

Charge Transport through Osmium-Containing Redox Polymers in Nitrophenyl-Based Solvents: Effect of Solvent Size

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Most studies on osmium-containing redox polymers have been carried out in aqueous media. The rate of charge transport through the osmium-containing redox polymer as a function of solvent properties has not been investigated. This paper reports studies of osmium-containing redox polymers in five nitrophenyl-based solvents: nitrobenzene, 2-nitrotoluene, 3-nitro-*o*-xylene, 2-nitrophenyl pentyl ether, and 2-nitrophenyl octyl ether. These solvents differ from solvents conventionally used for studying osmium-containing redox polymers, such as water and methanol, in that they have both high dipolarities and larger molecular sizes. Both chronoamperometry and cyclic voltammetry studies on those solvents indicate that it is the solvent size rather than the solvent polarity that determines the rate of charge transport through the osmium-containing redox polymer. The larger the solvent size, the slower the charge transport. We also found that the type of counterion has a strong effect on the cyclic voltammetry of the osmium-containing redox polymers in nitrophenyl-based solvents. No cyclic voltammetry waves were observed when using tetraphenylborate-based supporting electrolyte. Charge transport activation enthalpy–entropy compensation was observed for the redox reactions of the osmium-containing polymer in methanol, nitrobenzene, and 2-nitrotoluene. This suggests that the effect of solvent on the rate of charge transport is likely to involve ion pairing and the associated solvation and polymer rearrangements accompanying the making and breaking of the ion pairs.

Introduction

Osmium-containing redox polymers have been widely used for charge transport in enzyme sensors.^{1–4} However, most of the investigations of osmium- or ruthenium-containing redox polymers have been conducted in aqueous media,⁵ with very few exceptions.^{6,7} We have recently been developing a solid-state PVC membrane-based device for performing liquid/liquid interfacial voltammetry^{8–12} at the PVC plasticizer/water interface. In this application, we desired to use osmium-containing redox polymers in 2-nitrophenyl octyl ether (*o*-NPOE), a PVC plasticizer.¹³ However, we have found that the rate of charge transport through the osmium-containing redox polymers in *o*-NPOE is poor. This motivated us to investigate the effect of solvent properties on the rate of charge transport through the osmium-containing redox polymers.

The function of this osmium-containing redox polymer in interfacial voltammetry^{8–12} is shown in Figure 1. The redox polymer-coated carbon electrode is expected to act as a counter electrode which both maintains its potential and carries current. If this can be achieved by the osmium-containing redox polymer, then a potentiostat can control the potential applied at the PVC membrane/water interface using a three-electrode cell configuration.⁸ For optimal performance, the osmium-containing redox polymer should satisfy two criteria. First, the charge transport through the osmium-containing redox polymer should be fast in nitrophenyl-based PVC plasticizers. This ensures that the rate-limiting step of this device is the charge transfer at the

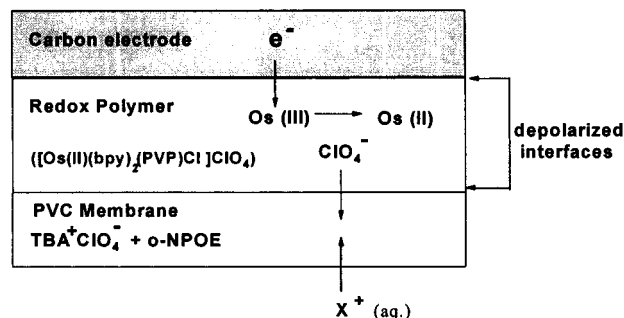


Figure 1. Schematics of the design of a PVC membrane-based liquid–liquid interfacial voltammetry device using an osmium-containing redox polymer-coated carbon electrode as a counter electrode.

PVC membrane/water interface. Second, the osmium-containing redox polymer film needs to supply a large number of charges, so that the electrode can carry some current without causing a large potential shift. Therefore, it is important to find an optimal solvent for achieving facile charge transport through the osmium-containing redox polymer.

The dynamics of charge transport through redox polymers are described by the electron-hopping theory.^{14–18} Parameters that affect the rate of charge transport are self-exchange rate constant,¹⁴ counterion transport,^{19–23} and polymer segment mobility.^{2,24,25} In this work, we seek to understand how the solvent properties affect the rate of charge transport through the osmium-containing redox polymer. We used a group of nitrophenyl-based solvents: nitrobenzene, 2-nitrotoluene, 3-nitro-*o*-xylene, 2-nitrophenyl pentyl ether, and 2-nitrophenyl octyl ether (Figure 2). More traditional organic solvents were also studied for comparison. Both cyclic voltammetry and chrono-

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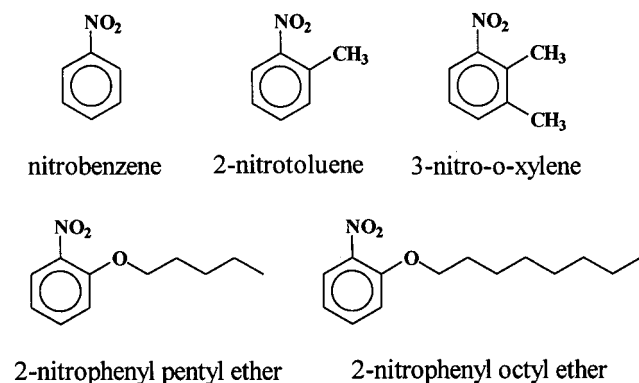


Figure 2. Structure of nitrophenyl-based solvents.

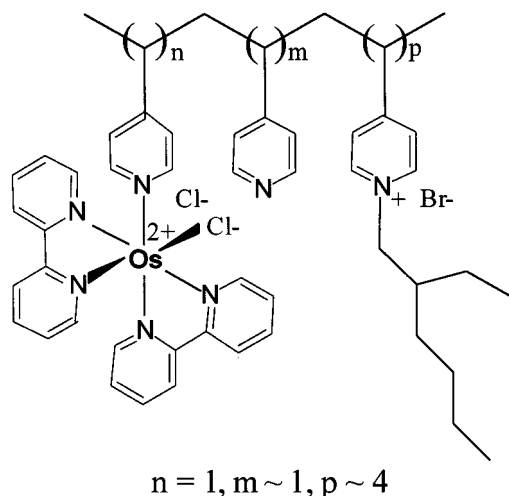


Figure 3. Structure of the osmium-containing redox polymer used in this work.

amperometry were used to study the effect of solvent on the rate of charge transport through the osmium-containing redox polymer. Ultramicroelectrodes were used for chronoamperometry studies in order to minimize the iR drop.

Experimental Section

Materials. Nitrobenzene and 2-nitrophenyl pentyl ether were obtained from Fluka (Switzerland). 2-Nitrotoluene, 3-nitro-*o*-xylene, 2-nitrophenyl octyl ether, 2-ethylhexyl bromide (95%), and 1,10-dibromodecane were obtained from Aldrich (Milwaukee, WI). Potassium hexachloroosmate(IV) was obtained from Alfa (Ward Hill, MA). Poly(4-vinylpyridine) (PVP) (molecular mass $\approx 50\,000$) was obtained from Polysciences, Inc. (Warrington, PA). Reichardt's dye was obtained from Aldrich. Tetrabutylammonium perchlorate was obtained from GFS Chemicals (Columbus, OH). Tetrabutylammonium chloride and sodium tetraphenylborate were obtained from Aldrich. Tetrabutylammonium tetraphenylborate salt was prepared by coprecipitating aqueous solutions of tetrabutylammonium chloride and sodium tetraphenylborate. House deionized water from the Milli-Q system was used in this work.

Synthesis of $[\text{Os}(\text{II})(\text{bpy})_2((2\text{EH}-\text{PVP})\text{Br})\text{Cl}]\text{Cl}$ Polymer (Figure 3). $[\text{Os}(\text{II})(\text{bpy})_2(\text{PVP})\text{Cl}]\text{Cl}$ polymer was synthesized according to the literature³ using potassium hexachloroosmate(IV) as the starting material. The alkylation of PVP polymer was achieved by refluxing a methanol solution (10 mL) of 50 mg of $[\text{Os}(\text{II})(\text{bpy})_2(\text{PVP})\text{Cl}]\text{Cl}$ and 80 mg of 2-ethylhexyl bromide under nitrogen for 4 h. After cooling to room temperature, the reaction mixture was evaporated to about 1–2

TABLE 1: Solvent Properties

solvent	solubility		π^* ^c	ϵ^d
	Os–2-EH ^a	no 2-EH ^b		
water	no ^e	yes ^f	1.09	78.5
acetonitrile (ACN)	no	no	0.75	37.5
methanol	yes	yes	0.60	32.7
water/ACN (v/v:10/90)	yes	yes	NA ^g	NA
nitrobenzene	yes	yes	0.85 ^h	34.8
2-nitrotoluene	no	no	0.81 ^h	26.3
3-nitro- <i>o</i> -xylene	No	no	0.77 ^h	NA
2-nitrophenyl pentyl ether	no	no	0.82 ^h	NA
2-nitrophenyl octyl ether	no	no	0.81 ^h	23.1

^a Osmium-containing redox polymer modified with 2-ethylhexyl groups (Figure 3). ^b Osmium-containing redox polymer without the modification of 2-ethylhexyl groups. ^c Abboud–Kamlet–Taft solvent dipolarity parameter. ^d Dielectric constant. ^e Not soluble. ^f Highly soluble. ^g Data not available. ^h Measured in this work; other π^* and ϵ values were obtained from the literature.²⁹

mL and was added dropwise to a stirred beaker containing 200 mL of diethyl ether. The $[\text{Os}(\text{II})(\text{bpy})_2((2\text{EH}-\text{PVP})\text{Br})\text{Cl}]\text{Cl}$ polymer was precipitated while the unreacted 2-ethylhexyl bromide remained in the solution. The precipitate was collected by filtration and rinsed with 50 mL of diethyl ether. Then, the $[\text{Os}(\text{II})(\text{bpy})_2((2\text{EH}-\text{PVP})\text{Br})\text{Cl}]\text{Cl}$ polymer was dried at 40–50 °C under vacuum for 12 h. The final product was characterized by UV–visible spectroscopy and cyclic voltammetry.²⁶ Elemental analysis (Atlantic Microlab, Inc.) and proton NMR were performed to confirm the structure shown in Figure 3. About 67% of the total pyridine groups were alkylated with 2-ethylhexyl groups.

Determination of Solvent Dipolarity (π^* Value). The Abboud–Kamlet–Taft solvatochromic comparison method^{27,28} was used for measuring the dipolarity (π^*) of the nitrophenyl-based solvents using Reichardt's dye. Approximately 1 mM Reichardt's dye solutions in nitrobenzene, 2-nitrotoluene, 3-nitro-*o*-xylene, 2-nitrophenyl pentyl ether, and 2-nitrophenyl octyl ether were measured using an HP8452 diode array UV–vis spectrophotometer (Hewlett-Packard). A 0.1 cm path length quartz cell was used. The π^* values of the five nitrophenyl-based solvents (Table 1) were determined based on a calibration curve of π^* vs λ_{max} using DMSO, methylene chloride, and benzene. The π^* values of these three solvents were obtained from the literature.²⁹

Preparation of Osmium-Containing Redox Polymer-Coated Electrodes. For all cyclic voltammetry studies, 3 mm diameter glassy carbon electrodes were used. The osmium-containing redox polymer coating was prepared by directly applying a 2 μL portion of a 10 mg/mL methanol solution of the osmium-containing redox polymer. The coating was air-dried without cross-linking. The surface coverage was estimated to be $1.4 \times 10^{-7} \text{ mol/cm}^2$ based on the loading.

In all the chronoamperometry studies, we used 10 μm diameter carbon fiber disk ultramicroelectrodes. These ultramicroelectrodes were constructed according to the literature.³⁰ An osmium-containing redox polymer solution for coating was prepared by mixing a solution of 1 mg of $[\text{Os}(\text{II})(\text{bpy})_2((2\text{EH}-\text{PVP})\text{Br})\text{Cl}]\text{Cl}$ in 100 μL of methanol, with a solution of 2 mM 1,10-dibromodecane in methanol, at a 1:1 (v/v) ratio. A drop of this solution was evaporated in air until highly viscous so that the ultramicroelectrodes could be paint-coated. The coated electrodes were incubated in an open vessel in a water bath at ~ 90 °C for 2 h to cross-link the polymer. Finally, the osmium-

containing redox polymer-coated electrodes were thoroughly rinsed with methanol to remove the un-cross-linked polymer. Typical surface coverage of these electrodes was 3.7×10^{-9} mol/cm² estimated by cyclic voltammetry at a sweep rate of 80 mV/s, 50 °C.

Electrochemical Experiments. For experiments using 3 mm diameter glassy carbon electrodes, a platinum mesh was used as the auxiliary electrode, and a 1 mm diameter Ag wire was used as a pseudoreference electrode. For experiments using ultramicroelectrodes, the auxiliary electrode was eliminated, and a 1 mm diameter Ag wire counter electrode was used. The potentiostat used for both cyclic voltammetry and chronoamperometry was a Cypress Systems model CS1090. All experiments were performed at room temperature except for those for Arrhenius plots. For chronoamperometry studies, the potential step at each temperature and solvent conditions was determined based on the $E_{1/2}$ of the cyclic voltammetry wave and an overpotential of +1.0 V. The Cottrell plot in the region of 15.6–62 ms was used for the calculation of the apparent diffusion coefficient $D^{1/2}C^*$, where C^* is the osmium concentration in the film.

Results

Solubility of the Osmium-Containing Redox Polymer. We did a qualitative comparison of the solubility of the two types of osmium-containing redox polymer in various solvents (Table 1). Unlike the unmodified polymer, the 2-ethylhexyl-modified polymer is insoluble in water. This is probably a result of the increased hydrophobicity of the 2-ethylhexyl groups. The modified polymer is highly soluble in methanol and acetonitrile–water mixtures but insoluble in pure acetonitrile. Methanol has a smaller dipolarity based on the Kamlet–Taft π^* values in Table 1. Therefore, the high solubility of the osmium-containing redox polymer in methanol is likely due to H bonding between the methanol and the pyridine groups on the polymer. The fact that the polymer is insoluble in either pure water or acetonitrile but highly soluble in their mixtures also suggests the importance of H-bond-donating solvents. Because the nitrophenyl-based solvents are not H-bond donors, solvent properties other than H-bond acidity should affect the solubility of the osmium-containing redox polymers. By measuring the Kamlet–Taft π^* values of these nitrophenyl-based solvents (Table 1), we found that their dipolarities are not significantly different. Therefore, the fact that the osmium-containing redox polymers are soluble in nitrobenzene but not in other nitrophenyl-based solvents suggests weak dependence of the solubility of the polymer on the dipolarity of the nitrophenyl-based solvents. Further detailed investigations were conducted by electrochemistry.

Cyclic Voltammetry. The effect of various nitrophenyl-based solvents on the cyclic voltammetry of the osmium-containing redox polymer is compared as shown in Figure 4. The peak current of cyclic voltammograms decreases and the peak split, ΔE_p , increases (Table 2) in the order of nitrobenzene, 2-nitrotoluene, 3-nitro-*o*-xylene, 2-nitrophenyl pentyl ether, and 2-nitrophenyl octyl ether. The same correlation was observed for the unalkylated polymer and polymer films cross-linked with 1,10-dibromodecane. This confirms that the solvent dependence is not due to the 2-ethylhexyl group or whether the polymer is cross-linked or not. We were surprised to find that such dramatic effects of solvent are apparently not correlated to π^* . This observation suggests that dipolarity plays an insignificant role in determining charge transport through the osmium-containing redox polymer in these nitrophenyl-based solvents.

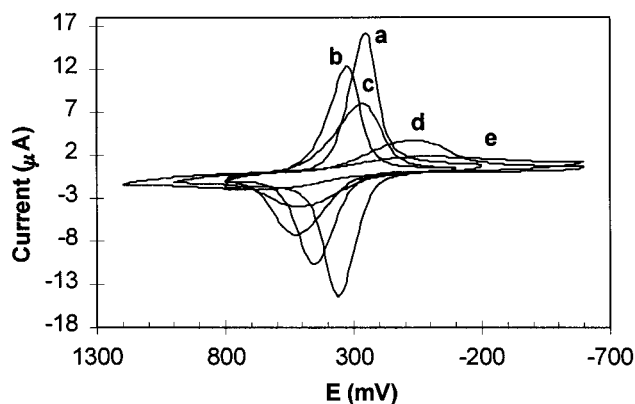


Figure 4. Cyclic voltammograms of an osmium-containing redox polymer-coated glassy carbon electrode in nitrophenyl-based solvents. The polymer was not cross-linked. The electrode surface coverage was 1.4×10^{-7} mol/cm². The electrode diameter was 3 mm. The supporting electrolyte was 0.1 M tetrabutylammonium perchlorate. The reference electrode was a 1 mm diameter Ag wire. The sweep rate was 50 mV/s, room temperature. (a) Nitrobenzene; (b) 2-nitrotoluene; (c) 3-nitro-*o*-xylene; (d) 2-nitrophenyl pentyl ether; (e) 2-nitrophenyl octyl ether.

TABLE 2: Anodic–Cathodic Peak Separation of Cyclic Voltammograms of Osmium-Containing Redox Polymer in Various Solvents^a

solvent	ΔE_p (mV)
nitrobenzene	102
2-nitrotoluene	125
3-nitro- <i>o</i> -xylene	273
2-nitrophenyl pentyl ether	450
2-nitrophenyl octyl ether	600

^a Experimental conditions are the same as that in Figure 4.

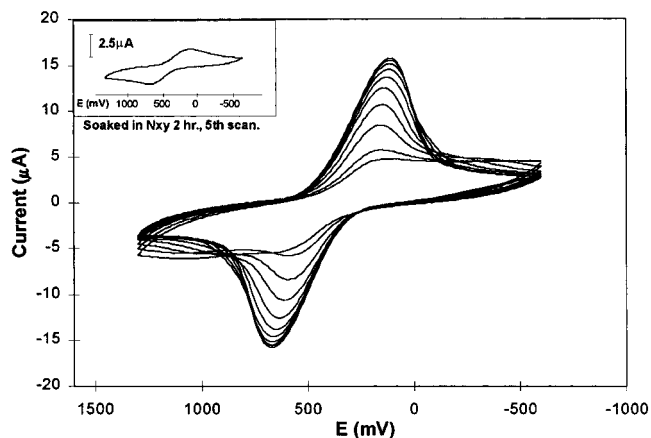


Figure 5. Continuous potential cycling of an osmium-containing redox polymer-coated glassy carbon electrode (3 mm diameter) in 3-nitro-*o*-xylene. The smallest wave corresponds to the third scan, and the largest wave corresponds to the 45th scan. The sweep rate was 100 mV/s, and the supporting electrolyte was 0.1 M tetrabutylammonium perchlorate. A silver wire was used as the reference electrode. The inset shows the fifth CV scan after the identical dry electrode being soaked in 3-nitro-*o*-xylene for 2 h.

The poor solvation of the osmium-containing redox polymer in nitrophenyl-based solvents is also reflected in the experiment shown in Figure 5. In 3-nitro-*o*-xylene, repeated potential cycling of an initially dry osmium-containing redox polymer-coated electrode was necessary in order to reach the steady state. The inset of Figure 5 shows the fifth CV scan after an identical dry osmium-containing polymer-coated electrode had been soaked in 3-nitro-*o*-xylene/0.1 M tetrabutylammonium perchlorate for 2 h. The peak current of the CV waves in the inset is small. Repeated potential cycling was needed to achieve the

TABLE 3: Approximate Number of Potential Cycles Needed for Reaching Steady State^a

solvent	no. of cycles
acetone	0
nitrobenzene	2
2-nitrotoluene	15
3-nitro- <i>o</i> -xylene	45
2-nitrophenyl octyl ether	75

^a Sweep rate was 20 mV/s, room temperature. The polymer was not cross-linked.

steady state. This indicates that it is the repeated potential cycling but not the exposure to the supporting electrolyte that helped the solvation of the polymer. We found that the number of potential cycles needed for reaching steady state was highly dependent on the size of the nitrophenyl-based solvents (Table 3). Thus, for both the (steady state) cyclic voltammetry and the process of wetting the films, the smaller, less alkylated solvents support more rapid kinetics.

Faulkner et al. demonstrated that using perchlorate-based supporting electrolyte can cause low permeability of the redox polymer.³¹ They found that low permeability can significantly retard the rate of charge transport due to poor accessibility of the counterion to the inner layer of the redox polymer film. Of course, the ion-pair formation constant depends on the dielectric constant of the solvent; lower dielectric constant solvents encourage ion pairing. We anticipated some effects of ion-pair formation in solvents with small dielectric constants such as *o*-NPOE ($\epsilon = 24$). We also found that no CV waves could be observed for the osmium-containing redox polymer when using tetrabutylammonium tetraphenylborate as the supporting electrolyte, in either *o*-NPOE or 2-nitrotoluene. We had hoped to be able to explore the effect of the counterion on the charge transport rate by studying a larger number of counterions, but we are unfortunately limited for the most part to perchlorate ion as the counterion.

Although cyclic voltammetry allows us to obtain useful comparisons of the effect of solvents on the redox behavior of the osmium-containing redox polymer, it is difficult to extract quantitative information from the cyclic voltammograms in Figure 4 has a ~ 0.74 power dependence on the scan rate, indicating that it has a behavior between a diffusion-limited thick film and a thin-layer film. This makes the peak currents of the CV waves have a complicated dependence on the rate of charge transport. Therefore, chronoamperometry³² at short times was used to obtain apparent charge diffusion coefficients in various solvent conditions.

Chronoamperometry. The limitation of the application of chronoamperometry to nonaqueous solvent systems is the large Ohmic resistance which can distort the current decay profile, leading to incorrect measurement of apparent diffusion coefficient.^{33,34} To minimize this problem,³⁰ we used carbon disk ultramicroelectrodes. The peak current of the CV waves of an osmium-containing redox polymer-coated electrode in 3-nitro-*o*-xylene has a 0.87 power dependence of the scan rate. The near-unity dependence illustrates that, at the long time scale (seconds), the behavior of the redox polymer coating is close to a thin-layer cell. On the other hand, at short times, less than about 100 ms, osmium-containing redox polymer-coated ultramicroelectrodes gave nearly ideal linear Cottrell plots (eq 1) with intercepts 0 ± 0.1 nA, in 2-nitrotoluene at room temperature, using 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte (Figure 6).

$$i(t) = nFAD^{1/2}C_{os}^*/(\pi t)^{1/2} \quad (1)$$

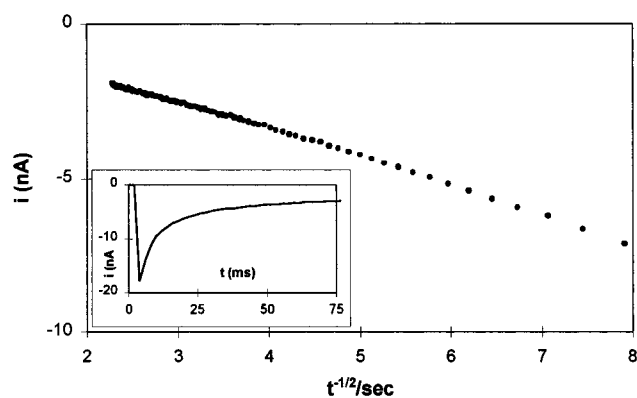


Figure 6. A Cottrell plot of current decay after applying a +1.0 V overpotential. The osmium-containing redox polymer film was coated on a 10 μ m diameter carbon disk ultramicroelectrode, cross-linked with 1,10-dibromodecane. The supporting electrolyte was 0.1 M tetrabutylammonium perchlorate in 2-nitrotoluene, 25 $^{\circ}$ C. The inset shows the current decay with time after applying the potential step.

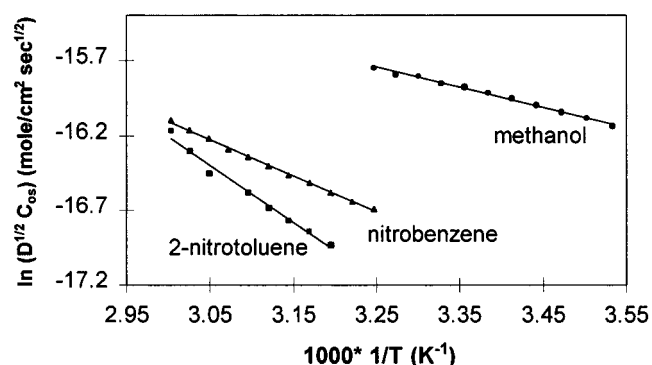


Figure 7. Chronoamperometry measurement of apparent charge diffusion coefficient as a function of temperature. A 10 μ m diameter carbon disk ultramicroelectrode was coated with an osmium-containing redox polymer and cross-linked with 1,10-dibromodecane. Supporting electrolyte was 0.1 M tetrabutylammonium perchlorate. Three solvents were studied: methanol, nitrobenzene, and 2-nitrotoluene.

TABLE 4: Comparison of the Effect of Solvent on Charge Transport

solvent	$D_{app} \times 10^8$ (35 $^{\circ}$ C), mol cm ⁻² s ^{-1/2}	ΔH^* , kJ/mol	ΔS^*_{300K} , J/(mol K)	ΔG^*_{300K} , kJ/mol
methanol	14.4	22	-40	34
nitrobenzene	5.6	40	10	37
2-nitrotoluene	3.0	64	80	40

Data collected in the time range of 15–62 ms were used for calculating the apparent charge diffusion coefficient $D^{1/2}C_{os}^*$ according to eq 1. We also measured the apparent charge diffusion coefficient of the osmium-containing redox polymer as a function of temperature in three solvents: methanol, nitrobenzene, and 2-nitrotoluene (Figure 7). Chronoamperometry experiments in 3-nitro-*o*-xylene, 2-nitrophenyl pentyl ether, and 2-nitrophenyl octyl ether were unfortunately not successful due to significant iR drop. Results of chronoamperometry are listed in Table 4. The apparent charge diffusion coefficient at 35 $^{\circ}$ C decreases from methanol (14.4×10^{-8} mol cm⁻² s^{-1/2}) to nitrobenzene (5.6×10^{-8} mol cm⁻² s^{-1/2}) and to 2-nitrotoluene (3.0×10^{-8} mol cm⁻² s^{-1/2}). This decrease in apparent charge diffusion coefficient is consistent with our cyclic voltammetry results on the dependence of the CV peak current on solvent size. We also compared the osmium-containing redox polymer with and without 2-ethylhexyl modifications. The result shown in Figure 8 indicates that there are no significant

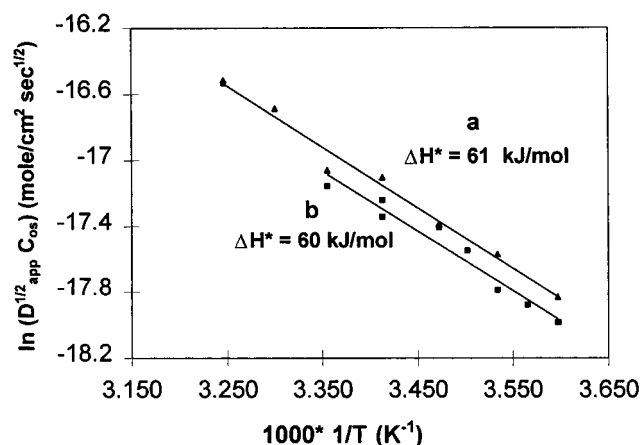


Figure 8. Comparison of the Arrhenius plots of two osmium-containing redox polymer films: (a) without the modification of 2-ethylhexyl groups and (b) modified with 67% 2-ethylhexyl group. Osmium-polymer films were coated on 10 μm diameter carbon disk ultramicroelectrodes and cross-linked with 1,10-dibromodecane. Supporting electrolyte was 0.1 M tetrabutylammonium perchlorate in 2-nitrotoluene.

differences in the rate of charge transport for these two polymers in 2-nitrotoluene/0.1 M tetrabutylammonium perchlorate.

Discussion

The solvent properties that affect the solvation of a single molecule are well summarized in solvatochromic studies.²⁷ They are solvent H-bonding acidity, H-bonding basicity, solvent dipolarity (π^*) and polarizability, solvent molar volume, and solvent cohesive energy density. The ionic nature of the osmium-containing redox polymer (Figure 3) will require a large solvent polarity, which is necessary to solvate the charged osmium and pyridinium groups. H-bond-donating solvents assist the solvation through H-bond formation with the pyridine groups. These properties are reflected qualitatively through the good solubility of the osmium-containing redox polymer in nitrobenzene, methanol, and acetonitrile/water mixtures but not pure acetonitrile (Table 1).

Cyclic voltammetry and chronoamperometry studies revealed that the predominant factor that influences the rate of charge transport is not related to the dipolarity but is related to the size of the nitrophenyl-based solvents. The dependence of solvation or complexation on solvent size is generally observed.^{7,35,36} The unfavorable effect of large solvent size on solvation is likely due to a smaller coordination number of solvent molecules surrounding a solute molecule. Thus, we may expect that larger solvents are less effective in breaking an ion pair. As we know that ion pairs exist between osmium-containing redox polymers and perchlorate ions,^{26,31} the influence of solvent size on the ion-pair solvation may also be an important contribution, in addition to the solvation of the redox polymer itself.

We compared an osmium-containing redox polymer modified (67% of pyridines alkylated) with 2-ethylhexyl groups and an unmodified polymer. The fact that the 2-ethylhexyl-modified polymer does not dissolve in water while the polymer without alkylation has good solubility in water demonstrates that the two polymers' solvation requirements are different. However, the Arrhenius plots of the effective diffusion coefficients of the two polymers in 2-nitrotoluene have very similar slopes and intercepts (Figure 8). There is no strong evidence in favor of considering that polymer solvation is a factor in limiting the charge transport in these systems.

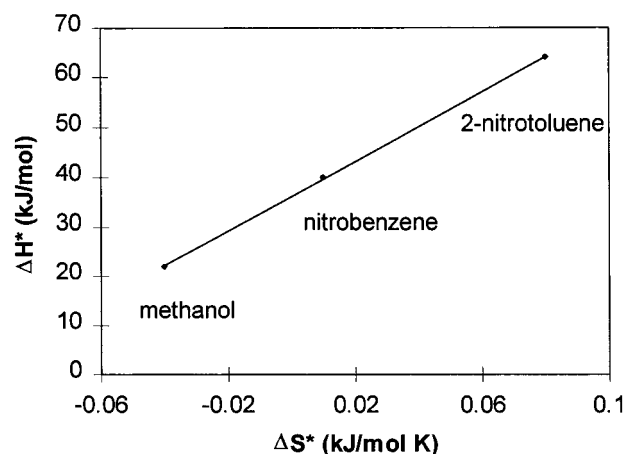


Figure 9. Charge transport activation enthalpy-entropy correlation for studies of the osmium-containing redox polymer in methanol, nitrobenzene, and 2-nitrotoluene. Data from Table 4 are plotted.

Mechanistic analysis has often used the activation enthalpy (ΔH^*) and activation entropy (ΔS^*).^{33,37-40} On the basis of the slope and the intercept of the Arrhenius plots (Figure 7), we can calculate the charge transport activation enthalpy ΔH^* , and activation entropy ΔS^* , according to the Arrhenius equation (eq 2) and the Eyring equation (eq 3). In eq 3, e is the base of the natural log, λ is the equilibrium separation of vicinal redox sites ($\lambda = 2.5 \text{ \AA}$ was used⁵), k is the Boltzmann constant, and h is Planck's constant.

$$D^{1/2}C_{\text{os}}^* = D^{0/2}C_{\text{os}}^*[\exp(-\Delta H^*/2RT)] \quad (2)$$

$$D^{0/2}C_{\text{os}}^* = e\lambda^2(kT/h)[\exp(\Delta S^*/R)] \quad (3)$$

While changes in ΔG^* are modest, the changes in ΔH^* and ΔS^* are large (Table 4). A large increase in charge transport activation enthalpy from methanol, nitrobenzene, to 2-nitrotoluene was observed, indicating increasing energy barrier of the charge transport through the osmium-containing redox polymer in this solvent.³⁹ The change in activation entropy is also dramatic, from a large negative value in methanol ($-40 \text{ J mol}^{-1} \text{ K}^{-1}$) to a large positive value in 2-nitrotoluene ($80 \text{ J mol}^{-1} \text{ K}^{-1}$). According to the report by Murray et al.,³⁷ the large positive activation entropy is an indication of polymer segmental mobility-limited behavior, while a negative activation entropy is an indication of counterion transport-limited behavior. It is not clear that such a detailed mechanistic conclusion is warranted from the analysis of the temperature dependence data. An alternative explanation invokes enthalpy-entropy compensation.

Enthalpy-entropy compensation is a general phenomenon that has been observed for many thermodynamic and kinetic systems.⁴¹⁻⁴⁴ In compensated systems, enthalpy linearly correlates to entropy, with a slope approximately equal to the temperature of the experiment. The almost constant activation free energy ΔG^* for the osmium-containing polymer in methanol, nitrobenzene, and 2-nitrotoluene (Table 4), and the linear relationship between the charge transport activation enthalpy and entropy (Figure 9), suggests that compensation exists in the systems under scrutiny. The fact that the slope ($\alpha = 349 \text{ K}$) of the enthalpy-entropy compensation plot is very close to the temperature at which the ΔS^* was calculated ($T = 300 \text{ K}$) indicates the near completeness of compensation.

Enthalpy-entropy compensation arises in processes involving many molecules or degrees of freedom. For example, en-

thalpy–entropy compensation can originate from solvation-related processes or complexation-related processes.⁴¹ Therefore, the observation of activation enthalpy–entropy compensation in our system indicates the involvement of many molecules in the rate-determining step of charge transport. For example, the solvation of the osmium-containing redox polymer, the solvation of the ion-pair between the osmium-containing redox polymer and the perchlorate ions, or the solvation of the perchlorate ion itself may be involved. Qualitative observations suggest that the polymer backbone solvation per se is not rate limiting as changing the backbone does not change the activation parameters. On the other hand, changing the counterion and the solvent do influence dramatically the rate of charge transport. Single ion transfer free energies⁴⁵ indicate that perchlorate ion is equally “soluble” in nitrobenzene and methanol (−0.9 kJ/mol from nitrobenzene to methanol⁴⁵). Tetraphenylborate is more soluble in nonaqueous solvents than perchlorate.⁴⁵ Yet changing the solvent from methanol to nitrobenzene has a significant influence on activation parameters, and changing the counterion from perchlorate to tetraphenylborate completely suppresses the voltammetry. Thus, it is not the solvation of the ions per se that is rate limiting.

It is known³¹ that ion pairing occurs in such systems. Ion pair formation will be favored in the more alkylated solvents. The charge transport process requires ion migration, and the mobile ions are the same set of ions as form the ion pairs, so liberation from the ion pair is essential for charge transport. The compensated activation parameters tell us that the process in methanol is enthalpically not very costly but that there are fewer degrees of freedom in the “activated complex” compared to the “ground state”. In the larger nitrobenzene and 2-nitrotoluene, the activation is enthalpically more costly, but degrees of freedom are created. It is speculation to fill in the picture more clearly, but worthwhile nonetheless. If we turn the picture around, and imagine a solution, fairly homogeneous, of the ionic redox polymer and soluble counterions in 2-nitrotoluene, then there is a considerable negative enthalpy, and negative entropy, associated with coming to equilibrium—where ion pairing, the necessary polymer structure, and solvent structure needed to accommodate the ion pairs exist. This may have to do with the formation of clusters of ion pairs; it may involve polymer self-solvation, and it may involve some solvent ordering. Solvent ordering arises in the larger solvents because they are highly asymmetrical molecules—one end is polar while the other is not. Further, they are large, and solvation by more than one solvent molecule must certainly involve steric interactions between adjacent solvent molecules that are exacerbated by the requirement to have their polar moieties arranged in a particular way to minimize electrostatic free energy.

Conclusions

For the redox reactions of the osmium-containing redox polymers in nitrophenyl-based solvents using perchlorate as the supporting electrolyte, the rate of charge transport has a strong dependence on solvent size but insignificant dependence on solvent dipolarity. Charge transport is slower in larger solvents. The activated process is compensated, so it involves many molecules. The most likely processes involved in the limitation of charge transport are ion pairing and the associated solvation and polymer rearrangements accompanying the making and breaking of the ion pairs.

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