58 *Chemistry of Materials* 1989, *1*, 58-63

Solid-State Voltammetric Measurement of Plasticization Transport Enhancement in Ionically Conducting Poly(ethylene oxide) Films

L. Geng,[†] M. L. Longmire, R. A. Reed,[‡] J. F. Parcher,[§] C. J. Barbour, and Royce W. Murray*

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

Received June 16, 1988

The diffusion coefficient D(Os) of the electroactive metal complex $[Os(phen)_3)]^{2+}$ (phen = phenanthroline) and the ionic conductivity $\sigma(LiCF_3SO_3)$ of the salt $LiCF_3SO_3$ in films of the polymeric electrolyte $PEO_{15}/LiCF_3SO_3$ (PEO = poly(ethylene oxide)) exposed to partial pressures of acetonitrile from P/P_0 = 0 to 0.8 increase as acetonitrile is sorbed into the polymer electrolyte. When compared with a free volume analysis, the changes in D(Os) and $\sigma(LiCF_3SO_3)$ are nearly identical. The temperature dependences of D(Os) and $\sigma(LiCF_3SO_3)$ in unplasticized $PEO_{15}/LiCF_3SO_3$ and of the gas chromatographically measured coefficient for partitioning of acetonitrile into $PEO_{15}/LiCF_3SO_3$ all display a discontinuity at the $PEO_{15}/LiCF_3SO_3$ melting temperature. Acetonitrile appears to partition only into the amorphous part of the $PEO_{15}/LiCF_3SO_3$ polymer. A model is presented that accounts for the enhancement of $\sigma(LiCF_3SO_3)$ induced by acetonitrile sorption ("plasticization") in terms of competitive displacement of Li^+ coordination to and Li^+ cross-linking of polyether chains by coordination to acetonitrile. There may also be some alteration in the degree of polymer crystallinity. Enhancement of D(Os) is proposed to occur as an indirect consequence of greater PEO chain segmental mobility resulting from diminution of Li^+/polyether coordination. In this sense the plasticization is a specific chemical effect related to plasticizer–electrolyte coordination.

Controlled-potential electrochemical techniques like cyclic voltammetry have become important tools in studies of heterogeneous and homogeneous electron-transfer dynamics. Because of the practical requirement that electrochemical experiments be done in solvents that are ionically conducting, such studies have traditionally been confined to *fluid* electrolyte solutions. It is significant, then, that it has recently become possible to apply electrochemical methods to electron-transfer phenomena in rigid and semirigid (*nonfluid*) media.[1] Contributing developments are thin-film electron[2] and ion[3] conducting polymers, novel, miniaturized electrochemical cells,[4] and microdimensioned electrodes,[5] which provide important experimental tactics to mitigate the relatively poor ionic conductivities and the slow transport dynamics typical of rigid and semirigid media.

We have in particular exploited[1a,6] the characteristics of disk microelectrodes to obtain solid-state voltammetry of diverse electroactive species like ferrocene, metallotetraphenylporphyrins, metal polypyridine complexes, and tetracyanoquinodimethane dissolved in films of the ionically conducting polymer electrolyte[3] poly(ethylene oxide)/lithium triflate, $PEO/LiCF_3SO_3$. Currents observed[1a,6] at a Pt disk microelectrode contacting a film of the semirigid polymer electrolyte reflect diffusion of the electroactive solute through the polymer to the Pt microelectrode to be reduced or oxidized, just as in fluid solutions, except that the diffusion is much slower. These currents measure diffusion[6a] and homogeneous/heterogeneous electron-transfer rates,[6b] formal potentials,[1a] and axial coordination reactions[6b,c] of the electroactive solute in the polymer phase, molecular phenomena that are familiar in fluid media but are relatively unstudied in solids. Given, for example, recent work[7] demonstrating changes in heterogeneous electron-transfer rates in high-viscosity fluids, experimental access to rigid solvents is timely for further inquiry about effects of solvent dynamics on electrochemical reactions and their associated chemistry.

It is conversely possible to exploit electrochemical reactions in polymers as tools to probe the polymeric phase itself. This paper illustrates the use of solid-state voltammetry to probe transport dynamics in $PEO/LiCF_3SO_3$ films that have been plasticized by gas-phase sorption of the organic monomer acetonitrile. In experiments using an electrochemical microcell (Figure 1A) in which the

---

[†] Present address: Brookhaven National Laboratory, Upton, Long Island, NY 11973.

[‡] Present address: Department of Chemistry, Princeton University, Princeton, NJ 08544.

[§] On leave from the University of Mississippi, University, MS 38677.

(1) (a) Reed, R. A.; Geng, L.; Murray, R. W. *J. Electroanal. Chem.* **1986**, *208*, 185. (b) Oliver, B. N.; Egekeze, J.; Murray, R. W. *J. Am. Chem. Soc.* **1988**, *110*, 2321. (c) Jernigan, J. C.; Chidsey, C. E. D.; Murray, R. W. *J. Am. Chem. Soc.* **1985**, *107*, 2824. (d) Jernigan, J. C.; Murray, R. W. *J. Am. Chem. Soc.* **1987**, *109*, 1738. (e) Skotheim, T. A. *Synth. Met.* **1986**, *14*, 31. (f) Skotheim, T. A.; Florit, M. I.; Melo, A.; O'Grady, W. E. *Mol. Cryst.* **1985**, *121*, 291. (g) Skotheim, T. A.; Inganas, O. *Mol. Cryst. Liq. Cryst.* **1985**, *121*, 285. (h) Skotheim, T. A.; Florit, M. I.; Melo, A.; O'Grady, W. E. *Phys. Rev. B: Condens. Matter* **1984**, *30*, 4846. (i) Inganas, O.; Skotheim, T. A.; Feldberg, S. W. *Solid State Ionics* **1986**, *18/19*, 332. (j) Raleigh, D. O. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1973; Vol. 6. (k) Bond, A. M.; Fleischmann, M.; Robinson, J. *J. Electroanal. Chem.* **1984**, *180*, 257. (l) Chao, S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 2197. (m) Stimming, U.; Schmickler, W. *J. Electroanal. Chem.* **1983**, *150*, 125.

(2) Murray, R. W. *Ann. Rev. Mater. Sci.* **1984**, *14*, 145.

(3) (a) Armand, M. B. *Ann. Rev. Mater. Sci.* **1986**, *16*, 245. (b) Vincent, C. A. *Prog. Solid State Chem.* **1987**, *17*, 145. (c) Ratner, M. A.; Shriver, D. F. *Chem. Rev.* **1988**, *88*, 109. (d) Armand, M. B.; Chabagno, J. M.; Duclot, M. J. In *Fast Ion Transport in Solids*; Mundy, J. N., Shenoy, G. K., Eds.; Pergamon: New York, 1979; p 131.

(4) (a) Chidsey, C. E. D.; Murray, R. W. *Science (Washington, D.C.)* **1986**, *231*, 25. (b) Wohltjen, H.; Barger, W. R.; Snow, A. W.; Jarvis, N. L. *IEEE Trans. Electron Devices* **1985**, *ED-32*, 1170. (c) Kittlesen, G. P.; White, H. S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 7373, and references therein. (d) Sanderson, D. G.; Anderson, L. B. *Anal. Chem.* **1985**, *57*, 2388.

(5) (a) Howell, J. O.; Wightman, R. M. *Anal. Chem.* **1984**, *56*, 524. (b) Bard, A. J.; Crayston, J. A.; Kittelsen, G. P.; Shea Varco T.; Wrighton, M. S. *Anal. Chem.* **1986**, *58*, 2321. (c) Wightman, R. M. *Science (Washington, D.C.)* **1988**, *240*, 415.

(6) (a) Reed, R. A.; Geng, L.; Longmire, M.; Murray, R. W. *J. Phys. Chem.* **1987**, *91*, 2908. (b) Geng, L.; Reed, R. A.; Kim, M.-H.; Wooster, T.; Oliver, B. N.; Egekeze, J.; Kennedy, R.; Jorgenson, J.; Parcher, J. F.; Murray, R. W. *J. Am. Chem. Soc.*, in press. (c) Reed, R. A. Ph.D. Thesis, University of North Carolina, 1987. (d) Diffusion enhancement is also found by using films of Nafion, sulfonated polystyrene, poly(vinyl chloride), and various polymer blends. (e) Geng, L. Ph.D Thesis, University of North Carolina, 1987.

(7) Zhang, X.; Yang, H.; Bard, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 1916.

0897-4756/89/2801-0058$01.50/0

polymer film solution is thin and readily equilibrated (transiently if desired[6b]) with volatile reagents, we found[1a,6a] that sorption of acetonitrile vapor into PEO/$LiCF_3SO_3$ films enhances currents for diffusion of electroactive monomer solutes in the polymer. Following the related ionic conductivity work of Hardy and Shriver[8] on poly(diallyldimethylammonium chloride), we qualitatively interpreted the transport enhancement as plasticization of the PEO/$LiCF_3SO_3$ solution by the sorbed acetonitrile vapor. It is known that low molecular weight solutes (plasticizers) in polymers act to increase polymer chain flexibility by reducing intermolecular interactions and increasing free volume.

This paper presents a quantitative study of how the diffusion coefficient D(Os) of the electroactive probe complex $[Os(phen)_3]^{2+}$ and the ionic conductivity $\sigma(LiCF_3SO_3)$ of the $LiCF_3SO_3$ electrolyte respond to sorption of various amounts of acetonitrile into PEO_{15}/$LiCF_3SO_3$ films. Our analysis uses free volume theory[9,10] as a vehicle to compare D(Os) and $\sigma(LiCF_3SO_3)$ and to demonstrate that these transport parameters respond in almost identical fashion to acetonitrile sorption. This is an interesting result inasmuch as transport of polyether-coordinated Li^+ has been proposed to involve cooperative polymer conformational fluctuations[3,11] whereas specific binding of polyether to $[Os(phen)_3]^{2+}$ is not expected.

Experimental Section

Voltammetry of $[Os(phen)_3](PF_6)_2$ Solutions in PEO_{15}/$LiCF_3SO_3$. Poly(ethylene oxide) (Aldrich, average MW 600 000) purified by column chromatography, $LiCF_3SO_3$ prepared according to a published procedure,[12] and the probe complex $[Os(phen)_3](PF_6)_2$ were codissolved in a 9:1 CH_3CN/CH_3OH casting solution in an ether O:Li ratio of 15:1. Films of PEO_{15}/$LiCF_3SO_3$ containing $[Os(phen)_3]^{2+}$ were cast on the top of the Figure 1A microcell so as to contact the three electrodes. By evaporating multiple solution droplets, a film at least 50 μm (dry) thick was built up. The thickness was established by peeling an example film off the microcell surface.

Voltammetry was observed in these films after equilibrating the microcell with a stream of dry N_2 or with acetonitrile-vapor-saturated N_2 quantitatively diluted (by control of relative flow rates) with dry N_2. For experiments above room temperature, the equilibration temperature was varied by passing the bathing gas feed line through a heated oil bath; a thermocouple in contact with the microcell monitored its temperature. The microcell and the low current potentiostat were housed in a Faraday cage.

Alternating Current Impedance of PEO_{15}/$LiCF_3SO_3$ Films on Interdigitated Array Electrodes. The ionic conductivity of polymer containing only $LiCF_3SO_3$ (no metal complex) was measured by complex ac impedance of ca. 0.3-μm films cast from 9:1 CH_3CN/CH_3OH solution onto a lithographically defined interdigitated array (IDA) electrode that has 20 and 21 Pt fingers, each 3.5 μm wide, extending from opposing contact pads[13] (Figure 1B). The film thickness is just sufficient to "fill" the interfinger gap, which is 2.5 μm wide and 0.3 μm deep, and give a parallel plate arrangement for ionic conductivity measurements. The coated IDA electrode was bathed in dry N_2 or acetonitrile vapor–N_2 mixture as above. The complex impedance analysis for the film ionic conductivity was conducted with a Solartron Model 1186 electrochemical interface connected to a Solartron frequency response analyzer driven by a Hewlett-Packard Model 85B computer.

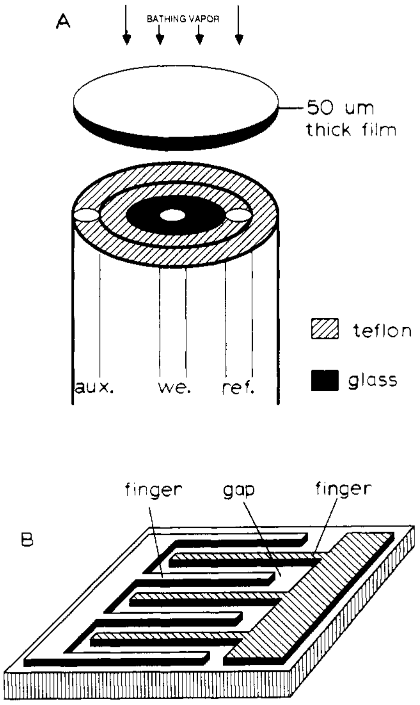

Figure 1. (A) Schematic diagram of three-electrode solid-state microelectrode cell.[1a,6a] The central electrode is the tip of a 10-μm Pt wire sealed in a glass capillary; the auxiliary and reference electrodes are tips of larger Pt and Ag wires sealed onto the glass capillary perimeter with shrinkable plastic. The microcell is polished so that the three electrodes lie in a common plane, over which is cast the polymer electrolyte solution of the electroactive probe complex. (B) Schematic diagram of interdigitated array electrode,[13] consisting of microlithographically defined interdigitated Pt film fingers each 3.5 μm wide and 0.3 μm high, resting on a glass substrate, and separated by 2.5-μm gaps. These gaps comprise the parallel plates of the conductivity cell. The actual IDA has 20 and 21 Pt fingers (more than are shown in the figure); they extend from contact pads, on the left and right of the diagram, that are masked off so that the film of polymer electrolyte contacts only the interdigitated finger part of the device.

Acetonitrile Sorption by PEO_{15}/$LiCF_3SO_3$ films. Acetonitrile sorption into the film was measured gravimetrically by using a Model TGS-2 Perkin-Elmer thermogravimetric instrument. A ca. 2-mg film was dried at 30 °C for several hours in the evacuated sample compartment before isothermal mass measurements in N_2–acetonitrile gas mixtures were done (after 15–20 min of equilibration in each case) at room temperature. The mass changes were reproducible and in a series of measurements did not depend on whether the acetonitrile vapor pressure was increasing or decreasing.

The temperature dependence of acetonitrile sorption into PEO_{15}/$LiCF_3SO_3$ was measured with inverse gas chromatography.[14] The capacity factor k' for elution of acetonitrile bands from a column packed with chromosorb C (dimethyldichlorosilane treated), 10% loaded with PEO_{15}/$LiCF_3SO_3$ as the stationary phase, was determined at a series of column temperatures.

Results

Sorption of Acetonitrile Vapor by PEO_{15}/$LiCF_3SO_3$. Gravimetric results for acetonitrile sorption into films at room temperature as a function of relative vapor pressure P/P_0 of acetonitrile (P_0 is saturated vapor pressure at 25

---

(8) Hardy, L. C.; Shriver, D. F. *J. Am. Chem. Soc.* **1985**, *107*, 3823.

(9) Flory, P. J. *J. Chem. Phys.* **1950**, *18*, 108.

(10) (a) Suwandi, M. S.; Stern, S. A. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 663. (b) Stern, S. A.; Saxena, V. *J. Membr. Sci.* **1980**, *7*, 47. (c) Fujita, H.; Kishimoto, A.; Matsumoto, K. *Trans. Faraday Soc.* **1960**, *56*, 424. (d) Stern, S. A., Frisch, H. L. *Ann. Rev. Mater. Sci.* **1981**, *11*, 523.

(11) (a) Watanabe, M.; Sanui, K.; Ogata, N. *Macromolecules* **1986**, *19*, 815. (b) Stainer, M.; Hardy, L. C.; Whitmore, D. H.; Shriver, D. F. *J. Electrochem. Soc.* **1984**, *131*, 784.

(12) (a) Papke, B. L.; Ratner, M. A.; Shriver, D. F. *J. Phys. Chem. Solids* **1981**, *42*, 493. (b) Bhattacharja, S.; Smoot, S. W.; Whitmore, D. H. *Solid State Ionics* **1986**, *18/19*, 306. (c) Hotzel, G.; Weppner, W. *Solid State Ionics* **1986**, *18/19*, 1223.

(13) Chidsey, C. E. D.; Feldman, B. J.; Lundgren, C.; Murray, R. W. *Anal. Chem.* **1986**, *58*, 601.

(14) (a) Guillet, J. E.; Stein, A. N. *Macromolecules* **1970**, *3*, 103. (b) Gray, D. G.; Guillet, J. E. *Macromolecules* **1971**, *4*, 129. (c) Courval, G.; Gray, D. G. *Macromolecules* **1975**, *8*, 326. (d) Mori, S. *J. Chromatogr.* **1977**, *135*, 261.

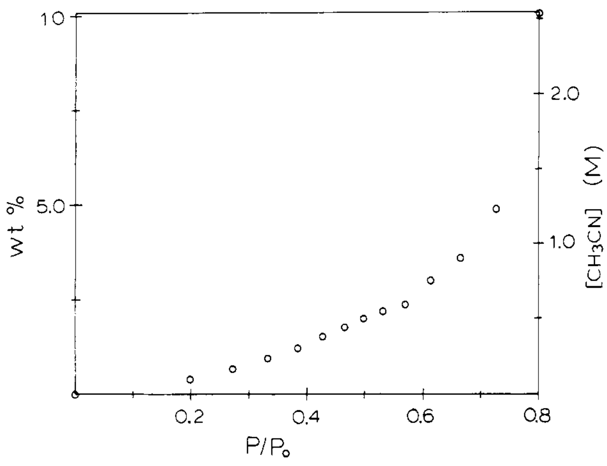

Figure 2. Uptake of sorbed acetonitrile by PEO_{15}/LiF_3SO_3 film as a function of acetonitrile partial pressure P/P_0.

Table I. $[Os(phen)_3]^{2+}$ Acetonitrile Sorption and Diffusion Coefficient Results in $PEO_{15}/LiCF_3SO_3$

P/P_0	% wt[a]	$[CH_3CN]$,[b] M	$10^9D(Os)$,[c] cm^2/s	X[d]	υ[b]	10^9D_T,[e] cm^2/s
0	0	0	0.1			
0.20	0.35	0.10	0.16	2.65	0.005	0.16
0.27	0.59	0.17	0.32	2.45	0.0091	0.32
0.33	0.83	0.24	0.37	2.33	0.013	0.37
0.38	1.08	0.31	0.48	2.24	0.016	0.48
0.43	1.35	0.39	0.58	2.14	0.021	0.58
0.47	1.56	0.45	0.66	2.10	0.024	0.66
0.50	1.77	0.50	0.79	2.06	0.027	0.79
0.53	1.94	0.55	0.93	2.04	0.030	0.93
0.57	2.12	0.60	0.99	2.04	0.032	0.99
0.62	2.71	0.76	1.45	1.91	0.041	1.46
0.67	3.26	0.91	2.38	1.84	0.048	2.43
0.73	4.51	1.23	4.63	1.68	0.066	4.85
0.80	10.07	2.55	16.9	1.22	0.136	21.2

[a] Percentage weight increase upon CH_3CN sorption at indicated P/P_0. [b] Molar concentration and volume fraction (υ) of CH_3CN calculated assuming additive volumes. [c] From data in Figure 4 and eq 1. [d] From eq 4. [e] From eq 3.

°C) reveal a sorption isotherm (Figure 2) with a positive deviation from Henry's law. The apparent strong interaction between acetonitrile and the polymer and/or electrolyte is consistent with the fact that PEO and $LiCF_3SO_3$ are both freely soluble in liquid acetonitrile. Table I presents the sorption data and the corresponding acetonitrile concentrations and volume fractions. At the highest volume fraction, ca. 0.14, the polymer film is noticeably softened but remains semirigid.

The chromatographic capacity factor k' for acetonitrile sorption into $PEO_{15}/LiCF_3SO_3$ depends on temperature as shown in Figure 3. (Capacity factor is proportional to the amount of acetonitrile sorbed at each temperature.) The symmetry of the observed chromatographic peaks indicates that these data correspond to sorption equilibria on the low P/P_0, linear part of the sorption isotherm of Figure 2. The capacity factor results are notable in several respects: (i) As the temperature is raised, a discontinuity in k' occurs beginning at 52 °C, which corresponds to the thermally detectable melting feature,[3] T_m, associated with melting of PEO microcrystallites dispersed in amorphous PEO material. (ii) The slopes of the linear segments in Figure 3, which are proportional to the heat of solution of acetonitrile into $PEO_{15}/LiCF_3SO_3$, are nearly identical above and below T_m. Since above T_m the polymer is mainly in an amorphous state, we infer that, below T_m, acetonitrile is *also partitioning into an amorphous polymer phase*. (iii) Following ii, if the 10-fold change in k' at T_m is taken to represent a corresponding 10-fold change in the amount of amorphous PEO phase in the column, then the polymer is ca. 10% amorphous below T_m. This gas chromatographic approach to measure polymer crystallinity is well-known[14] but has not been applied to polymer electrolytes. The result is consistent with an NMR-based study[15] of $PEO_8/LiCF_3SO_3$.

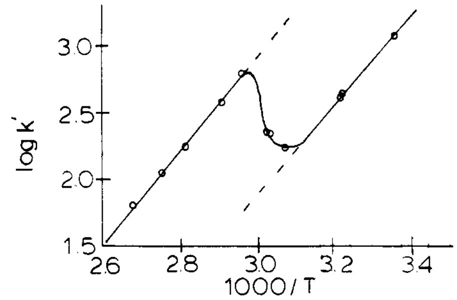

Figure 3. Temperature dependence of the capacity factor for elution of 0.5-μL samples of acetonitrile from a 2-m gas chromatography column packed with 10 wt % $PEO_{15}/LiCF_3SO_3$ on chromosorb C (dimethyldichlorosilane treated, acid washed). Temperatures were measured with an Omega TAC-386-JC thermocouple.

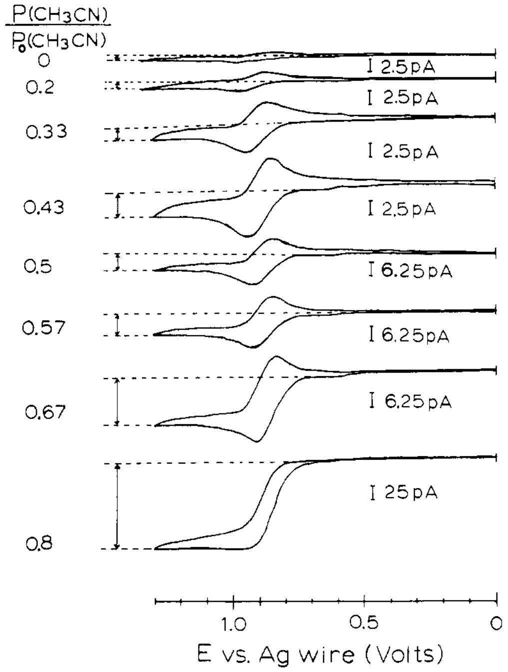

Figure 4. Microelectrode cyclic voltammetry of 4.9×10^{-5} mol/cm³ $[Os(phen)_3]^{2+}$ dissolved in a ca. 50-μm-thick film of $PEO_{15}/LiCF_3SO_3$ on the miniature electrochemical cell of Figure 1A, at various partial pressures of CH_3CN in the bathing gas.

Diffusion of $[Os(phen)_3]^{2+}$ in $PEO_{15}/LiCF_3SO_3$ Solution. Currents for oxidation of this complex (to $[Os(phen)_3]^{3+}$) in room-temperature $PEO_{15}/LiCF_3SO_3$ solutions, barely perceptible (Figure 4, top curve) in dry N_2 bathing gas, are readily measurable when the polymer is exposed to acetonitrile vapor (Figure 4). The larger currents reflect increasingly rapid diffusion of $[Os(phen)_3]^{2+}$ in the polymer solvent as the concentration of sorbed acetonitrile increases at higher P/P_0.

At $P/P_0 = 0.8$ (lowest curve, Figure 4), the oxidation voltammogram exhibits a well-defined limiting current i_L, which shows that diffusion of $[Os(phen)_3]^{2+}$ to the disk microelectrode is rapid enough (on the time scale of the

---

(15) Berthier, C.; Gorecki; Minier, M.; Armand, M. B.; Chabagno, J. M.; Rigand, P. *Solid State Ionics* **1983**, *11*, 91.

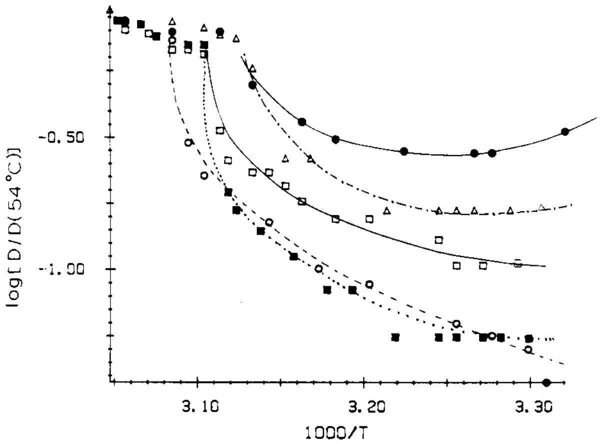

Figure 5. Diffusion coefficients of $[Os(phen)_3]^{2+}$ dissolved in $PEO_{15}/LiCF_3SO_3$, measured by cyclic voltammetry as in Figure 4, normalized to that at 54 °C, as a function of temperature and bathing gas: ○, dry N_2; ■, $P/P_0 = 0.33$; □, $P/P_0 = 0.43$; △, $P/P_0 = 0.57$; ●, $P/P_0 = 0.67$.

potential sweep) to establish an approximately hemispherically shaped radial diffusion field deeper than the 5-μm microdisk radius. The 50-μm polymer film thickness acts as a semiinfinite solvent volume, so that i_L can be expressed as[16]

$$i_L = 4nrFDC \tag{1}$$

where r is 5 μm and D and C are the diffusion coefficient and concentration, respectively, of the $[Os(phen)_3]^{2+}$ complex in the polymer. (The slight swelling of the film by sorbed acetonitrile vapor was neglected in figuring concentration.) The limiting current at $P/P_0 = 0.8$, where the concentration of sorbed acetonitrile is 2.6 M, gives $D(Os) = 1.7 \times 10^{-8}$ cm²/s. This diffusion constant is over 10^2 times smaller than $D(Os)$ in pure liquid acetonitrile solvent.[1]

At lower P/P_0, $[Os(phen)_3]^{2+}$ diffusion is slower, and the radial diffusion field develops more slowly; this causes the voltammograms to exhibit a current peak before the current settles to a steady value near the terminus (1.3 V) of the voltage sweep. (Scanning the potential more slowly, at 2 mV/s rather than 5 mV/s, gives less pronounced current peaks but practically identical limiting currents at 1.3 V.) Measuring i_L as indicated in Figure 4 gives the values for $D(Os)$ listed in Table I.

We should note at this point that the $D(Os)$ results in Table I probably include a charge-transport contribution from homogeneous electron self-exchange between $[Os(phen)_3]^{2+}$ and electrogenerated $[Os(phen)_3]^{3+}$ and thus overestimate the actual physical diffusion rate of $[Os(phen)_3]^{2+}$. The effect is analogous to that reported for $[Co(bpy)_3]^{+/2+}$ self-exchange by Buttry and Anson[17] in liquid-wetted Nafion films and will be more fully discussed in a separate publication.[6c] The error is not thought to be serious, since the electron self-exchange rate is itself diffusion-limited, meaning that the measured diffusion coefficients in Table I are all enhanced by similar amounts.

Figure 5 shows the temperature dependence of $[Os(phen)_3]^{2+}$ diffusion in $PEO_{15}/LiCF_3SO_3$ films exposed to various acetonitrile vapor pressures and to dry N_2. The data are normalized to $D(Os)$ measured at 54 °C, for ease of comparison. For polymer bathed only in dry N_2 (open circles), diffusion is slow at room temperature but increases rapidly with temperature to an abrupt "knee" at 52 °C, thereafter following an Arrhenius-like behavior. Like the capacity factor feature in Figure 3, the knee in the $[Os(phen)_3]^{2+}$ diffusion rate occurs near the PEO microcrystallite melting temperature T_m. An analogous knee is known to occur in the temperature dependence of the ionic conductivity of PEO–$LiCF_3SO_3$ polymer electrolyte.[18]

Table II. Ionic Conductivity of $PEO_{15}/LiCF_3SO_3$ as a Function of Sorbed Acetonitrile at 25 °C

P/P_0	$[CH_3CN]$, M	$10^7\sigma(LiCF_3SO_3)$, Ω^{-1} cm^{-1}	X^a	$10^7\sigma_T{}^b$
0	0	1.54		1.54
0.23	0.13	1.65	2.52	1.64
0.32	0.24	2.10	2.29	2.08
0.41	0.39	2.7	2.12	2.70
0.50	0.52	4.52	2.05	4.53
0.59	0.73	4.88	1.92	4.93
0.68	0.91	5.52	1.77	5.67
0.77	1.87	8.00	1.18	9.41

[a] From eq 4. [b] From eq 3.

Clearly the presence of the PEO microcrystallites strongly depresses both diffusion of $[Os(phen)_3]^{2+}$ and mobilities of electrolyte charge carriers in PEO below T_m. Transport of alkali-metal salts dissolved in PEO is thought to occur predominantly in the amorphous regions[3,15] and for Li^+ to occur by sequential cooperative segmental motions of polyether chains to which it is coordinated.[3,11] Diffusion of the $[Os(phen)_3]^{2+}$ complex is expected to be also confined to the amorphous regions and to depend on segmental motions of PEO chain segments, but not necessarily cooperative ones in the manner imagined for Li^+ ion transport.

When the polymer electrolyte is equilibrated with acetonitrile at various P/P_0, $[Os(phen)_3]^{2+}$ diffusion rates (Figure 5) are enhanced at all temperatures below T_m but are enhanced most at the lower temperatures and least at temperatures near T_m. This temperature dependence of plasticization is undoubtedly associated with the decreasing extent of acetonitrile sorption as temperature is increased (cf. Figure 3). This explanation is reinforced by observing that under conditions of extensive sorption (lowest temperatures and $P/P_0 = 0.67$), the temperature dependence of acetonitrile sorption, which is opposite to that of $[Os(phen)_3]^{2+}$ diffusion, begins to dominate, causing $D(Os)$ to actually *increase* in an absolute sense as temperature *decreases.*

Figure 5 also shows that the T_m melting feature persists even at high P/P_0 values, indicating that PEO retains part or all of its microcrystallinity when acetonitrile is sorbed. This observation is consistent with our interpretation of Figure 3 (vide supra). In that light, it is interesting that the ca. 10-fold increase between 50 and 66 °C in amorphous phase volume into which acetonitrile can partition (cf. Figure 3) is mirrored by sharp increases in $D(Os)$ between ca. 44 and 51 °C (cf. Figure 5). While the temperature offset between these events is puzzling, they do support prior suggestions[3b,c] that microcrystalline regions serve to impose a tortuosity on the diffusion pathway available for transport and, probably by amorphous and crystalline regions sharing individual PEO molecules, also act to cross-link the polymer.

Ionic Conductivity of $PEO_{15}/Li(CF_3SO_3)$ Solutions. Ionic conductivities of polymer electrolyte, containing no Os complex, were measured in films coated on interdigitated array electrodes (Figure 1B) as described in the Experimental Section, by using an ac complex impedance analysis. Straightforward RC semicircles were observed

---

(16) Wightman, R. M. *Anal. Chem.* **1981**, *53*, 1125A.

(17) Buttry, D. A.; Anson, F. C. *J. Am. Chem. Soc.* **1983**, *105*, 685.

(18) Weston, J. E.; Steele, B. C. H. *Solid State Ionics* **1981**, *2*, 347.

over a range of frequencies of 1 Hz to 66 kHz for the 2.5-μm-wide segment of polymer in the IDA interelectrode gap. Conductivities thus derived, $\sigma(\mathrm{LiCF_3SO_3})$, are given in Table II. The plasticization-derived ionic conductivity enhancement in Table II is less than that observed by Hardy and Shriver in an analogous study.[8,11b]

Discussion

To examine the transport data in Tables I and II, we make use of free volume theory originally designed[9,10] for analysis of gas permeation through polymeric membranes. The analysis accounts for (i) how sorption of the permeant (in our case the plasticizing acetonitrile) into the polymer film depends on its gas pressure and (ii) how transport rates of the permeant (in our case the transport rates are $D(\mathrm{Os})$ and $\sigma(\mathrm{LiCF_3SO_3})$) in the polymer depend on the amount of sorbed permeant. Our application of the theory neglects the facts that the polymer is not entirely amorphous at room temperature, that the sorbed acetonitrile is concentrated into the amorphous regions, and that the transference numbers of $\mathrm{Li^+}$ and $\mathrm{CF_3CO_3^-}$ (which are not known in the room-temperature material) might vary with acetonitrile sorption. The main purpose of applying the free volume theory (there are alternative approaches[3]) is simply as a convenient vehicle for comparing the responses of $D(\mathrm{Os})$ and $\sigma(\mathrm{LiCF_3SO_3})$ to acetonitrile sorption within a common theoretical framework.

The relationship connecting[10c,d] sorption and diffusion rate is

$$(\ln [D_T/D_0])^{-1} = v(0,T)/B_d + [v(0,T)]^2/[B_d r(T)](1/v) \tag{2}$$

where D_T is the thermodynamic diffusion coefficient of $[\mathrm{Os(phen)_3}]^{2+}$ and v the volume fraction of sorbed acetonitrile. D_0 is the $[\mathrm{Os(phen)_3}]^{2+}$ diffusion coefficient at zero sorbed acetonitrile, and the other terms are free volume parameters: $v(0,T)$ is the free volume of pure polymer, B_d is a constant related to the minimum hole size required for diffusion, and $r(T)$ is a proportionality factor.

D_T is related to the experimental diffusion coefficient $D(\mathrm{Os})$, by[10a,c]

$$D_T = \{D(\mathrm{Os})/(1 - v)^3\}\{\delta \ln (v)/\delta \ln (a)\} = D(\mathrm{Os})/\{(1 - v)^3[1 - (1 - 2X)v + 2Xv^2]\} \tag{3}$$

where a is the activity of sorbed acetonitrile, the $(1 - v)^3$ term takes the intrinsic diffusion coefficient of the polymer as negligible, and the $\{\delta \ln (v)/\delta \ln (a)\}$ term represents the thermodynamic Flory–Huggins equation[9,10]

$$\ln (a) = \ln (v) + (1 - v) + X(1 - v)^2 \tag{4}$$

in which the strength (substantially heat of mixing) of interaction between acetonitrile and the polymer–solvent is parameterized as X, the Flory–Huggins interaction parameter.

Taking activity $a = P/P_0$ gives from eq 4 and 3 and from the volume fractions v and experimental diffusion coefficients $D(\mathrm{Os})$ listed in Table I the interaction parameters X and thermodynamic diffusion coefficients D_T, respectively, also listed in Table I. X varies with acetonitrile volume fraction; for a strictly amorphous polymer, X should be independent of concentration, but it is known to vary in partially crystalline materials. The variation in X is of little consequence, however, since D_T and $D(\mathrm{Os})$ measurably differ only at the highest acetonitrile concentrations.

Equation 2 predicts that $[\ln (D_T/D_0)]^{-1}$ should vary linearly with $1/v$. Because the room-temperature $[\mathrm{Os(phen)_3}]^{2+}$ voltammetry at $P/P_0 = 0$ is poorly defined (Figure 4, top), D_0 was obtained by comparing the data to an empirical relation known to describe gas permeation systems:[10a,19]

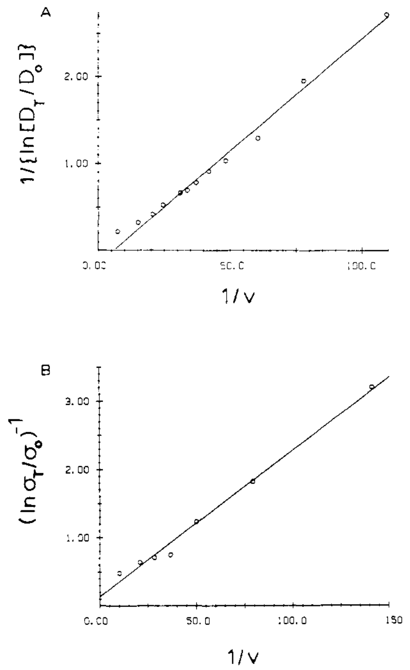

Figure 6. Plot of eq 2 for diffusion coefficients D_T of $[\mathrm{Os(phen)_3}]^{2+}$ (panel A) and σ_T of $\mathrm{LiCF_3SO_3}$ (panel B).

$$D(\mathrm{Os}) = D_0 \exp(\beta C) \tag{5}$$

where β is a constant and C is sorbed acetonitrile concentration. Extrapolation of the linear log $[D(\mathrm{Os})]$ vs C plot gives $D_0 = 0.2 \times 10^{-9}$ cm^2/s, which when used with D_T and $1/v$ from Table I according to eq 2 gives the analysis shown in Figure 6A. The excellent fit (correlation coefficient 0.9944) shows that the plasticization enhancement of $[\mathrm{Os(phen)_3}]^2$ can be represented by this free volume theory.

The $\mathrm{LiCF_3SO_3}$ conductivity data (Table II) were similarly analyzed. In this case the measured quantity is ionic conductivity $\sigma(\mathrm{LiCF_3SO_3})$ which is the product of n_T, the number of carrier ions per unit volume, and μ_T, their mobility. We assume, for the moment, that plasticization occurs more through enhancement of carrier mobility than by changes in carrier generation, i.e., that $\sigma(\mathrm{LiCF_3SO_3})$ is proportional to μ_T and that $\ln [\sigma_T/\sigma_0]$ can be substituted for $\ln [D_T/D_0]$ in eq 2. Application of eq 5 gives $\sigma_0 = 1.2 \times 10^{-7}\ \Omega^{-1}\ \mathrm{cm}^{-1}$, which plotted according to eq 2 with the σ_T values in Table II gives Figure 6B. Again, the free volume theory gives a good representation of the variation of PEO/$\mathrm{LiCF_3SO_3}$ ionic conductivity with the volume fraction of sorbed acetonitrile.

Comparison of the analyses in Figure 6A and 6B shows that the $[\mathrm{Os(phen)_3}]^{2+}$ diffusion coefficient $D(\mathrm{Os})$ and the electrolyte ionic conductivity $\sigma(\mathrm{LiCF_3SO_3})$ *respond virtually identically to acetonitrile plasticization.* The intercepts of Figure 6A and 6B are both nearly zero, and their slopes differ by only about 10%. This similarity could be fortuitous, but we believe it more plausible that acetonitrile *plasticization occurs by influencing event(s) that exert common control over the values of both* $D(\mathrm{Os})$ *and* $\sigma(\mathrm{LiCF_3SO_3})$. We next consider the possibilities for such a common factor: changes in ion–ion association equilibria, in chemical interactions of the ionic participants

---

(19) Mauze, G. R.; Stern, S. A. *J. Membr. Sci.* **1982**, *12*, 51.

with the polymer, or in polymer microcrystallinity.

There is substantial evidence[3b,c,11,20] that ionic conductivity in polymer electrolytes is affected by ion association equilibria. One mode of action by which sorbed acetonitrile might increase $\sigma(\mathrm{LiCF_3SO_3})$ then is to alter, by competitive solvation of $\mathrm{Li^+}$ and $\mathrm{CF_3SO_3^-}$, the extent of their ion association or clustering. From this viewpoint, the changes in $\sigma(\mathrm{LiCF_3SO_3})$ shown in Table II could reflect changes in carrier generation as well as carrier mobility. This viewpoint is, however, not successful in understanding changes in $D(\mathrm{Os})$ that occur upon acetonitrile sorption, because $[\mathrm{Os(phen)_3}]^{2+}$,$\mathrm{CF_3SO_3^-}$ ion pairing is both less likely and of minor consequence since (redox) charge carrying is accomplished equally well (except for the influence of molecular volume) by an ion-paired and a dissociated electroactive species. On the basis of the virtually identical responses of $D(\mathrm{Os})$ and $\sigma(\mathrm{LiCF_3SO_3})$ to acetonitrile sorption (Figure 6), we suggest that, while $\mathrm{LiCF_3SO_3}$ charge-carrier densities may change somewhat upon acetonitrile sorption, the main effect on $\sigma(\mathrm{LiCF_3SO_3})$ is due to an increase in carrier mobility, i.e., mobility of the $\mathrm{Li^+}$ and $\mathrm{CF_3SO_3^-}$ electrolyte ions.

That alkali-metal cations are strongly coordinated to polyether oxygen in polymer electrolytes and that ionic conductivity occurs predominantly in the amorphous regions of PEO are well established.[3b,c,15] Transport of alkali-metal cations has been proposed[11] to occur by cooperative fluctuations of the polymer chains to which they are coordinated. It must also be true that alkali-metal cations, by coordination to segments of adjacent macromolecules, act as ionic cross-linking sites, which would strongly reduce overall segmental mobility within the polymer. Such electrolyte cross-linking would have the strongest mobility consequences for polymer chains already partially ordered by being partly embedded[21] in crystalline regions.

We suggest that alteration of the above alkali metal–polyether cross-linking, either in amorphous or in near-crystalline regions, is an important component of acetonitrile plasticization of this polymer electrolyte. This alteration could occur through competitive coordination or by a change in the degree of crystallinity, or most likely both. Lithium salts are well solvated by acetonitrile, they are typically quite soluble in the liquid solvent, and lithium–acetonitrile coordination is to be expected in the plasticized polymer solvent. Competitive coordinative replacement of $\mathrm{Li^+}$/ether oxygen interactions with $\mathrm{Li^+/CH_3CN}$ interactions would diminish electrolyte cross-linking and at the same time lessen the dependency of $\mathrm{Li^+}$ motion on cooperative polymer chain segmental motions and yield larger uncoordinated polymer chain segmental mobility.

The above arguments also serve to explain how sorbed acetonitrile enhances $D(\mathrm{Os})$. It is expected that $[\mathrm{Os(phen)_3}]^{2+}$ diffusion is controlled by segmental motions of PEO chains, so that any factor, like decreasing interchain cross-linking by competitive $\mathrm{Li^+}$/acetonitrile coordination or decreasing microcrystallinity, would produce a concomitant increase in the metal complex diffusion rate. This explanation is consistent with the fact that appreciable transport enhancements are produced by sorbed concentrations of acetonitrile (Table I) that are much lower than the 1.5 M $\mathrm{LiCF_3SO_3}$ electrolyte concentration, yet are much higher than the 0.05 M concentration of $[\mathrm{Os(phen)_3}]^{2+}$.

Major changes in the degree of crystallinity in $\mathrm{PEO_{15}/LiCF_3SO_3}$ upon acetonitrile sorption can be ruled out by the data in Figure 5, which shows that the T_m melting feature is retained even at large P/P_0. Additionally, we have observed[6b] in gas plug flow experiments in which the transient sorption and desorption of acetonitrile into $\mathrm{PEO_{15}/LiCF_3SO_3}$ is observed through changes in $D(\mathrm{Os})$, that such changes can be observed on time scales (seconds) much too short to imagine reversible melting and refreezing of large quantities of microcrystallites to be the source of the effect. On the other hand, it must be admitted that transport processes in $\mathrm{PEO_{15}/LiCF_3SO_3}$ may be extremely sensitive to even tiny changes in microcrystallinity, so involvement of this property of $\mathrm{PEO_{15}/LiCF_3SO_3}$ in the plasticization phenomenon cannot be entirely ruled out.

In summary of the above considerations, we propose that Figure 6 should be interpreted in terms of a common factor controlling both electrolyte ion and $[\mathrm{Os(phen)_3}]^{2+}$ mobility, that factor being the mobility of polymer segments whose fluctuations are intrinsically associated with electrolyte ion and $[\mathrm{Os(phen)_3}]^{2+}$ transport, and that sorption of the acetonitrile plasticizer increases polymer segmental mobility by competitive coordination of polymer chain cross-linking $\mathrm{Li^+}$ ions and possibly also by reduction of PEO microcrystallinity. This explanation of the acetonitrile plasticization is thus a chemically specific one, in the sense of being evoked by plasticizer–electrolyte coordination.

Finally we should note that free volume increases due to strictly nonspecific effects of freely rotating acetonitrile molecules dissolved in the amorphous phase of the $\mathrm{PEO/LiCF_3SO_3}$ medium are not likely to play a significant role in transport rate effects. Shriver et al.[11b] have shown, for example, that dissolution of ammonia in the strictly amorphous form of $\mathrm{PEO/NH_4CF_3SO_3}$ causes little if any change in ionic conductivity in that polymer solvent. And we have observed[6c] that while toluene is sorbed by $\mathrm{PEO/LiCF_3SO_3}$ to an extent nearly the same as acetonitrile, it is less effective at plasticizing the solvent (for $[\mathrm{Os(phen)_3}]^{2+}$ diffusion) than acetonitrile by ca. 20-fold. It is expected that toluene is a less potent ligand for $\mathrm{Li^+}$ than is acetonitrile.

Acknowledgment. This research was supported in part by a grant from the National Science Foundation. We gratefully acknowledge technical and equipment assistance with the ac impedance measurements from M. Iglehart and Prof. R. P. Buck, of UNC.

Registry No. $\mathrm{LiCF_3SO_3}$, 33454-82-9; PEO, 25322-68-3; $\mathrm{Os(phen)_3(PF_6)_2}$, 75441-76-8; acetonitrile, 75-05-8.

---

[20] Dupon, R. W.; Papke, B. L.; Ratner, M. A.; Whitmore, D. H.; Shriver, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 6247.

[21] Boyer, R. F. *J. Macromol. Sci. Phys. B* **1973**, *8*, 503.