1E) is approximately the same as that in Figure 1D but become nearly 1 at higher electrolyte concentrations. Thus, while secondary effects from electron self-exchange transport (as with **I** above) and from changes in the interfacial melt liquid structure[4] may contribute, the observed electrolyte concentration dependencies suggest ionic migration as the primary cause of the two unequal oxidation steps for **II** and for **III**.

Ferrocenecarboxylic acid, when esterified with an ethylene glycol trimer tail, is a soft wax, as was a previously described longer-chain derivative.[15] However, esterification with an analogous, but atactic, poly(*propylene* glycol) trimer produces the ferrocene **IV**, which is rich in redox sites ($\sim$2.5 M) and dissolves >1 M $LiClO_4$ electrolyte yet remains a viscous liquid. Figure 1F shows cyclic voltammetry at a 1:3 Li^+/**IV** ratio; chronoamperometric measurements indicate that $D_{app,0/+} = 2 \times 10^{-9}$ cm^2/s in this material. Given its large ferrocene site concentration and the large k_{ex} values typical of ferrocenes in solution, this $D_{app,0/+}$ is probably enhanced by diffusion–electron-transfer coupling.[10]

The above results show that undiluted **I**–**IV** are bulky-site materials with transport properties intermediate between those of dilute fluid solutions and fixed-site polymers. These materials may permit an improved understanding of distinctions between microscopic and macroscopic mobility and viscosity. Compounds **I**–**IV** are, in effect, pseudopolymers, offering large, controllable viscosities and a potential for blending without microphase segregation. Additionally, they may exhibit interesting spectroscopic and thermal properties involving respectively site–site electron and self-entanglement interactions. The structural diversity among **I**–**IV** furthermore suggests that our synthetic approach may have general utility for transforming additional redox and other species into room temperature liquids.

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[11] Andrieux, C. P.; Savéant, J.-M. *J Phys. Chem.* **1988**, *92*, 6761–6767.

[12] (a) Watanabe, M.; Wooster, T. T.; Murray, R. W. *J. Phys. Chem.* **1991**, *95*, 4573–4579. (b) Wooster, T. T.; Watanabe, M.; Murray, R. W. *Ibid.* **1992**, *96*, 5886–5893.

[13] Zhang, H.; Murray, R. W. *J. Am. Chem. Soc.* **1991**, *113*, 5183–5187.

[14] (a) The ionic conductivity of **III** being too low to produce recognizable voltammetry, Figure 1D was produced using CH_3CN vapor-plasticization in the manner described previously. (b) Parcher, J. F.; Barbour, C. J.; Murray, R. W. *Anal. Chem.* **1989**, *61*, 584–589.

[15] Pinkerton, M. J.; LeMest, Y.; Zhang, H.; Watanabe, M.; Murray, R. W. *J. Am. Chem. Soc.* **1990**, *112*, 3730–3736.