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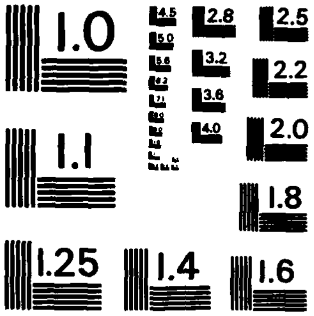

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ESTIMATION OF THE RATE OF ELECTRON TRANSFERS BETWEEN TWO CONTACTING POLYMER SURFACES

C. R. Leidner[†] and Royce W. Murray*
Kenan Laboratories of Chemistry
University of North Carolina
Chapel Hill, NC 27514

ABSTRACT

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A bilayer of redox polymer films, Pt/poly-$[Os(bpy)_2(vpy)_2]^{2+}$/poly-$[Ru(vbpy)_3]^{2+}$, is coated on a Pt electrode. Reduction of the poly-$[Ru]^{3+}$ outer film of a pre-oxidized bilayer, Pt/poly-$[Os]^{3+}$/poly-$[Ru]^{3+}$ is controlled by the rate of electron diffusion through the inner, poly-$[Os]^{2+/3+}$ film. When oxidizing the outer poly-$[Ru]^{2+}$ film of a reduced Pt/poly-$[Os]^{2+}$/poly-$[Ru]^{2+}$ bilayer, however, the rate of oxidation depends largely on the kinetics of electron transfer between the *ca.* monolayer of poly-$[Os]^{3+}$ and poly-$[Ru]^{2+}$ sites in contact at the interface between the two polymer films. The electron diffusion kinetics in the two polymer films perturb the interfacial reaction rate only slightly, so that a lower limit to the interfacial electron transfer rate constant is available. Remarkably, this value is within a factor of *ca.* 20 of that calculated from the Marcus relation for the corresponding homogeneous cross electron transfer reaction in acetonitrile.

[†] Present address: Department of Chemistry, Stanford University, Stanford, CA.

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Ultra-thin (10-1,000nm), stable, and adherent films of the electroactive transition metal polymers poly-$[M(bpy)_2(vpy)_2]^{2+}$ and poly-$[Ru(vbpy)_3]^{2+}$ where M = Os or Ru, vbpy = 4-vinyl-4'-methyl-2,2'-bipyridine and vpy = 4 vinylpyridine, are easily electropolymerized onto Pt electrodes from monomer complex solutions[1,2]. These films and those of analogous complexes have provided a number of important insights into the internal electron self exchange[3,4], permeation[5-7], and electron transfer mediation chemistry[6-9] of transition metal polymers. This paper further exploits this electron transfer chemistry to arrive at an estimate of the rate of an electron transfer reaction between two different, contacting polymer film surfaces. The rate of such a polymer surface to surface electron transfer has eluded us in previous experiments[3,4,10], and as far as we are aware has never before been reported for any pair of contacting polymer films or biological membrane materials.

The experiment is based on a Pt electrode coated first with a thin (30-80 monolayer-equivalents) poly-$[Os(bpy)_2(vpy)_2]^{2+}$ film ($E^{o'}$ = 0.73V vs. SSCE), which is then over-coated with a similarly thin poly-$[Ru(vbpy)_3]^{2+}$ film ($E^{o'}$ = 1.14V vs. SSCE). Since the inner, poly-$[Os]^{2+}$ film is

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relatively pinhole free[6], electron transfers between the Pt electrode and the outer, poly-[Ru]$^{2+}$ film are, like our previous bilayer electrodes, constrained to occur at the poly-[Os]/poly-[Ru] film/film interface, via the poly-[Os] film. By control of the Pt electrode potential, electron transfer reactions which can be driven across the film/film interface are:

$$\mathrm{Pt/poly\text{-}[Os]^{2+}/poly\text{-}[Ru]^{3+}} \longrightarrow \mathrm{Pt/poly\text{-}[Os]^{3+}/poly\text{-}[Ru]^{2+}} \quad (1)$$

starting with both films oxidized and sweeping the potential negatively, and

$$\mathrm{Pt/poly\text{-}[Os]^{3+}/poly\text{-}[Ru]^{2+}} \longrightarrow \mathrm{Pt/poly\text{-}[Os]^{2+}/poly\text{-}[Ru]^{3+}} \quad (2)$$

starting with both films reduced and sweeping potential positively.

Reaction 1 is thermodynamically favored. Reaction 2 is unfavorable but is driven nonetheless by continous regeneration of the inner film poly-[Os]$^{3+}$ state. By analogy with experiments in which such transition metal polymer films were used to drive thermodynamically favored and unfavored oxidation (or reduction) of solutions of metal complexes[6-9] and thermodynamically favored reactions in other bilayer electrodes[3,4-10], we can guess at the likely rate controlling steps of Reactions 1 and 2. Specifically, Reaction 1 is likely to be controlled by the rate of electron diffusion in the inner, poly-[Os] film (controls the supply of poly-[Os]$^{2+}$ sites). The rate of the thermodynamically favored electron transfer cross-reaction in Reaction 1 should be much faster than the electron diffusion step. And, we hoped that, as found[6] for the solution complex reactions, the opposite situation would be found in Reaction 2, where the rate of the thermodynamically unfavored and thus much slowed electron transfer cross reaction should become less than that of the electron diffusion process. The Pt/poly-[Os]/poly-[Ru] bilayer was designed on this basis. The specific polymers were furthermore selected to provide both a rather large unfavorable free energy change ($E^{o'}_{Ru} - E^{o'}_{Os}$ $= 0.40_5V$; $K_{eq} = 1.4x10^{-7}$), and an inner film polymer with a high electron diffusion rate (the poly-$[Os]^{2+/3+}$ film).

Expectations with respect to rate control in Reaction 1 were realized. Expectations with respect to the more significant Reaction 2 are realized to a first approximation only, but nonetheless constitute the first data available on the rate of electron transfers between contacting polymer surfaces.

EXPERIMENTAL

Syntheses of $[Os(bpy)_2(vpy)_2](PF_6)_2$ and $[Ru(vbpy)_3](PF_6)_2$ have been described earlier[1,2], as has the electrochemical apparatus[6-9]. Tetraethylammonium perchlorate, Et_4NClO_4, (Eastman) was thrice recrystallized from water and stored in vacuo at 50°C. Acetonitrile (Burdick and Jackson) was stored over molecular sieves. All experiments were performed in 0.1M Et_4NClO_4/CH_3CN with standard three electrode instrumentation.

The Pt/poly-$[Os(bpy)_2(vpy)_2]^{2+}$/poly-$[Ru(vbpy)_3]^{2+}$ bilayers were prepared as follows. A Pt/poly-$[Os(bpy)_2(vpy)_2]^{2+}$ electrode was prepared by reductive electropolymerization from a ca. 0.5 mM solution of the monomer and the inner film coverage determined by cyclic voltammetry in monomer-free 0.1M Et_4NClO_4/CH_3CN. The outer poly-$[Ru(vbpy)_3]^{2+}$ film was next electropolymerized from a ca. 0.1mM monomer solution. All inner films and resultant bilayer films were visibly smooth (shiny). Outer film coverages Γ_{outer} were obtained in 0.1<u>M</u> Et_4NClO_4/CH_3CN by applying 1.4V <u>vs</u>. Ag/AgCl to the bilayer electrode for 20-45 minutes (to drive the thermodynamically unfavorable Eq. (2) to completion). A potential scan was then initiated from 1.4 to 0.4V to produce the $Pt/Os^{2+}/Ru^{3+}$ trapping peak (Reaction 1). Γ_{outer} was obtained by integrating the charge under this trapping peak. The Ag/AgCl pseudo-reference was used in place of the conventional SSCE in these experiments, to prevent leakage of Cl^- into the working compartment during the long wait at 1.4V. In all other experiments, potentials were referred to the SSCE.

$[Os(Me_2bpy)_3](PF_6)_2$ was prepared by a modification of a standard method[11]. 200.85 mg (0.458 mmole) $(NH_4)_2OsCl_6$ (Englehard) and 421.7 mg (2.29 mmole) 4,4'-Me_2bpy (Reilley Chemicals) were refluxed for 5 hours under N_2 in 30 ml 2-(2-methoxyethoxy)ethanol (Aldrich). The dark green reaction mixture was cooled to room temperature under N_2, and 50 ml H_2O was added. Saturated NH_4PF_6/H_2O was added to the stirred solution until precipitation ceased. The green solid was collected by suction filtration and washed with 200 ml H_2O and 200 ml Et_2O. The crude product was purified by chromatography on Al_2O_3 using 3:2 toluene/CH_3CN as the eluent. The main green band was collected and taken to dryness by rotary evaporation. The solid was dissolved in a minimum of CH_3CN and added dropwise into a stirring solution of Et_2O. The green solid was collected by suction filtration. Yield: 327 mg (79%).

RESULTS AND DISCUSSION

Cyclic Voltammetry of the Pt/poly-[Os]/poly-[Ru] Bilayer. In order to observe Reaction 1, starting with both the poly-[Os] and poly-[Ru] films in the $[M]^{3+}$ state, a positive potential was applied to the bilayer for a period. Full oxidation of the poly-$[Os]^{2+}$ film proceeds quickly, but the poly-[Ru] film is oxidized via Reaction 2 which is slow. For the film coverages employed here, potentiostatting at +1.4V for at least 20 minutes was satisfactory.

The cyclic voltammetry of a thus pre-oxidized bilayer is shown in Figure 1. The sharp reduction current peak at ca. +0.95V is due to the bilayer electrode charge trapping Reaction 1, in which the very small quantity of poly-$[Os]^{2+}$ states generated at this potential is rapidly consumed at the film/film interface by the poly-$[Ru]^{3+}$ film. The quantity of electroactive poly-$[Ru]^{3+}$ sites in the outer film was ascertained by integration of the charge under this peak. If the pre-potentiostating period is shortened, to 5 minutes for instance, the trapping peak is appreciably smaller (~60%) because Reaction 2 has not proceeded to completion.

The shape and behavior of the sharp reduction peak in Figure 1 for Reaction 1 is similar to that observed for earlier bilayer electrode (thermodynamically favorable) trapping reactions[3,4,10]. The peak is however much better resolved than most we have reported[4,5]. Using a theory assigning control of the current to electron diffusion in the inner film, we analyzed the reduction peak in Figure 1 by plotting the current on the rising part of the sharp peak according to the equation[3,4]

$$i = (nFAD_{ct}C^2/\Gamma_{inner})\ \exp[(gnF/RT)(E - E^{o'}_{inner})] \qquad (3)$$

where D_{ct} is the electron diffusion coefficient and C is the polymer site concentration ($\sim 1.5\times10^{-3}$ mol/cm^3) in the inner film. The log i vs E - $E^{o'}_{inner}$ plots are linear up to 90% of the current peak. For a series of experiments, the slopes and intercepts of these plots yield, respectively, the interaction parameter g (describes the Nernstian shape function of the Os(III/II) wave[12]) and electron diffusion constant for the poly-[Os] film in Table I. The lack of dependence on Γ_{inner} and Γ_{outer} and agreement of the electron diffusion parameter with other, independent results for the same poly-[Os] film, $D^{1/2}_{ct}C = 1.1\times10^{-7}$ and 1.3×10^{-7} mol/cm^{2}s$^{1/2}$, confirms the expected, that the sharp peak reduction currents in Figure 1, and the rate of Reaction 1, is governed by the rate of electron diffusion in the inner, poly-[Os] film.

The second reduction peak observed at +0.73V vs SSCE for a pre-potentiostatted, Pt/poly-[Os]$^{3+}$/poly-[Ru]$^{3+}$ bilayer, is due to reduction of the main portion of the poly-[Os(bpy)$_2$(vpy)$_2$]$^{2+}$ inner film. This and the ensuing reoxidation peak at the same potential can be observed without the pre-potentiostatting routine since the poly-[Os] film is in direct contact with the Pt electrode. The charge under the poly-[Os]$^{2+/3+}$ wave measures the inner film coverage, Γ_{inner}, which was found to be the same before and after electropolymerizing the poly-[Ru] outer film layers. At potential sweep rates employed here, peak currents for the poly-[Os]$^{2+/3+}$ wave are proportional to sweep rate.

Continuation of the return, positive going potential scan reveals in Figure 1 a shallow oxidation current peak (*) at ca. 1.0V. The * peak is attributed to Reaction 2. (In bilayers where the difference in inner and outer $E^{o'}$ values is great, no peak would be observed here at all; in those cases the outer film is more stably trapped in its oxidation state[3,4].) For the Pt/poly-[Os]/poly-[Ru] bilayer, the rate of the Reaction 2 is, while quite slow, still rapid enough to give a peak in the voltammetry. We have previously[4] referred to peaks such as this as the "back reaction" as they are deleterioes to charge storage applications of bilayer electrodes.

That the shallow (*) current peak in Figure 1 is due to Reaction 2, and is small and shallow because it is kinetically controlled, was confirmed by sweeping the potential at different rates, starting at +0.3V with the film in its reduced state (Figure 2). Adjusting the recorder current sensitivity in concert with (proportional to) the potential sweep rate normalizes the current scale for the poly-$[Os]^{3+/2+}$ peak, so that it appears unchanged in Figure 2. The shallow (*) peak at 1.0V, however, is definitely enhanced by the use of slower potential scan rates. This observation confirms its kinetic control.

<u>Redox Pumping of the Outer Film</u>. The potential scan rate dependency of the peak current for Reaction 2 (*) in Figure 2 could, in principle, be employed to extract the rate of Reaction 2. Rather than employ the rather complex, time dependent reversible kinetic theory required for this, we adopted a simpler approach, using a rotated disk bilayer electrode in a solution of the reductant $[Os(Me_2bpy)_3]^{2+}$. The reductant ($E^{o'}$ = +0.66V vs. SSCE) serves to prevent depletion of poly-$[Ru]^{2+}$ states in the outer film during Reaction 2, and the rotated disk arrangement provides a steady mass transfer of $[Os(Me_2bpy)_3]^{2+}$. The redox energy level scheme for this arrangement is

illustrated in Figure 3.

Note from the scheme that the function of the electrode potential is to lower the poly-$[Os]^{2+}$/poly-$[Os]^{3+}$ ratio sufficiently in the inner film to initiate a net rate of electron transfers from poly-$[Ru]^{2+}$ to poly-$[Os]^{3+}$ greater than that from (the ordinarily more favorable) poly-$[Ru]^{3+}$ to poly-$[Os]^{2+}$. Expressing the poly-$[Os]^{2+}$/poly-$[Os]^{3+}$ ratio with the Nernst equation (plus g interaction parameter as used in Eq. (3)) and assigning rate control to the film/film electron transfer of Reaction 2, leads to the equations for the voltammetric response of a Pt/poly-[Os]/poly-[Ru] rotated disk electrode in a solution of reductant, $[Os(Me_3bpy_3)]^{2+}$,

$$i_{lim} = nFAk\phi_{inner}\,\phi_{outer} \tag{4}$$

$$\text{and } E = E_{\frac{1}{2}} + (RT/gnF)\ln[i/(i_{lim} - i)] \tag{5}$$

$$\text{where } E_{\frac{1}{2}} = E^{o'}_{outer} + (RT/gnF)\ln[i_{lim}/i_{ct,outer}] \tag{6}$$

in which i_{lim} is the limiting current of the rotated disk voltammogram, k is the second order cross electron transfer rate constant of Reaction 2 between the contacting polymer film surfaces, each containing *ca.* a monolayer of poly-[Os] and poly-[Ru] sites (assume $\phi_{inner} \cong \phi_{outer} \cong 1\times10^{-10}$ mol/cm^2), $E_{\frac{1}{2}}$ is the half wave potential of the rotated disk voltammogram, and $i_{ct,outer}$ is the current through the outer film that would be limited by electron diffusion ($i_{ct,outer} = nFAD_{ct,outer}C^2_{outer}/\Gamma_{outer}$).

The rotated disk voltammetric response of a Pt/poly-$[Os(bpy)_2(vpy)_2]^{2+}$/poly-$[Ru(vbpy)_3]^{2+}$ bilayer with $\Gamma_{inner} = 3.65\times10^{-9}$ and

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$\Gamma_{outer} = 1.92\times10^{-9}$ mol/cm^2 in a $3.5m\underline{M}$ $[Os(Me_2bpy)_3]^{2+}$ solution is shown in Figure 4. A steady state kinetic wave with $E_{1/2} = 0.93V$ and $i_{lim} = 25.2\mu A$ (current density $j_{lim} = 458\mu A/cm^2$) is observed. Of Eqs. 4 and 5, application of Eq. 4 is the more significant in that it predicts no dependency on electrode rotation rate (none observed) or upon Γ_{inner} and Γ_{outer}. Limiting current results from voltammograms for a series of bilayer electrodes are shown in Table II. The experimental scatter is fairly appreciable, but to a first approximation (see below), i_{lim} appears to be constant and Eq. 4 is satisfied. Values of the film/film electron transfer rate $k\phi^2$ fall in the range 2 to 5×10^{-9} mol/cm^{2}s.

Eqs. 5 and 6 are also satisfied by voltammetry like Figure 4, for Eq. 5 by the linearity of plots of E <u>vs</u>. $\log[i/(i_{lim}-i)]$ whose slope = 0.063V gives g = 0.94 agreeing with Table 1, and for Eq. 6 the $E_{1/2}$ observed in the voltammetry. Eq. 6 predicts that the $E_{1/2}$ potential for poly-$[Ru]^{2+}$ oxidation should occur at a less positive potential than $E^{o'}_{outer}$ (+1.14V) according to the ratio $i_{lim}/i_{ct,outer}$. With a value of $D^{1/2}_{ct,outer}C_{outer} = 6\times10^{-8}$ mol/cm^{2}s$^{1/2}$ determined elsewhere[3], Eq. 6 predicts an $E_{1/2}$ *of* 0.97_2 *to* 0.99_9V *for* the i_{lim} and Γ_{outer} given in Table II. These lie with 39 to 65mV of the $E_{1/2}$ actually observed.

The redox pumping by reductant outlined in Figure 3 can also be used in cyclic voltammetry. Here again, the reductant $[Os(Me_2bpy)_3]^{2+}$ serves the function of consuming outer film poly-$[Ru]^{3+}$ sites generated by Reaction 2 at the bilayer/solution interface. Figure 5 illustrates the cyclic voltammetry of the Pt/poly-$[Os(bpy)_2(vpy)_2]^{2+}$/poly-$[Ru(vbpy)_3]^{2+}$ bilayer of Figure 1 in the $3.55\ m\underline{M}$ $[Os(Me_2bpy)_3]^{2+}$ solution. Compared to Figure 1, and as in the rotated disk experiment, an enhanced current is observed for Reaction 2. At

500 mV/s a well-defined, sigmoidal wave centered at <u>ca.</u> 0.95V <u>vs.</u> SSCE is evident in Figure 5. The limiting currents observed at 100, 200, and 500mV/s, after baseline current corrections, are roughly the same as those observed in the rotated disk experiment (500, 510, 510μA/cm^2 respectively). Evidently, the concentration - distance profiles through the two films are established rapidly enough on the timescale of the potential scan for steady state current flow to exist. This limiting current persists until sufficient time has elapsed during the continuing positive potential scan for concentration polarization of the $[Os(Me_2bpy)_3]^{2+}$ solution to occur, at which point the concentration gradient of $[Os(Me_2bpy)_3]^{2+}$ becomes too small to support the limiting kinetic current of Reaction 2 and the current is seen to decay. At slower scan rates, this concentration polarization is more substantial and the pumped currents are lower. Figure 5 illustrates the virtue of using the rotated electrode format to avoid depletion of the pumping reductant.

<u>Discussion and Examination of Assumptions</u>. Before considering the measured Reaction 2 film/film rate of Table II, four important assumptions of the experiment should be examined.

First assumed is that the pumping reductant $[Os(Me_2bpy)_3]^{2+}$ does not penetrate the outer, poly-$[Ru]^{2+}$ film to either the inner film or to the Pt electrode (both would give a wave near the $E^{\circ\prime} = +0.66V$ for $[Os(Me_2bpy)_3]^{2+}$ oxidation). Previous explicit permeation measurements of bulky, dicationic complexes by Ikeda[5] through the poly-$[Ru(vbpy)_3]^{2+}$ film show that permeation of a complex like $[Os(Me_2bpy)_3]^{2+}$ through the present films should not give significant currents on the scale of Figure 4. The pumping reductant was chosen on this basis. That the pumping reductant also does not encounter film imperfections (as opposed to permeation) allowing access to the Pt/poly-[Os] interface is clearly satisfied by the absence of a 0.66V wave in Figure 4. That, further, the reductant does not encounter outer film imperfections allowing access to the poly-$[Os]^{3+}$ sites at the film/film interface is also satisfied by the absence in Figures 4 and 5 of a wave at 0.66V for the reaction of $[Os(Me_2bpy)_3]^{2+}$ with poly-$[Os(bpy)_2(vpy)_2]^{3+}$. Thus, all assumptions surrounding the pumping reductant seem satisfied.

The second assumption is that there are no significant inner film imperfections through which direct outer film electron transfer with the Pt electrode might occur. This assumption is satisfied by the absence of peaks at the poly-$[Ru]^{2+/3+}$ potential ($E^{o'}_{outer} = + 1.14V$) in Figures 1 and 2.

The third assumption deals with *absence of rate* control of Reaction 2, even partially, by electron diffusion rates in the inner or outer films. Calculations of the electron diffusion <u>limited</u> inner and outer film currents give values of ≥ 0.15 and ≥ 0.05 A/cm^2, far larger than the j_{lim} values in Table II. This by itself does not totally exclude electron diffusion rate interference, however. Another criterion is independence of $k\phi^2$ on the inner and outer film coverages, Γ_{inner} and Γ_{outer}. Close inspection of Table II reveals no obvious correlation of $k\phi^2$ with Γ_{inner}, but a slight trend in $k\phi^2$ seems to exist with Γ_{outer}. $k\phi^2$ increases by about a factor of two-fold as Γ_{outer} changes from $5x10^{-9}$ to $1.4x10^{-9}$ mol/cm^2. The implication of this trend may be a slight bias of $k\phi^2$ due to the electron diffusion rate in the outer, poly-[Ru] film. The electron diffusion rate in poly-$[Ru(vbpy)_3]^{2+/3+}$ is, indeed, slower than that in poly-$[Os(bpy)_2(vpy)_2]^{2+/3+}$. Electron diffusion limitations also might rise from the thermodynamically favorable reverse of Reaction 2. Electron diffusion is necessary to maintain the proper C_{ox}/C_R ratio within both films at the reacting interface, and slow electron diffusion within either film may not supply the reacting sites at a rate required by the interfacial reaction. The kinetic data in Table II exhibit a decrease of only _ca_. 2.5 over the range of film thickness. Either form of electron diffusion kinetics might be contributing to this small trend in the observed $k\phi^2$ values. On this basis, the most reliable values of $k\phi^2$ in Table II should be those obtained at the lowest Γ_{outer}, _i.e._, $k\phi^2 \simeq 5\times10^{-9}$ mol/cm^{2}s. Conservatively, even this value may represent a lower limit on $k\phi^2$.

The fourth assumption concerns the quality of the contact between the poly-[Os] and poly-[Ru] films. The geometrical electrode area (A) was used in Eq. 4 to calculate the value of $k\phi^2$ in Table II. This assumes that at the film/film interface, the outermost monolayer (Γ_{inner}) of sites on a smooth poly-[Os] film is contacted smoothly and uniformly by the innermost monolayer (Γ_{outer}] of sites in the poly-[Ru] film. Interfacial roughness of either film would affect this assumption by change in area, A, in Eq. 4. Roughness of one film surface mirrored by and (_exactly_) in register with the other film wouldd enhance the apparent $k\phi^2$, while roughness leading to interruptions (solvent-filled voids) in the interface diminishes the apparent $k\phi^2$. Both effects might be present simultaneously, in different regions of the interface. We will return to this difficult and quite possibly imperfect assumption later.

Now examine the $\geq 5\times10^{-9}$ mol/cm^{2}s rate assigned to the poly-[Os]$^{3+}$/poly-[Ru]$^{2+}$ film/film reaction. We have established[6] that reactions of metal complex solutes at polymer/solution interfaces of poly-[Os] or poly-[Ru] (single layer) films have cross electron transfer rates quantitatively correlatable with the reaction free energy using the well-known Marcus relation[13]

$$k_{12} = (k_{11}\ k_{22}\ K_{12}\ f)^{\frac{1}{2}}$$

$$\log f = (\log K_{12})^2/[4 \log (k_{11}k_{22}/Z^2)] \qquad (7)$$

Since Reaction 2 is at least formally analogous to these previous correlations, it seems reasonable to estimate, *a priori*, the rate that Reaction 2 would have were it to follow Eq. 7. Using the known homogeneous solution electron self exchange rates for $[Ru(bpy)_3]^{2+/3+}$ and $[Os(bpy)_3]^{2+/3+}$ complexes[14], and the K_{eq} 1.4×10^{-7} of Reaction 2 and estimating ϕ_{inner} and ϕ_{outer} as 10^{-10} mol/cm^2, we calculate that $(k\phi^2)_{theor}$ should be 1.4×10^{-7} mol/cm^{2}s. Put in different terms, with $\phi_{inner} = \phi_{outer} = 10^{-10}$ mol/cm^2, a homogeneous second order rate constant for Reaction 2 of 32 $M^{-1}s^{-1} = k^{homo}$ can be calculated from the experimental $k\phi^2 \_ 5 \times 10^{-9}$ mol/cm^{2}s. This experimental rate is a factor of 28X slower than the $(k^{homo})_{theor}$ = 910 $M^{-1}s^{-1}$ calculated from Eq. 7 with the $[Ru(bpy)_3]^{2+/3+}$ and $[Os(bpy)_3]^{2+/3+}$ self exchange rates.

CONCLUSIONS

The results of Table II constitute the first estimate of how fast electron transfers can occur across the interface between two polymeric phases. Based on its reaction free energy and the premises of the Marcus relation Eq. 7, the maximum rate that Reaction 2 could exhibit is $(k\delta^2)_{theor} = 1.4\times10^{-7}$ mol/cm^{2}s in interfacial rate constant terms, or $(k^{homo})_{theor} = 910$ $M^{-1}s^{-1}$ in more familiar homogeneous solution dimensions. It is remarkable that the observed rate is (at a minimum) only 28X smaller. The actual difference may be even less, considering our discussion of possible electron diffusion rate limitations, above.

Consider this remarkable result, however, in the light of salient features of the previously ascertained electron transfer properties of these two polymers: (*i*) Values of the electron diffusion coefficients D_{ct} in poly-$[Os(bpy)_2(vpy)_2]^{2+/3+}$ and poly-$[Ru(vbpy)_3]^{2+/3+}$ translate[6,15] to homogeneous electron self exchange constants similar to the known homogeneous values[14] for $[Os(bpy)_3]^{2+/3+}$ and $[Ru(bpy)_3]^{2+/3+}$, implying that electron transfers in these polymers involve surmounting the same (intrinsic, outer sphere) barrier as in homogeneous solutions. (*ii*) The rates of electron transfers between metal poly-pyridine complex solutes and the surfaces of poly-$[Os(bpy)_2(vpy)_2]^{2+/3+}$ and poly-$[Ru(vbpy)_3]^{2+/3+}$ films follow[6-9] the free energy-rate dictates of Eq. 7. Points (*i*) and (*ii*) say, in effect that both the internal and the polymer/solution electron transfer chemistry of the two polymers essentially follow the Marcus theory[13]. Viewed in this light, one might expect that the value of $k\delta^2$ for Reaction 2 could be anticipated from Eq. 7, rather than being 28X (or less) smaller.

It is appropriate, then, to consider the factors which might impede electron transfers at the film/film interface. The most likely factor is the quality of contact between the two polymer surfaces (the fourth assumption discussed above). Firstly, in these experiments, the two polymer films were not grown in such a way as to ensure chemical bonding between the monolayer of poly-$[Os(bpy)_2(vpy)_2]^{2+/3+}$ and poly-$[Ru(vbpy)_3]^{2+/3+}$ sites at the interface. To the extent that several solvent layers (or larger solvent voids) exist either in places, or generally, between the two site monolayers, the effective, microscopic, contacting area of the bilayer interface might be diminished and/or additional polymer chain motions might be required to displace intervening solvent to achieve the Reaction 2 transition state. The observation that $k\phi^2$ is less than $(k\phi^2)_{theor}$ suggests that such interrupted interfacial contact may be more prevalent than in-register interfacial roughness[16], which would act to enhance, not depress, the apparent $k\phi^2$. Secondly, Reaction 2 occurs while most of one film is in the M^{2+} state with most of the other film in the M^{3+} state. To the extent that swelling of the two polymer states differs, the lateral stresses on the film/film interface may degrade the quality of the adhesive contact between poly-[Ru] and poly-[Os] and thereby decrease the electron transfer rate. The limiting currents of voltammograms like that in Figure 4 do in fact decay with time more rapidly than do currents in a continuously scanned cyclic voltammogram like Figure 2. Furthermore, with a different but related (Ru/Fe) bilayer assembly, we found[5] that the limiting current decay could be partially reversed by "resting" the bilayer in the all Ru^{2+}/Fe^{2+} or all Ru^{3+}/Fe^{3+} states. Differential swelling may well therefore be a crucial factor.

Another possible factor is the rate at which charge compensating counterions cross the film/film interface. Although we have no direct evidence for bilayers, considering that the kinetic measurements were carried out under steady state conditions, and that previous data indicate that small anions are quite mobile in similar non-bilayer films[5,15], we are inclined to eliminate counterion effects for the present bilayer.

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16. We have no evidence that the surface of poly-[Os] films are substantially rougher than the gently undulating topology (roughness factor of < 2) suggested by surface profilometry[17], of $4x10^{-9}$ mol/cm^2 poly-[Os] films deposited on (sputtered) Pt film electrode on smooth glass substrates, with a Sloan Dektak profilometer set to minimum status pressure. The poly-[Os] films employed in Table II were all shiny (grainy specimens were discarded), and serious roughness was not revealed in previous kinetic studies[6]. The profilometry does reveal an occassional dendrite; we believe these contribute minimally to enhancing the interfacial area since Reaction 2 rates at dendrite surfaces will be greatly attenuated by the required high electron diffusion flux through the dendrite cross-section.

17. E. Wilbourn, University of North Carolina, unpublished results, 1984.

TABLE I

Electron Diffusion Rates in the Inner Film of a Pt/poly-$[Os(bpy)_2(vpy)_2]^{2+}$/poly-$[Ru(vbpy)_3]^{2+}$ Bilayer

$\Gamma_{inner} x10^9$ mol/cm^2	$\Gamma_{outer} x10^9$ mol/cm^2	s [a]	$D_{ct}^{\frac{1}{2}}C$ x10^7 [a] mol/cm^{2}s$^{\frac{1}{2}}$
2.51	1.97	0.92	2.2
2.73	1.96	0.92	2.8
2.87	3.09	0.93	2.0
3.27	5.53	0.94	2.5
3.53	3.11	0.96	2.9
3.65	1.92	0.94	2.7
3.90	2.69	0.93	2.1
3.99	1.35	0.93	2.4
4.13	3.79	0.97	2.1
4.47	4.25	0.96	2.3
4.60	5.68	0.96	2.3
4.61	1.48	0.95	2.6
5.08	2.98	0.91	2.8
5.46	4.18	0.97	2.8
5.68	2.77	0.97	2.8
6.89	1.39	0.92	2.4
7.04	2.67	0.95	3.0
7.21	2.07	0.96	2.8
7.84	4.63	0.92	1.9
7.91	5.07	0.94	2.4
		0.94(±0.02)	2.5(±0.3)

a. Obtained from a log i *vs*. $E - E^{o'}_{inner}$ plot, Eq. (3).

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TABLE II

Electron Transfer Kinetic Data for
$Pt/poly\text{-}[(bpy)_2Os(vpy)_2]^{2+}/poly\text{-}[(vbpy)_3Ru]^{2+}$

$\Gamma_{inner} \times 10^9$ mol/cm^2	$\Gamma_{outer} \times 10^9$ mol/cm^2	j_{lim} μA/cm^2	$k\phi^2 \times 10^9$ mol/cm^{2}s	$E_{\frac{1}{2}}$ V vs. SSCE
2.73	1.96	504	5.2	0.93_0
2.92	3.39	390	4.0_5	0.94_2
3.27	5.53	329	3.4	0.94_2
3.38	4.14	337	3.5	0.93_8
3.53	3.11	317	3.3	0.93_4
3.65	1.92	458	4.7_5	0.92_5
4.36	2.30	314	3.3	0.93_8
4.47	4.25	256	2.7	0.93_9
4.60	5.68	231	2.4	0.94_6
4.61	1.48	458	4.7_5	0.91_9
5.08	2.98	395	4.1	0.93_2
5.46	4.18	268	2.6	0.93_5
5.68	2.77	268	2.8	0.92_8
6.89	1.39	473	4.9	0.91_2
7.06	2.67	403	4.2	0.92_1
7.91	5.07	196	2.0	0.93_8

$E_{\frac{1}{2}}$ <u>V vs. SSCE</u>
0.93_0
0.94_2
0.94_2
0.93_8
0.93_4
0.92_5
0.93_0
0.93_9
0.94_6
0.91_9
0.93_2
0.93_5
0.92_8
0.91_2
0.92_1
0.93_8

FIGURE LEGENDS

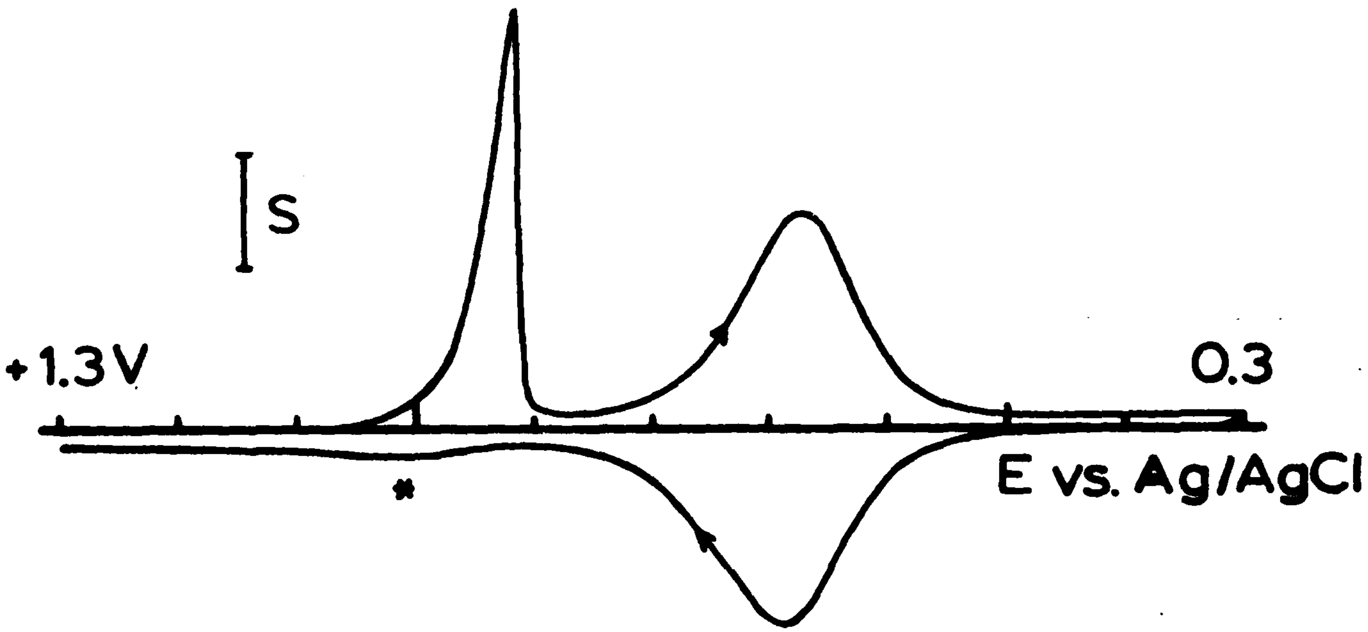
Figure 1. Cyclic voltammetry of a Pt/poly-$[Os(bpy)_2(vpy)_2]^{2+}$/poly-$[Ru(vbpy)_3]^{2+}$ bilayer with $\Gamma_{inner} = 3.65\times10^{-9}$ and $\Gamma_{outer} = 1.92\times10^{-9}$ mol/cm^2 at 50mV/s in 0.1<u>M</u> Et_4NClO_4/CH_3CN. S = 73 μA/cm^2. Bilayer was potentiostatted at +1.4V vs. Ag/AgCl (add 50mV to correct to SSCE) for 20 minutes before initiating the negative potential scan shown. The sharp reduction peak at +0.95V is Reaction 1; the symmetrical reduction/oxidation peaks at +0.68V (+0.73V vs. SSCE) are the poly-$[Os]^{2+/3+}$ couple of the inner film.

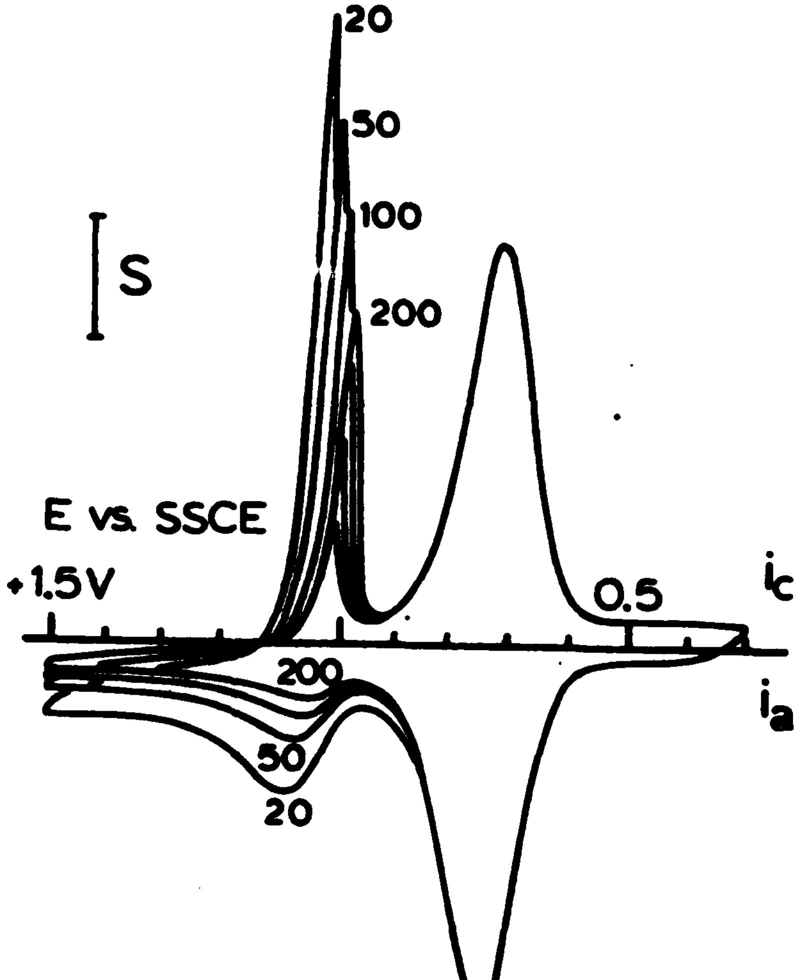
Figure 2. Cyclic voltammetry starting from +0.3V of Pt/poly-$[Os(bpy_2(vpy)_2]^{2+}$/poly-$[Ru(vbpy)_3]^{2+}$ bilayer with $\Gamma_{inner} = 2.73\times10^{-9}$ and $\Gamma_{outer} = 1.96\times10^{-9}$ mol/cm^2 at 20, 50, 100 and 200mV/s. S = 5.43, 13.6, 27.2 and 54.4 μA/cm^2 for 20, 50, 100 and 200 mV/s, respectively.

Figure 3. Energy level diagram for rotated disk redox pump experiment (and the cyclic voltammetric experiment in Fig. 5); dashed line represents Reaction 2.

Figure 4. Rotated disk voltammogram of the Pt/poly-$[Os(bpy)_2(vpy)_2]^{2+}$/poly-$[Ru(vbpy)_3]^{2+}$ bilayer of Fig. 1 in 3.55 m<u>M</u> $[Os(Me_2bpy)_3]^{2+}$ solution in 0.1<u>M</u> Et_4NClO_4/CH_3CN. v = 10 mV/s, S = 91 μA/cm^2 and w = 4900 r.p.m. The (non-steady state) wave at +0.7V for the oxidation of poly-$[Os]^{2+}$ does not appear in voltammograms obtained by halting the potential scan for a short interval before current measurement.

Figure 5. Cyclic voltammetry of Pt/poly-$[Os(bpy)_2(vpy)_2]^{2+}$/poly-$[Ru(vbpy)_3]^{2+}$ bilayer in Figure 1 in 3.55 m<u>M</u> $[Os(Me_2bpy)_3]^{2+}$ solution in 0.1<u>M</u> Et_4NClO_4/CH_3CN at 20, 50, 100 and 200 mV/s. S = 182 μA/cm^2


S
+1.3V
0.3
*
E vs. Ag/AgCl


20
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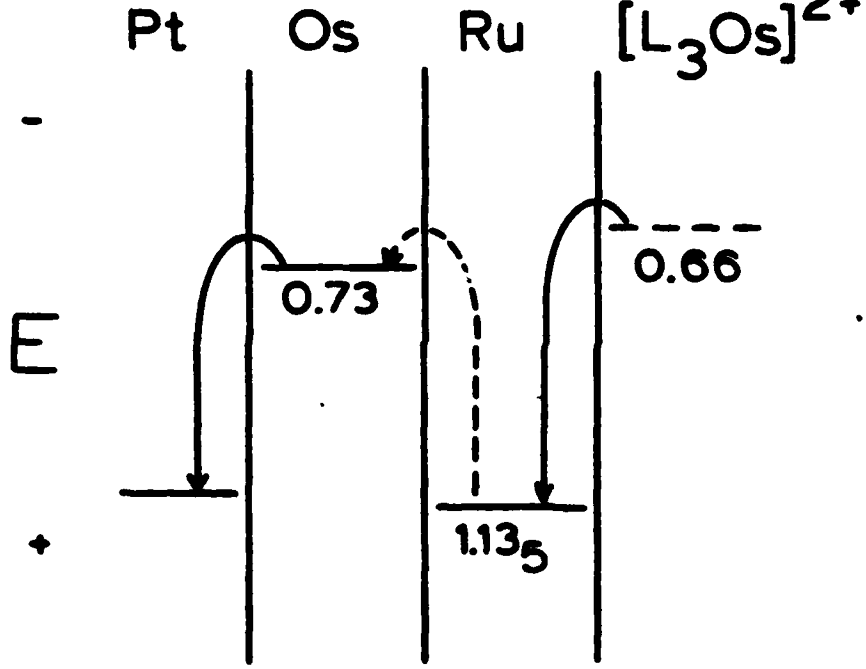
Pt
Os
Ru
$[L_3Os]^{2+}$
-
E
+
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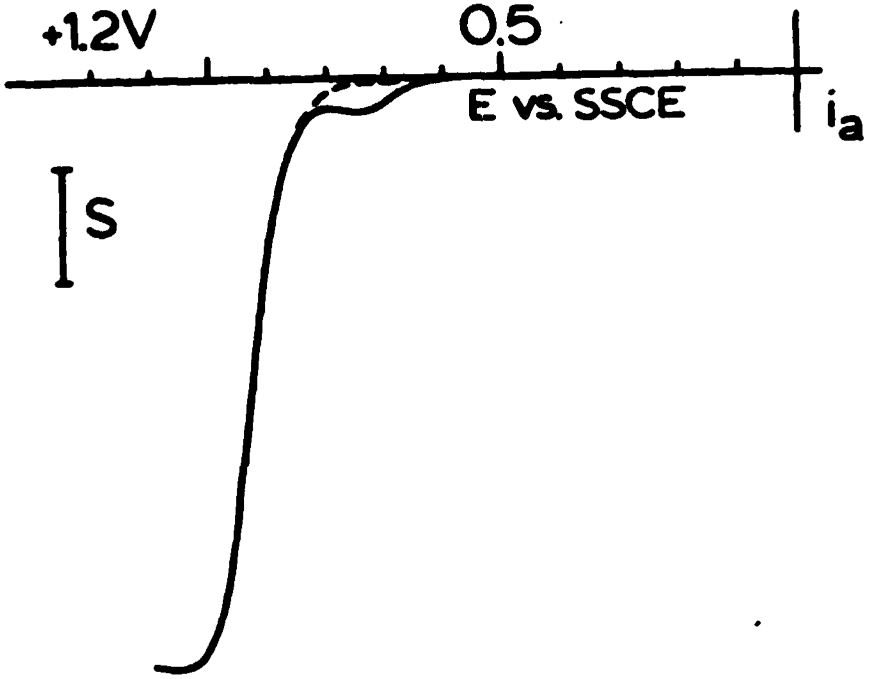
0.66
1.13_5



$_3$Os]$^{2+}$

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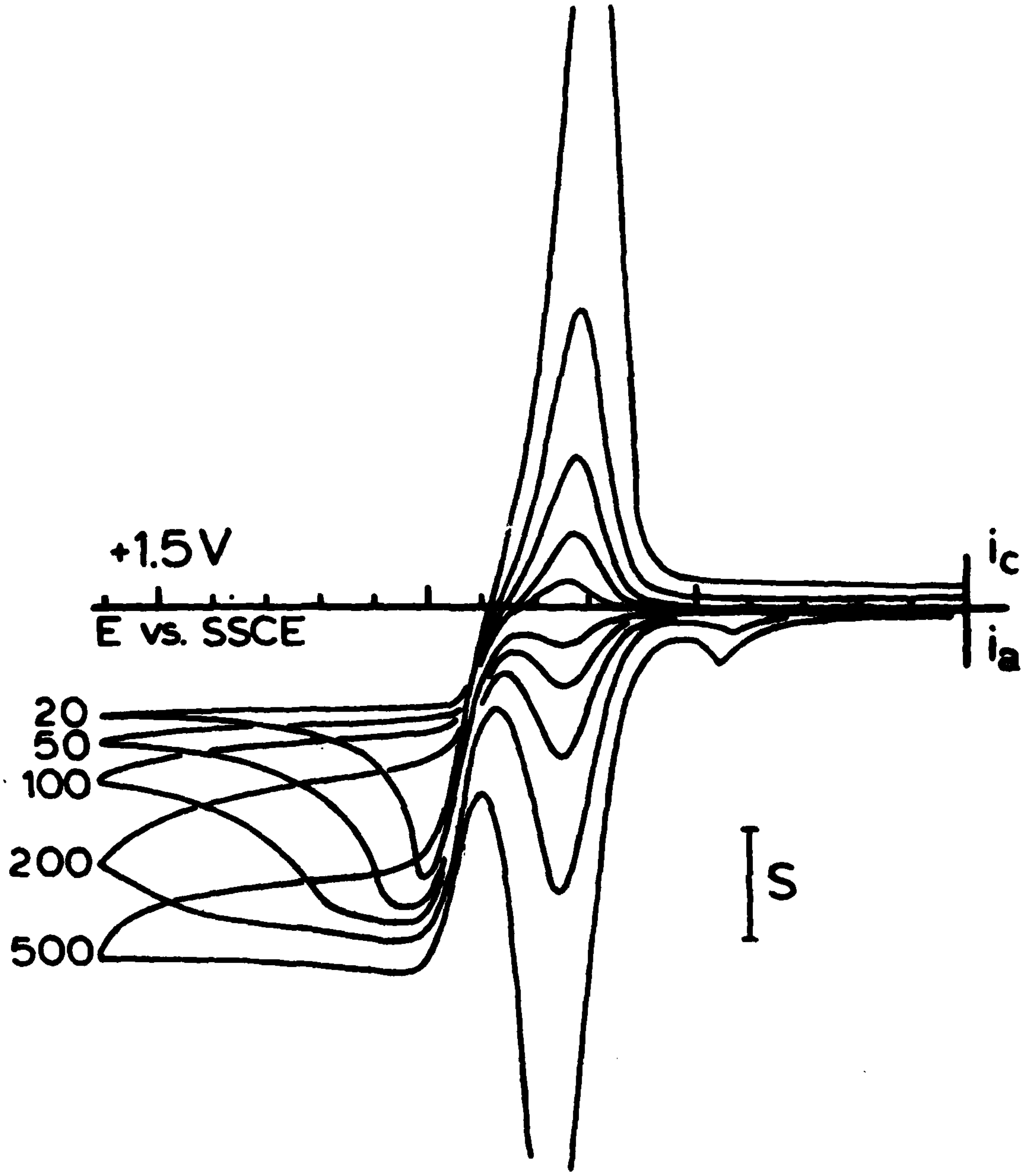
+1.5V
E vs. SSCE
i_c
i_a
20
50
100
200
500
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TECHNICAL REPORT # 12

ESTIMATION OF THE RATE OF ELECTRON TRANSFERS BETWEEN TWO CONTACTING POLYMER SURFACES

by

Royce W. Murray, Principal Investigator

Prepared for Publication

in the

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University of North Carolina
Department of Chemistry
Chapel Hill, North Carolina 27514

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A bilayer of redox polymer films, Pt/poly-$[Os(bpy)_2(vpy)_2]^{2+}$/poly-$[Ru(vbpy)_3]^{2+}$ is coated on a Pt electrode. Reduction of the poly-$[Ru]^{3+}$ outer film of a pre-oxidized bilayer, Pt/poly-$[Os]^{3+}$/poly-$[Ru]^{3+}$ is controlled by the rate of electron diffusion through the inner, poly-$[Os]^{2+/3+}$ film. When oxidizing the outer poly-$[Ru]^{2+}$ film of a reduced Pt/poly-$[Os]^{2+}$/poly-$[Ru]^{2+}$ bilayer, however, the rate of oxidation depends largely on the kinetics of electron transfer between the ca. monolayer of poly-$[Os]^{3+}$ and poly-$[Ru]^{2+}$ sites in contact at the interface between the two polymer films. The electron diffusion kinetics in the two polymer films perturb the interfacial reaction rate only slightly, so that a lower limit to the interfacial electron transfer rate constant is available. Remarkably, this value is within a factor of ca. 28 of that calculated from the Marcus relation for the corre-