

Kinetics of Electron-Transfer Cross-Reactions within Redox Polymers. Coatings of a Protonated Polylysine Copolymer with Incorporated Electroactive Anions

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Abstract: The kinetics of the cross-reaction between $\text{Co}(\text{typ})_2^{2+}$ ($\text{typ} = 2,2',2''\text{-terpyridine}$) and $\text{Mo}(\text{CN})_8^{3-}$ or $\text{W}(\text{CN})_8^{3-}$ were measured within coatings of a protonated poly-L-lysine copolymer on rotating graphite disk electrodes. The anionic octacyano complexes were bound electrostatically within the polycationic coatings. The $\text{Co}(\text{typ})_2^{2+}$ was dissolved in the solution that occupied the pores within the swollen coatings. The kinetic data were compared with the predictions of a recent theoretical analysis of reversible cross-reactions in electrode coatings⁷ and good agreement was obtained. The magnitudes of the cross-reaction rate constants evaluated from the data were remarkably similar despite a large difference in the equilibrium constants for the two cross-reactions. Some possible reasons for this behavior are examined.

Electrodes coated with polymers and polyelectrolytes in which redox sites are incorporated have rapidly become one of the most popular types of modified electrode surfaces.¹ Potential applications in catalysis of electrochemical reactions have provided much of the incentive for this development as has the relative ease of preparation of many electrode coatings. Catalysis by redox mediator couples attached to the electrode surface has the advantage over homogeneous catalysis that smaller quantities of catalyst are required and cumbersome separation problems are avoided. However, part of the efficacy of homogeneous catalysis is inherently related to the three-dimensional distribution of the catalytic centers as opposed to the essentially two-dimensional geometry operating with direct reactions at uncoated electrodes^{2a,c} or with reactions catalyzed by a single monolayer of attached catalyst.^{2b,c} Coatings consisting of electroactive polymers are particularly attractive in this connection because, in principle, they combine the advantages of an attached catalyst with the three-dimensional distribution of catalytic centers prevailing in homogeneous catalysis.^{2b,c} An illustration of this case is simple "redox catalysis"^{2a} in which the electron-transfer reactions of the substrate at the electrode and with the mediator redox couple (the catalyst) have a purely outer-sphere character and are not subject to particular steric requirements. In such cases, a monolayer of "catalyst" attached to the electrode surface is predicted to produce only small, if not negligible, catalytic effects even when significant catalysis does occur with the same redox centers dispersed homogeneously in the solution or within a polymeric coating.^{2b,c} Indeed, in the latter cases, the "catalysis" is essentially a reflection of the three-dimensional distribution of the catalytic centers. An experimental illustration of the validity of these assertions about monolayer coatings of redox mediators is available in a recent investigation of electron transfer mediated by polymeric films of [ruthenium(4-vinyl-4'-methyl-2,2'-bipyridine)]₃²⁺.³ These coatings are impermeable to components of the solution so that only their outer-most layer participates in the mediation.

It does not follow that catalysis of electrochemical reactions by monolayers is impossible. It may well occur when chemistry more intricate than simple outer-sphere electron transfer is involved in the catalytic process ("chemical catalysis"^{2a}) or when the reactions involve special steric requirements as illustrated in a number of recent examples.^{4,5} However, the use of polymeric rather than monolayer catalyst might further enhance the catalytic

efficiency in such cases because of the three-dimensional arrangement of the catalytic sites.

The attractive potentialities of three-dimensional arrays of catalysts within electrode coatings are now understood to be subject to possible kinetic limitations imposed by the rates of substrate permeation^{2b,d,6,7} and charge propagation^{2d,7,8} through the coatings, steps that are inescapably associated with the catalytic reaction itself in the overall catalytic process. Several investigations have shown that redox polymer films may even behave as a single monolayer located either at the film-solution interface^{3a,b,4c,5} or at the electrode-film interface,⁹ corresponding to the case where the catalytic step is faster than the permeation of the substrate or charge propagation through the film, respectively. In such cases, the advantage resulting from the three-dimensional distribution of the redox sites in the polymer film is obviously lost so that monolayer coatings may prove more advantageous under such circumstances.

Models devised for analyzing the kinetic factors that control the catalytic efficiency of redox polymer films have been progressively developed.^{2a,4e,6,7,10-13} Redox polymer coatings will

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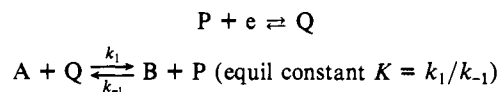
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function most efficiently when the catalytic reaction takes place within a substantial portion of the film rather than at one of its external interfaces. Rigorous analyses of the interplay between the three possible rate-limiting factors mentioned above are now available for several cases of practical interest.^{7,13,14} They concern the generalized reactions in Scheme I, where P/Q is the mediator

Scheme I



couple and A/B the substrate couple, i.e., the system whose reduction (or oxidation) is mediated by the P/Q couple. The equilibrium constant of the cross-reaction is related to the standard potentials of the two couples E_{PQ}° and E_{AB}° through:

$$(RT/F) \ln K = \pm(E_{AB}^\circ - E_{PQ}^\circ) \quad (1)$$

where the + or - sign corresponds to reduction or oxidation of the substrate, respectively.

Under steady-state conditions for the mass-transfer processes in solution (e.g., in rotating disk electrode voltammetry), the influence of the three rate-limiting factors in the film can be conveniently expressed by three characteristic current densities:^{7c}

permeation of the substrate

$$i_S = FC_A^\circ \kappa D_S / \phi \quad (2)$$

diffusion-like charge propagation

$$i_E = FC_P^\circ D_E / \phi = F\Gamma_P^\circ D_E / \phi^2 \quad (3)$$

rate of the cross-reaction

$$i_k = FC_A^\circ \kappa k C_P^\circ \phi = FC_A^\circ \kappa k \Gamma_P^\circ \quad (4)$$

where C_A° is the concentration of substrate in the bulk of the solution, Γ_P° is the total amount of mediator present in the film per unit surface area, $C_P^\circ (= \Gamma_P^\circ / \phi)$ is the concentration of mediator in the film, ϕ is the film thickness, κ is the partition coefficient of the substrate between the film and the solution, D_S is the diffusion coefficient of the substrate in the film, and D_E is the diffusion coefficient for the diffusion-like propagation of charge through the film. The electrochemical response obtained from a coated electrode is a function of these three current densities, of the equilibrium constant K (Scheme I), and of a fourth characteristic current density:

$$i_A = FC_A^\circ D / \delta \quad (5)$$

governing the rate of supply of the substrate to the film/solution interface. (D is the diffusion coefficient of the substrate in solution and δ is the thickness of the diffusion layer under stationary state conditions.)

The kinetics of the overall mediated electron-transfer process take simple limiting forms when one or two of the rate-limiting factors predominate(s) over the others. These limiting cases have been identified by various combinations of the three letters S, E, and R (representing substrate permeation, charge transport, and cross-reaction, respectively) to indicate the rate-limiting factors that predominate in each sub-case.⁷

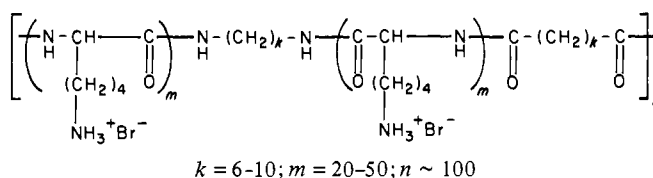
To establish the practical applicability as well as the reliability of these kinetic models, comparisons with experimental results are needed. For the most interesting cases, where a significant portion of the film actually participates in the mediation of the electron-transfer process, experimental tests of the theoretical analysis have dealt with polyelectrolyte coatings in which charged redox mediators are incorporated by electrostatic (ion-exchange) attachment. Such films possess a number of advantages, particularly when a variety of redox couples can be incorporated into a given polymeric structure.^{10,11,15-19} In the few cases where

experimental data suitable for comparison with theory were available encouragingly good agreement was obtained for both irreversible cross-reactions^{7b,10a,15} ($K = \infty$) and one self-exchange reaction^{17a} ($K = 1$). However, tests of the theory for cross-reactions^{7b,10a,15} have been incomplete because of the lack of precise data on substrate permeation or charge transport through the films considered. A complete analysis that produced excellent agreement with the theoretical predictions was possible in the particular case of a self-exchange reaction.^{17a}

The need remains for further analysis of systems involving cross-reactions with equilibrium constants differing from unity. That was a primary objective of the work described herein. Our purposes include the design of procedures for deciphering the roles of each of the three rate-limiting factors on a quantitative basis so that the operating efficiency of catalytic devices based on redox polymer coatings can be optimized.

Experimental Section

Materials. $[\text{Co}(\text{tpy})_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$,^{2a} $\text{K}_4[\text{Mo}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$,^{2b} and $\text{K}_4[\text{W}(\text{CN})_8]^{2c}$ were prepared and purified according to procedures given in the cited references. All other chemicals were reagent grade and used without further purification. Laboratory distilled water was further purified by passage through a purification train (Barnsted Nanopure). Pyrolytic graphite electrodes were obtained and prepared as previously described.^{22a} The electrodes were mounted to expose 0.17 cm² of the basal plane of the graphite to the solution. Mounted electrodes were coated with the polylysine copolymer as previously described.^{17a} The coating material was incorrectly identified as poly-L-lysine in ref 17a. Subsequent tests have disclosed that the polyelectrolyte employed is actually a block copolymer of polylysine with the following structure:



Apparatus and Procedures. The instrumentation and procedures used to record the cyclic and rotating disk voltammograms have been described.^{10a} The incorporation of desired quantities of $\text{Mo}(\text{CN})_8^{4-}$ or $\text{W}(\text{CN})_8^{4-}$ in polylysine copolymer coatings was achieved by continuously scanning the potential of a coated electrode over the oxidation-reduction wave of the complex in a dilute solution (0.1 to 0.5 mM) while monitoring the peak current. When the peak current reached the selected value the electrode was quickly removed from the solution, washed, and transferred to pure supporting electrolyte where the quantity of incorporated reactant was determined by coulometric assay. The latter was performed by integrating the current that flowed as the electrode potential was scanned from values more negative than the oxidation wave to values well beyond the peak potential where it was maintained until the current decreased to background levels.

Chronocoulometric measurements were conducted with a computer-based instrument previously described.^{22b} Positive feedback was employed to provide as much compensation as possible of the additional resistance associated with the polylysine coatings. Measurements were

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(14) The situation where the polymer coating functions as a monolayer located at one of the two interfaces of the film can be treated either as limiting cases of these analyses^{4,13} or directly.^{3a,4e,6,12}

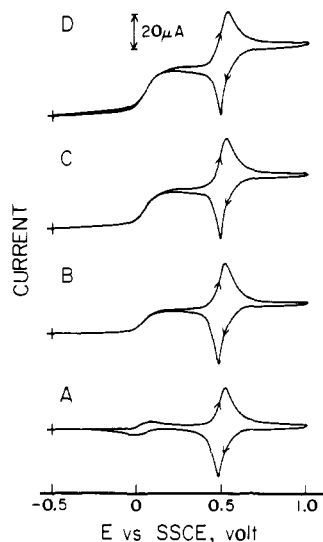


Figure 1. Current-potential curves for oxidation of 0.5 mM $\text{Co}(\text{tpy})_2^{2+}$ at a rotating graphite disk electrode coated with PLC- $\text{Mo}(\text{CN})_8^{4-}$. The coating contained 2.8×10^{-7} mol cm^{-2} of PLC and 3.5×10^{-8} mol cm^{-2} of $\text{Mo}(\text{CN})_8^{4-}$. Supporting electrolyte: 0.2 M acetate buffer at pH 5.5. Electrode rotation rates: (A) 0; (B) 400; (C) 1600; (D) 3600 rpm. Electrode potential was scanned at 10 mV s^{-1} .

confined to times sufficiently short to ensure that semi-infinite linear diffusion prevailed.

Measurements were conducted at 22 ± 2 °C in solutions that were deaerated with prepurified argon. Potentials were measured and are quoted with respect to a sodium chloride saturated calomel electrode, SSCE.

Results

The Experimental Systems. Pyrolytic graphite electrodes coated with protonated poly-L-lysine copolymer (PLC) were used to incorporate anionic mediator complexes. Previous investigations of this polyelectrolyte coating¹⁷ have shown it to yield a highly swollen structure through which substrates permeate rapidly and which supports remarkably high charge propagation rates along the polymer chains. PLC coatings have been modeled in terms of two interacting domains:^{17a} the tangled, polyelectrolyte chains with their accompanying counterions (Donnan domains) are separated by pores²³ that are filled up by the electrolyte solution with which the coating is in contact (see Figure 1 in ref 17a).

When $\text{Mo}(\text{CN})_8^{4-}$ or $\text{W}(\text{CN})_8^{4-}$ was incorporated in PLC coatings, stable reversible cyclic voltammetric responses were obtained when the electrodes were transferred from the incorporating solution to pure supporting electrolyte. Similar behavior has been reported when the same complexes were incorporated in protonated poly(vinylpyridine) coatings.^{16c,f} In order to observe the effects of electron transfer between the incorporated complex and a second, non-incorporating complex, the coated electrodes were utilized as rotating disk electrodes in solutions containing $\text{Co}(\text{tpy})_2^{2+}$ ($\text{tpy} \equiv 2,2',2''\text{-terpyridine}$). This complex was selected because the relatively small self-exchange constant for the $\text{Co}(\text{tpy})_2^{3+/2+}$ couple ($k_{\text{ex}} \sim 10 \text{ M}^{-1} \text{ s}^{-1}$ at 0 °C)²⁴ suggested that the cross-reaction with the incorporated anions would proceed at easily measured rates.

Mediation of $\text{Co}(\text{tpy})_2^{2+}$ Oxidation by $\text{Mo}(\text{CN})_8^{3-}$. The set of current-potential curves shown in Figure 1 resulted when $\text{Mo}(\text{CN})_8^{4-}$ was incorporated in the coating and the electrode potential was scanned from -0.5 V to more positive potentials in a 0.5 mM solution of $\text{Co}(\text{tpy})_2^{2+}$. The first wave with $E_{1/2}$ near +0.05 V represents the oxidation of the $\text{Co}(\text{tpy})_2^{2+}$ that penetrates the coating to react directly at the graphite surface. A similar response

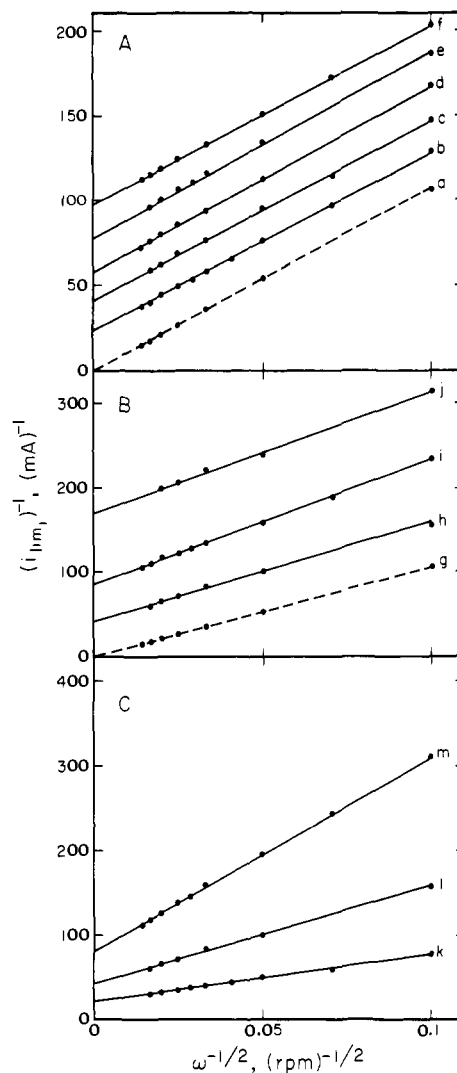


Figure 2. Koutecky-Levich plots prepared from the plateau currents of the first wave for the oxidation of $\text{Co}(\text{tpy})_2^{2+}$ at rotating graphite disk electrodes coated with PLC- $\text{Mo}(\text{CN})_8^{4-}$. (A) $[\text{Co}(\text{tpy})_2^{2+}] = 0.5$ mM: (a) bare electrode; (b-f) $\Gamma_{\text{PLC}} = 2.8 \times 10^{-7}$ mol cm^{-2} , $\Gamma_{\text{Mo}(\text{CN})_8^{4-}} = 4.9$ (b), 3.5 (c), 2.1 (d), 1.5 (e), 0×10^{-8} (f), mol cm^{-2} . (B) $[\text{Co}(\text{tpy})_2^{2+}] = 0.5$ mM: (g) bare electrode; (h) $\Gamma_{\text{PLC}} = 2.8 \times 10^{-7}$, $\Gamma_{\text{Mo}(\text{CN})_8^{4-}} = 3.5 \times 10^{-8}$ mol cm^{-2} ; (i) $\Gamma_{\text{PLC}} = 5.6 \times 10^{-7}$, $\Gamma_{\text{Mo}(\text{CN})_8^{4-}} = 7.1 \times 10^{-8}$ mol cm^{-2} ; (j) $\Gamma_{\text{PLC}} = 11.2 \times 10^{-7}$, $\Gamma_{\text{Mo}(\text{CN})_8^{4-}} = 14.1 \times 10^{-8}$ mol cm^{-2} . (C) $\Gamma_{\text{PLC}} = 2.8 \times 10^{-7}$, $\Gamma_{\text{Mo}(\text{CN})_8^{4-}} = 3.5 \times 10^{-8}$ mol cm^{-2} . $[\text{Co}(\text{tpy})_2^{2+}] = 1.0$ (k), 0.5 (l), 0.25 (m) mM. Supporting electrolyte as in Figure 1.

is obtained at electrodes coated with PLC in which no $\text{Mo}(\text{CN})_8^{4-}$ had been incorporated. The current peak at the beginning of the second wave in the curves of Figure 1 arises from the oxidation of the incorporated $\text{Mo}(\text{CN})_8^{4-}$ to $\text{Mo}(\text{CN})_8^{3-}$. The peak is followed by a second plateau with a current that is larger than the plateau current of the wave preceding the peak even though both of these plateau currents correspond only to the oxidation of $\text{Co}(\text{tpy})_2^{2+}$. The second plateau current is larger because the oxidation of $\text{Co}(\text{tpy})_2^{2+}$ is mediated by the $\text{Mo}(\text{CN})_8^{3-}$ now present in the coating so that the $\text{Co}(\text{tpy})_2^{2+}$ can be oxidized without having to reach the underlying electrode surface. The clear separation of these two plateau currents provides an ideal situation for inspecting separately the parameters that limit each of the currents. To do so, the two plateau currents were measured as a function of the electrode rotation rate, ω , and Koutecky-Levich plots²⁵ of $(i_{\text{lim}})^{-1}$ vs. $\omega^{-1/2}$ were prepared.^{10a}

Representative plots corresponding to various experimental parameters are shown in Figures 2 and 3 for the first and second

(23) These pores are not pinholes. Although their average diameters are larger than molecular dimensions, they are much smaller than the thickness of the diffusion layer in solution. Electron micrographs of coatings reveal no holes or other imperfections with diameters greater than ca. 1 μm .

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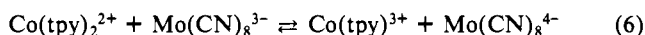
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Table I. Permeation Currents, i_S , for the Direct Oxidation of $\text{Co}(\text{tpy})_2^{2+}$ at Graphite Electrodes Coated with PLC

$10^7 \Gamma_{\text{PLC}}^a$ mol cm^{-2}	$10^8 \Gamma_{\text{Mo}(\text{CN})_8^{4-}}^b$ mol cm^{-2}	$[\text{Co}(\text{tpy})_2^{2+}]^c$ mM	$10^5 i_S^d$ A cm^{-2}	$10^{-9} i_S$	
				$[\text{Co}(\text{tpy})_2^{2+}] \Gamma_{\text{Mo}(\text{CN})_8^{4-}}^7$ $\text{A cm}^3 \text{mol}^{-2}$	
2.8	3.5	0.25	7.2		8.2
2.8	3.5	0.5	14		8.0
2.8	3.5	1.0	27		7.8
2.8	0	0.5	5.9		
2.8	1.5	0.5	7.4		9.9
2.8	2.1	0.5	9.9		9.4
2.8	4.9	0.5	24		9.8
5.6	7.1	0.5	6.7		
11.2	14	0.5	3.3		

^a Total quantity of PLC in the rotating disk electrode coating. ^b Total quantity of $\text{Mo}(\text{CN})_8^{4-}$ incorporated in the PLC coating. ^c Bulk concentration of $\text{Co}(\text{tpy})_2^{2+}$ in the test solution where the rotating disk measurements were made. Solution also contained 0.2 M acetate buffer at pH 5.5. ^d Permeation currents obtained from the intercepts of Koutecky-Levich plots such as those in Figure 2.

plateau currents, respectively. The linearity (or lack of it), slopes, and intercepts of such plots provide an entry to the available theoretical analyses⁷ of the behavior to be expected from electrodes coated with redox polymer films. Both the $\text{Co}(\text{tpy})_2^{3+/2+}$ and $\text{Mo}(\text{CN})_8^{3-/4-}$ redox couples are electrochemically reversible (Figure 1, curve A). The rate of direct electron transfer between the electrode and the $\text{Co}(\text{tpy})_2^{3+/2+}$ couple is not depressed significantly by the protonated PLC coating in contrast to the behavior observed with the $\text{Fe}^{3+/2+}$ couple in protonated poly(vinylpyridine) coatings.^{10a,26} The standard potential of the substrate couple, $\text{Co}(\text{tpy})_2^{3+/2+}$, E_{AB}° , is less positive than that of the mediator couple, $(\text{Mo}(\text{CN})_8^{4-/3-})$, E_{PQ}° , by 456 mV. Thus, equilibrium for the cross-reaction



strongly favors the products ($K = 6 \times 10^7$; eq 1). Since the reversible response of the substrate couple occurs at potentials ahead of that for the mediator couple, the kinetic situation corresponds to that termed "case C" in previous theoretical analyses.^{7d} The pertinent equations governing the plateau currents of the first and second waves are therefore those given in Table 5 of ref 7d.

It should be pointed out that the mediated reactions investigated in the present study are not catalytic in the sense that the oxidation of the substrate proceeds at less positive potentials in the presence of the mediator. This is because the direct oxidation of the substrate at the electrode surface precedes the oxidation of the mediator at both bare and coated electrodes. However, the rate of substrate oxidation at potentials on the second current plateau is increased by the introduction of the mediator so that this system is useful for modeling catalytic processes.

Koutecky-Levich plots of the plateau currents from the first wave in Figure 1 are shown in Figure 2. They exhibit features expected for a permeation limited current, i_S (eq 2). In particular, the plots are linear with slopes that match that obtained at a bare electrode and intercepts that are linear functions of the coating thickness (Figure 2B) and of the reciprocal concentration of $\text{Co}(\text{tpy})_2^{2+}$ (Figure 2C). These properties are summarized in Table I. The increase in the values of i_S as the quantity of $\text{Mo}(\text{CN})_8^{4-}$ incorporated in the coating is increased is most likely produced by shrinkage in the coating thickness resulting from electrostatic cross-linking by the incorporated, multiply-charged anions.^{10a} The permeation current is fourfold larger in a PLC coating containing $4.9 \times 10^{-8} \text{ mol cm}^{-2}$ of $\text{Mo}(\text{CN})_8^{4-}$ than in a pure PLC coating (Table I). This change in i_S probably reflects a decrease in coating thickness that is larger than fourfold because the rate of diffusional motion of the reactant ($\text{Co}(\text{tpy})_2^{2+}$) is likely to decrease with increased cross-linking.¹⁷ For a given amount of PLC in the coating, the permeation current is approximately proportional to the amount of mediator present in the coating (last column of Table I). This empirical observation reflects the combined influences of $\text{Mo}(\text{CN})_8^{4-}$ incorporation on the film thickness and

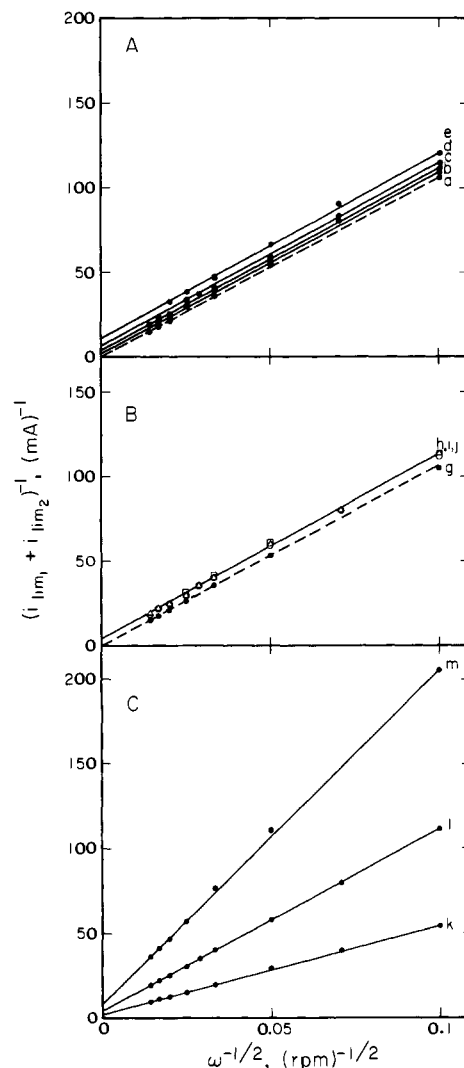


Figure 3. Koutecky-Levich plots prepared from the total plateau current of the second wave for the oxidation of $\text{Co}(\text{tpy})_2^{2+}$ at rotating graphite disk electrodes coated with PLC- $\text{Mo}(\text{CN})_8^{4-}$. The experimental situations correspond to those specified in the caption to Figure 2.

on the permeation diffusion coefficient of the substrate.

The most important point for the purposes of the present discussion is that the first wave of the current-potential curves in Figure 1 provides a direct measure of i_S under all experimental conditions. (We have assumed that i_S is not significantly affected by the oxidation of the incorporated $\text{Mo}(\text{CN})_8^{4-}$ to $\text{Mo}(\text{CN})_8^{3-}$.) The plateau current of the second wave (that follows the transient, peaked response from the incorporated $\text{Mo}(\text{CN})_8^{4-}$ anions) is larger than that on the first wave because of the additional Co-

Table II. Mediator Propagation Currents, i_E , for $\text{Mo}(\text{CN})_8^{4-}$ and $\text{W}(\text{CN})_8^{4-}$ in Coatings of PLC^a

$10^8 \Gamma_P^b$ mol cm ⁻²	$10^3 S^c$ C cm ⁻² s ^{-1/2}	$10^3 i_E^d$ A cm ⁻²	$10^5 (i_E/\Gamma_P^0)$ A mol ⁻¹
$\text{Mo}(\text{CN})_8^{4-}$			
1.5	1.54	1.3	0.87
2.1	2.66	2.8	1.33
3.5	3.65	3.1	0.86
4.9	4.65	3.6	0.73
$\text{W}(\text{CN})_8^{4-}$			
1.5	1.47	1.2	0.80
2.1	2.63	2.7	1.29
3.3	3.62	3.0	0.91
4.9	4.74	3.7	0.76

^a All coatings contained 2.8×10^{-7} mol cm⁻² of PLC. ^b Total quantity of mediator incorporated in the PLC coating. ^c Initial chronocoulometric slope for oxidation of the incorporated mediator after electrode was transferred to pure supporting electrolyte. Slopes were measured within 50 ms after the potential step was applied. ^d Mediator propagation current calculated from eq 7.

(tpy)₂²⁺ that is oxidized by reacting with the $\text{Mo}(\text{CN})_8^{3-}$ anions that are generated electrochemically within the coating. To analyze the kinetic situation in the framework of "case C",^{7d} it is necessary to estimate the relative values of the three characteristic current densities, i_S , i_E , and i_k (eq 2–4). Values of i_S are available from Table I. i_E is the propagation current (eq 3) that measures the rate at which $\text{Mo}(\text{CN})_8^{3-}$ ions generated at the electrode surface are transported through the coating by ion-hopping or electron-hopping within the Donnan domains. i_k is the kinetic current that measures the rate of the cross-reaction between mediator and substrate (eq 4).

A convenient method for measuring i_E involves the transfer of a mediator-loaded electrode to a pure supporting electrolyte solution where the transient chronocoulometric^{27a} or chronoamperometric^{27b} responses to potential steps across the mediator wave are recorded. For example, eq 7 gives the relevant relation when

$$i_E = \frac{\pi S^2}{4F\Gamma_P^0} \quad (7)$$

chronocoulometric slopes per unit surface area, S , are measured in the pure supporting electrolyte. Table II summarizes values of i_E obtained in this way. Note that these values are much larger than the values of i_S measured under the same conditions (Table I).

The possible kinetic situations that might apply to the present system include those labeled (R + S), SR, and (SR + E) in ref 7d. The (R + S) case can be ruled out because it corresponds to a finite concentration of unoxidized $\text{Co}(\text{tpy})_2^{2+}$ at the electrode surface and this concentration is already decreased to zero by direct oxidation of the $\text{Co}(\text{tpy})_2^{2+}$ on the plateau of the first wave. Both the linearity of the Koutecky–Levich plots for the second wave (Figure 3) and the demonstration that $i_E \gg i_S$ (Table I) allow the (SR + E) case to be eliminated. Thus, the observed behavior seems most compatible with that expected for the SR case. Physically, this means that charge propagation is so fast that its rate does not affect the observed kinetics so that substrate permeation (S) and the cross-reaction itself (R) are the only factors that limit the rate of the overall process taking place in the film. The film current, i_F , i.e., the intercept of the Koutecky–Levich plot, is therefore expected to obey the simple relation^{7b}

$$i_F = (i_k i_S)^{1/2} \quad (8)$$

The product ($i_S i_k$) is independent of the coating thickness at constant concentration of incorporated mediator so that i_F should not depend on coating thickness according to eq 8. Similarly, eq 4 and 8 predict that the combination $i_F^2 (i_S \Gamma_P^0)^{-1}$ should be independent of Γ_P^0 at a constant concentration of substrate. Figure

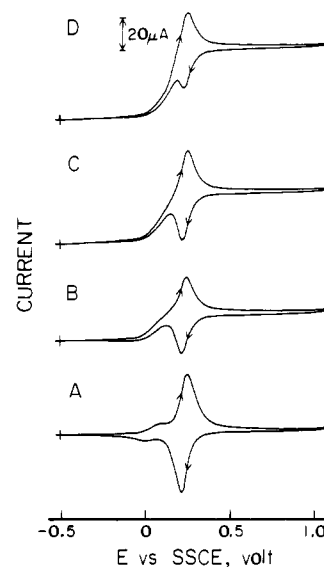


Figure 4. Current-potential curves for oxidation of 0.5 mM $\text{Co}(\text{tpy})_2^{2+}$ at a rotating graphite disk electrode coated with PLC- $\text{W}(\text{CN})_8^{4-}$. Experimental conditions correspond to those in Figure 1.

3B shows that essentially the same film current results for three different coating thicknesses as expected from eq 8. Additional experimental data are collected in Table III including values of $i_F^2 (i_S \Gamma_P^0)^{-1}$ for the first four entries. The relatively good constancy of these values also points to eq 8 as the appropriate governing equation. Thus, it may be concluded that the $\text{Co}(\text{tpy})_2^{2+}$ - $\text{Mo}(\text{CN})_8^{4-}$ system provides an example of the kinetic situation labeled case C, sub-class SR in the classification scheme of ref 7d. Physically, this corresponds to the case where all of the substrate reacts with the incorporated mediator in a thin reaction layer near the coating-solution interface. Thus, the $\text{Co}(\text{tpy})_2^{2+}$ that is oxidized only after it reaches the graphite surface when the electrode potential is held on the plateau of the first wave in Figure 1 is oxidized without reaching the electrode surface by means of its cross-reaction with $\text{Mo}(\text{CN})_8^{3-}$ when the potential is held on the plateau of the second wave.

Mediation of $\text{Co}(\text{tpy})_2^{2+}$ Oxidation by $\text{W}(\text{CN})_8^{4-}$. As shown by the current-potential curves in Figure 4, there is only a small separation between the potentials where $\text{W}(\text{CN})_8^{4-}$ and $\text{Co}(\text{tpy})_2^{2+}$ are directly oxidized at PLC-coated rotating disk electrode ($E_{AB}^0 - E_{PQ}^0 = 210$ mV; $K = 3.5 \times 10^3$). The consequent lack of a well-developed plateau for the first wave prevents the measurement of i_S for the permeation of $\text{Co}(\text{tpy})_2^{2+}$ of PLC coatings containing $\text{W}(\text{CN})_8^{4-}$. For this reason the i_S values needed to analyze the kinetics were assumed to be the same as those measured with PLC coatings containing the same quantity of $\text{Mo}(\text{CN})_8^{4-}$. Considering the similarity in the size and charge of the two anions this approximation seems well justified.

The values of i_E for the PLC- $\text{W}(\text{CN})_8^{4-}$ coatings were measured by the same chronocoulometric procedure employed with $\text{Mo}(\text{CN})_8^{4-}$ and the results, included in Table II, indicate similarly high propagation rates through the coating of the oxidized form of the incorporated complex. Koutecky–Levich plots of the second, well-formed plateau currents in the rotating disk current-potential curves for the $\text{Co}(\text{tpy})_2^{2+}$ - $\text{W}(\text{CN})_8^{4-}$ system exhibited the same characteristics as those for the $\text{Co}(\text{tpy})_2^{2+}$ - $\text{Mo}(\text{CN})_8^{4-}$ system (Figure 5). Film currents obtained from the intercepts of the Koutecky–Levich plots are summarized in Table III. As was true for $\text{Mo}(\text{CN})_8^{4-}$, the combination $i_F^2 (i_S \Gamma_P^0)^{-1}$ was reasonably independent of Γ_P^0 (Table III, last column) and the film current remained independent of coating thickness at a fixed level of mediator loading (Figure 5B). Thus, the film currents in the case of mediation by $\text{W}(\text{CN})_8^{4-}$ also obey eq 8.

Kinetic Currents, Cross-Reaction Rate Constants, Reaction-Layer Thickness. The characteristic kinetic currents, i_k , and the corresponding rate constants for the cross-reaction between $\text{Co}(\text{tpy})_2^{2+}$ and $\text{Mo}(\text{CN})_8^{3-}$ or $\text{W}(\text{CN})_8^{3-}$ were calculated from the

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Table III. Film Currents, i_F , for the Mediated Oxidation of $\text{Co}(\text{tpy})_2^{2+}$ at Graphite Electrodes Coated with PLC-Mo(CN) $_8^{4-}$ or PLC-W(CN) $_8^{4-}$

$10^8 \Gamma_P^\circ$, mol cm $^{-2}$	[Co(tpy) $_2^{2+}$], mM	$10^5 i_S^c$, A cm $^{-2}$	$10^5 i_F^d$, A cm $^{-2}$		$10^5 i_F^2 (i_S \Gamma_P^\circ)^{-1}$, A mol $^{-1}$	
			Mo(CN) $_8^{4-}$	W(CN) $_8^{4-}$	Mo(CN) $_8^{4-}$	W(CN) $_8^{4-}$
1.5	0.5	7.4	46	57	1.9	2.9
2.1	0.5	9.9	72	96	2.5	4.4
3.5	0.5	14	96	144	2.9	4.2
4.9	0.5	24	144	229	1.8	4.5
3.5	0.25	7.2	57	72		
3.5	1.0	2.7	230	287		
7.1	0.5	6.9	96	144		
14	0.5	3.3	96	144		

^a All electrodes were coated with 2.8×10^{-7} mol cm $^{-2}$ of PLC except for the final two entries for which Γ_{PLC} was twice and four times as large, respectively. ^b Total quantity of mediator, Mo(CN) $_8^{4-}$ or W(CN) $_8^{4-}$, incorporated in the PLC coatings. ^c Permeation currents from Table I. ^d Film current evaluated from the intercepts of Koutecky-Levich plots such as those in Figures 3 and 5.

data in Table III with use of eq 4 and 8. (The data allow the evaluation only of the product of the rate constant, k , and the substrate partition coefficient, κ . The latter is probably within an order of magnitude of unity.) The results are summarized in Table IV.

The cross-exchange reaction takes place essentially within a reaction layer of thickness μ located inside the film at the film-solution interface. The dimensionless concentration profile of Co(tpy) $_2^{2+}$ in the film can be calculated from eq 9, where $C_A(x)$

$$\frac{C_A(x)}{\kappa C_A^\circ} = \exp[-(i_k/i_S)^{1/2}(1-x/\phi)] [1 + (i_k i_S)^{1/2}/i_A]^{-1} \quad (9)$$

is the concentration of A at distance x from the electrode surface. The ratio of the reaction layer and film thicknesses as calculated from eq 10^{7b,d} are given in Table IV. As expected, this ratio is

$$\mu/\phi = (i_S/i_k)^{1/2} \quad (10)$$

independent of the substrate concentration. It is also approximately independent of the quantity of mediator present in the film at a given value of Γ_{PLC} (first six entries of Table IV). This is because i_k is directly proportional to Γ_P° and i_S is approximately proportional to Γ_P° because of the decrease in film thickness as the concentration of the mediator in the film increases (Table I). Increasing the film thickness at a fixed concentration of mediator produces essentially no change in the reaction layer thickness (e.g., compare entries 3, 7, and 8 in Table IV). This is the behavior expected for an "SR" situation^{7d} in which the kinetics of the substrate in the film is compensated by the kinetics of the cross-reaction to limit the region in the film where substrate and mediator encounter each other.

On the basis of previous measurements of PLC films^{17b} we estimate that coatings consisting of 2.8×10^{-7} mol cm $^{-2}$ of PLC will have film thicknesses between ca. 0.5 and 2×10^{-3} cm depending on the concentration of mediator in the film. The smallest reaction layer thickness in Table IV is thus ca. 5×10^{-5} cm (5000 Å). This is considerably larger than molecular dimensions and shows that the cross-reaction really proceeds within the bulk of the polymer coating and is not a surface reaction occurring only at the film-solution interface.

We concluded that the propagation of charge within the coating does not interfere in the overall kinetics because i_E was always significantly larger than i_S . This conclusion is also consistent with the fact the i_E exceeded i_A , the Levich current density (eq 5), under all of the experimental conditions. Thus, the value of i_A corresponding to the largest values of C_A° and ω was only 7.3×10^{-4} A cm $^{-2}$ while the smallest value of i_E was 1.2×10^{-2} A cm $^{-2}$ (Table II).

Another test of self-consistency of our analysis concerns the first wave. The theoretical predictions indicate that the film current at the plateau of the first wave should be equal to i_S only if $(i_k/Ki_S)^{1/2}$ is small enough so that both $\cosh [(i_k/Ki_S)^{1/2}]$ and $(Ki_S/i_k)^{1/2} \tanh [(i_k/Ki_S)^{1/2}]$ are essentially equal to unity (see Table 5 in ref 7d). With Mo(CN) $_8^{4-}$, in the most unfavorable case, these conditions are fulfilled with a high precision: $\cosh [(i_k/Ki_S)^{1/2}] = 1 + 7 \times 10^{-6}$, $(Ki_S/i_k)^{1/2} \tanh [(i_k/Ki_S)^{1/2}] = 1$

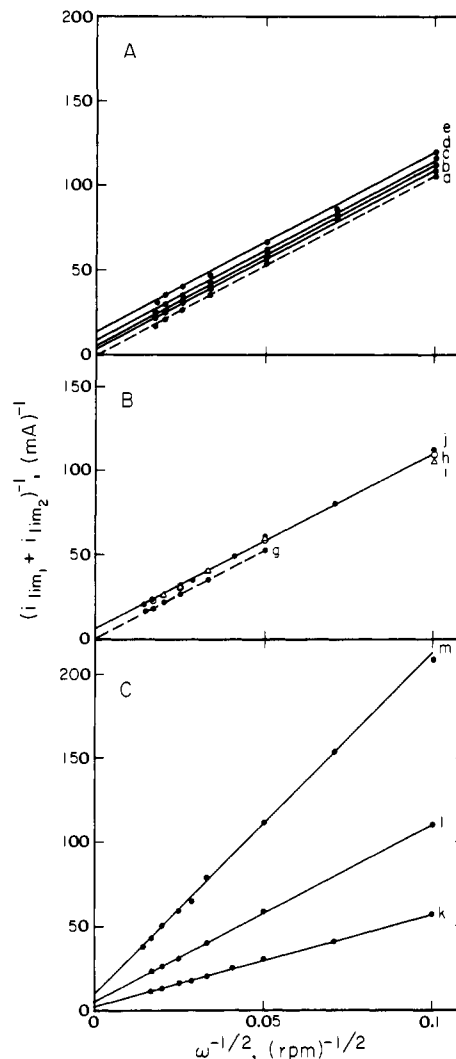


Figure 5. Koutecky-Levich plots of the plateau current of the second wave for the oxidation of $\text{Co}(\text{tpy})_2^{2+}$ at rotating graphite disk electrodes coated with PLC-W(CN) $_8^{4-}$. The experimental situations match those specified with the same letters in the caption to Figure 2 except for A, C ($\Gamma_{\text{W(CN)}_8^{4-}} = 3.3 \times 10^{-8}$ mol cm $^{-2}$).

$+ 5 \times 10^{-6}$. With W(CN) $_8^{4-}$ this criterion is not fulfilled in the most unfavorable case: $\cosh [(i_k/Ki_S)^{1/2}] = 1.29$, $(Ki_S/i_k)^{1/2} \tanh [(i_k/Ki_S)^{1/2}] = 0.85$, but this posed no problem because i_S was taken as equal to the value measured with Mo(CN) $_8^{4-}$ as the mediator.

Discussion

The results described above provide a good example of the usefulness of the theoretical analyses given in ref 7a-d for diag-

Table IV. Kinetic Currents and Rate Constants for the Cross-Reaction of $\text{Co}(\text{tpy})_2^{2+}$ with $\text{Mo}(\text{CN})_8^{3-}$ or $\text{W}(\text{CN})_8^{3-}$ within PLC Coatings^a

$10^8 \Gamma_{\text{P}}^{\circ},^b$ mol cm ³	[Co(tpy) ₂ ²⁺], mM	Mo(CN) ₈ ³⁻			W(CN) ₈ ³⁻		
		$10^3 i_{\text{k}},^c$ A cm ⁻²	$10^{-3} \kappa k,^d$ M ⁻¹ s ⁻¹	μ/ϕ^e	$10^3 i_{\text{k}},^c$ A cm ⁻²	$10^{-3} \kappa k,^d$ M ⁻¹ s ⁻¹	μ/ϕ^e
1.5	0.5	2.9	4.0	0.15	4.4	6.1	0.13
2.1	0.5	5.2	5.1	0.14	9.3	9.2	0.10
3.5	0.5	6.6	3.9	0.15	14.8	8.8	0.10
4.9	0.5	8.6	3.6	0.17	21.9	9.3	0.10
3.5	0.25	4.5	5.3	0.13	7.2	8.5	0.09
3.5	1.0	19.6	5.8	0.12	30.5	9.0	0.09
7.1	0.5	13.8	4.0	0.07	30.9	9.0	0.05
14	0.5	27.9	4.1	0.034	63	9.3	0.023
			av 4.5			av 8.7	

^a All electrodes were coated with 2.8×10^{-7} mol cm⁻² of PLC except for the final two entries for which Γ_{PLC} was twice and four times as large, respectively. ^b Symbols have same significance as in Tables I and II. ^c From eq 8. ^d Calculated from eq 4 with use of the values of i_{S} and i_{F} in Table III, i.e., $\kappa k = i_{\text{k}}(F^{\circ}_{\text{P}}[\text{Co}(\text{tpy})_2^{2+}])^{-1} = i_{\text{F}}^2(i_{\text{S}}F\Gamma_{\text{P}}^{\circ})^{-1}$. ^e Ratio of the reaction layer and film thicknesses; eq 11.

nosing the kinetics of redox cross-reactions occurring within coatings on rotated disk electrodes. The diagnosis is particularly simple when, as in the present instance, the characteristic current density for permeation of the substrate through the mediator-loaded coating, i_{S} , can be measured independently. The good agreement between the data in Tables III and IV and the predictions of the equations given in ref 7d for the appropriate case supports the analysis presented there. It is worth emphasizing that the entire treatment of the kinetic data that leads to the determination of the rate constant of the cross-reaction does not require that the film thickness be known.

It is noteworthy that incorporation of $\text{Mo}(\text{CN})_8^{4-}$ or $\text{W}(\text{CN})_8^{4-}$ in polyelectrolyte coatings on electrodes allows rate constants for the cross-reactions between $\text{Co}(\text{tpy})_2^{2+}$ and the oxidized forms of these anions to be obtained from the rotating disk data. If the same pairs of reactants are dissolved in solution, the two oxidation waves obtained at an uncoated rotating disk electrode both give linear Levich plots of i_{lim} vs. $\omega^{1/2}$ so that no kinetic information about the cross-reactions can be obtained. Thus, incorporation of one of the co-reactants into a polyelectrolyte coating that decreases the rate at which the other reactant diffuses to the electrode converts the system into a form where kinetic information becomes accessible.

No measurements of the rates of the cross-reactions examined in this study have been reported so that it is not possible to compare the values of κk given in Table IV with previous measured values of k . However, the values of the constants for the two mediators appear surprisingly similar considering that the equilibrium constants for the two cross-reactions differ by a factor of over 10^4 (3.5×10^3 vs. 6×10^7 for $\text{W}(\text{CN})_8^{3-}$ and $\text{Mo}(\text{CN})_8^{3-}$, respectively). In fact, the data in Table IV indicate that the rate of the reaction with $\text{W}(\text{CN})_8^{3-}$ is larger than that with $\text{Mo}(\text{CN})_8^{3-}$ while the equilibrium constants are in the opposite order. The apparent insensitivity of the cross-reaction rate to so large a difference in driving force²⁸ contrasts with the behavior reported for a different set of cross-reactions that proceed entirely at a polymer/solution interface.^{3a} This suggests that the rate-limiting factor involved in the present studies may not be electron transfer between the co-reactants. As has been pointed out in recent studies of electron-transfer reactions within polyelectrolyte coatings, accessibility^{7b,17a} and/or diffusion^{16d} factors operating in the polymer may produce smaller reaction rates than are observed in solution.

In the interior of the polyelectrolyte coating, the cross-reaction does not proceed homogeneously. It occurs at the boundary between two phases (the Donnan domains in which the mediator

anions are confined and the solution that occupies the pores in the coating^{17a}). From a dynamic viewpoint, the set of polymer chains might be regarded as a network of "wires" parallel and perpendicular to the electrode surface with the propagation of the charge taking place along the perpendicular "wires". The diffusive displacement coupled with the interfacial cross-reaction thus proceeds parallel to the electrode surface from the center of the pores to the neighboring "wires". If the distance involved is l cm, the time, τ , required for a reactant molecule to traverse it is given by

$$\tau = l^2/D_{\text{S}} \quad (11)$$

The diffusion coefficient of $\text{Co}(\text{tpy})_2^{2+}$ within the PLC coating, D_{S} (as calculated from the measured values of i_{S} , the estimated thicknesses of the PLC coating, and for $\kappa = 1$), is ca. 3×10^{-6} cm² s⁻¹ which is only slightly smaller than its diffusion coefficient in homogeneous solution, 4×10^{-6} cm² s⁻¹. For $\Gamma_{\text{PLC}} = 2.8 \times 10^{-7}$ mol cm⁻² the film thickness ranges from 2.8×10^{-3} cm (without incorporated anions) to smaller values. With the thickest film, the average distance between the NH_3^+ groups within the PLC and hence between the "wires" is ca. 25 Å if there is no preferred orientation of the polymer chains perpendicular to the electrode surface. (In the unlikely event that the latter were the case, the average distance between the "wires" would be ca. 70 Å.)

Thus, the time required for the substrate reactant to travel from the center of a pore to the neighboring wire is no more than ca. 2×10^{-8} s. The concentrations of mediator employed were at most 0.1 M which, combined with a rate constant of ca. 5×10^3 M⁻¹ s⁻¹, leads to a reaction half-life of the system of at least 2×10^{-3} s, i.e., more than four orders of magnitude larger than the lateral diffusion time. It follows that diffusion within the pores between the Donnan domains does not appreciably limit the rate of the cross-reaction. This is confirmed by the observation that if lateral diffusion were the slow step of the cross-reaction the overall rate should not depend upon the mediator concentration exactly as the rate of an electrochemical reaction does not depend upon the electrode potential in the region where the current is diffusion controlled. In the systems studied here a clean dependence of the film currents upon the amount of mediator present in the film was observed (Table III) and the dependence was that expected for a rate-limiting second-order reaction (Table IV).

Limits on the mutual accessibility of the substrate and attached mediator anions could arise in essentially two ways. One would involve steric requirements resulting from partial masking of the mediator centers by the polymer chains. As in the dimerization of radicals,³⁰ this would decrease the number of reactive collisions between the reactants and thereby lower the overall rate constant which should, nevertheless, be sensitive to differences in the thermodynamic driving force of the reaction. Alternatively, the

(28) Activation energies determined for the cross-reaction of similar complexes ($\text{Co}(\text{bpy})_3^{3+/2+}$ and $\text{Fe}(\text{CN})_6^{3-/4-}$)²⁹ make it seem extremely unlikely that the reaction of $\text{Co}(\text{tpy})_2^{2+}$ with $\text{Mo}(\text{CN})_8^{3-}$ or $\text{W}(\text{CN})_8^{3-}$ could fall in the "inverted region" of the activation-free energy reaction-free energy plot.

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mediator ions might be so completely encapsulated by the surrounding polymer chains that no particular orientation would be required for the electron transfer to occur. The formation of the precursor complex would then be limited by the activation energy necessary to cross this shell of polymer chains separating the mediator reaction site from the incoming co-reactant. The height of the energy barrier would be essentially a function of the charge and size of the reactants and if it were high enough the overall rate constant would no longer depend upon the redox driving force. Clearly, additional kinetic measurements (involving the use of mediator couples that differ not only in standard potential but also in charge and size and for which data on homogeneous self-

and cross-reaction kinetics are available) are needed to distinguish between these possibilities.

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Registry No. Co(tpy)₂²⁺, 18308-16-2; Mo(CN)₈³⁻, 17845-99-7; W(CN)₈³⁻, 17568-76-2; Mo(CN)₈⁴⁻, 17923-49-8; W(CN)₈⁴⁻, 18177-17-8; graphite, 7782-42-5.

Electrochemical Modulation of Fluorescence from Zinc Tetrphenylporphyrin on Electrode Surfaces

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Abstract: Zinc tetrphenylporphyrin (ZnTPP) has been studied as deposits on pyrolytic graphite, indium oxide coated glass, and thin films of gold. Deposits were made (a) by drying of an aliquot of solution in toluene that had been loaded onto a defined area by syringe or (b) by dipcoating from toluene solution. The dipcoating method provided apparently uniform coverages in the range $1-4 \times 10^{-10}$ mol/cm². Syringe-coating gave coverages that were larger by an order of magnitude. On graphite, only 1% of the molecules in a dipcoated deposit are electroactive, but oxidation of those sites results in strong quenching of luminescence from the deposit. The excitation spectrum of the luminescence on graphite and gold at low coverages features a very weak contribution from the Soret transition. At heavier coverages the transition reappears. On indium oxide, the degree of electroactivity is higher than on graphite, and similar degrees of quenching can be obtained upon oxidation, but there are no unusual spectral modifications in thin layers. A model for the structure of ZnTPP deposits is proposed on the basis of these observations.

Introduction

As research on electrode processes has become concerned with finer degrees of detail, a demand has developed for spectroscopic tools capable of characterizing interfacial structure. A large volume of research has been directed toward this end.¹ The more successful methods for observations in situ involve optical absorption,²⁻⁵ changes in reflectivity,⁶⁻⁸ or Raman scattering.⁹⁻¹¹ Useful information can also be gathered from observations of electrode surfaces by various ion- and electron-beam techniques,¹ but these methods do not allow study in situ.

Our concern here is with the development of fluorescence spectroscopy as a means for probing interfacial structure. There

are several reasons for interest in the approach. First, there is already a large volume of experience with fluorescent probes, particularly in the labeling of microstructures in biological systems.¹²⁻¹⁹ The probes are useful in defining local pH, polarity, fluidity, molecular rotational freedom, intermolecular spacings, and molecular orientation. Much of this kind of information cannot be obtained from existing optical tools for examining electrode surfaces. Second, fluorescence can be observed in the time domain, and the kinetics of fluorescence quenching, which are very well understood, can be used to examine a host of transport phenomena and bimolecular interactions. This aspect makes possible the observation of molecular events in electrochemical systems on a nanosecond time scale, which is simply not accessible to purely electrochemical modes of observation, or even to other spectroelectrochemical modes as they presently exist. Finally, fluorescence techniques are exquisitely sensitive. Detection

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