Acknowledgment. This work was supported by National Science Foundation Grant CHE 77-26473. Support to D.C. from CSIRO Australia is also acknowledged. We thank Professor F. A. L. Anet, Dr. Dan Terpstra, and Dr. J. F. Whidby for helpful discussions.

Appendix

Molecular tumbling in a magnetic field brings about a modulation of the $^{13}C-^{1}H$ dipole–dipole interaction, the frequency distribution of which is described by the spectral density function $J(\omega)$. The dipolar spin–lattice relaxation time (T_1^{DD}) for a single $^{13}C-^{1}H$ vector is linked to the spectral density function via eq A1.

$$\frac{1}{T_1^{DD}} = \left(\frac{1}{20}\right)\frac{\gamma_H^2\gamma_C^2\hbar^2}{r_{C-H}^6}[J(\omega_H - \omega_C) + 3J(\omega_C) + 6J(\omega_H + \omega_C)] \quad (A1)$$

Here the γ terms are the magnetogyric ratios, $\hbar$ is Planck's constant divided by 2π, r_{C-H} is the carbon–hydrogen internuclear distance, and the ω terms are the appropriate Larmor frequencies (in rad/s).

Woessner[15] originally derived expressions for the spectral density function in terms of both geometrical and motional parameters for a rigid molecule undergoing anisotropic motion. However, because of a singularity in the Woessner formalism for the case when motion is isotropic, we have used the transformed equations of Bleich et al.[6]

$$J(\omega_i) = \frac{12Rd(\omega_i^2 + 36L^2)}{(1/\tau_+^2 + \omega_i^2)(1/\tau_-^2 + \omega_i^2)} - \frac{12e(\omega_i^2 - 36L^2)}{(1/\tau_+^2 + \omega_i^2)(1/\tau_-^2 + \omega_i^2)} + \frac{C_1\tau_1}{(1 + \omega_i^2\tau_1^2)} + \frac{C_2\tau_2}{(1 + \omega_i^2\tau_2^2)} + \frac{C_3\tau_3}{(1 + \omega_i^2\tau_3^2)} \quad (A2)$$

where $R = {}^1/_3(R_1 + R_2 + R_3)$, $L^2 = {}^1/_3(R_1R_2 + R_1R_3 + R_2R_3)$, $1/\tau_+ = 6[R + (R^2 - L^2)^{1/2}]$, $1/\tau_- = 6[R - (R^2 - L^2)^{1/2}]$, $1/\tau_1 = 4R_1 + R_2 + R_3$, $1/\tau_2 = R_1 + 4R_2 + R_3$, $1/\tau_3 = R_1 + R_2 + 4R_3$, $d = {}^1/_2[3(l^4 + m^4 + n^4) - 1]$, $e = {}^1/_6\{\delta_1[(3l^4 + 6m^2n^2) - 1] + \delta_2[(3m^4 + 6l^2n^2) - 1] + \delta_3[(3n^4 + 6l^2m^2) - 1]\}$, $C_1 = 6m^2n^2$, $C_2 = 6l^2n^2$, $C_3 = 6l^2m^2$, $\delta_1 = R_1 - R$, $\delta_2 = R_2 - R$, and $\delta_3 = R_3 - R$.

In these equations l, m, and n are the direction cosines of the C–H vector with respect to the principal axes. R_1, R_2, and R_3 are the rotational diffusion coefficients about these axes.

In our program the calculated T_1^{DD} value was obtained by summing the contribution to eq A1 from every C–H interaction in the molecule.

Registry No. 2 (X = H), 4486-29-7; **2** (X = NO_2), 4228-30-2; **2** (X = NH_2), 35391-92-5; **2** (X = NH_2) trifluoroacetate salt, 79664-54-3; **2** (X = CH_3), 16499-70-0.

Propagation of a Redox Reaction through a Quinoid Polymer Film on an Electrode

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Abstract: Quinoid polymers were prepared by reacting acryloyl or methacryloyl chloride with dopamine. The polymers were coated onto glassy carbon electrodes. Using aqueous, pH 7 solutions and cyclic voltammetry, it is shown that for polymer layers with less than one equivalent monolayer of dopamine (<0.6 nmol cm^{-2}), most units are electroactive and can be converted to dopaquinone units. In thicker films only this inner monolayer is electroactive on the time scale of cyclic voltammetry. This behavior is compared with that for *N*-acetyldopamine as a soluble analogue. It is shown that the oxidation of the bulk polymer layer can be accelerated if compounds with reversible one-electron couples like bis(hydroxymethyl)ferrocene or *N,N,N',N'*-tetramethylphenylenediamine are present at millimolar levels in the solution. It is suggested that these couples mediate the oxidation past the inner layer. Using mixed organic/aqueous solvents also serves to propagate the oxidation through the bulk layer. In this case, the mixed solvents swell the layer, making polymer chain motion more rapid so that the oxidation rate goes up.

There is currently considerable interest in the properties of electrodes which have molecular surfaces.[1] One attractive method for producing such electrodes is to coat the surface of a conductor with an ultrathin, 10–1000 Å, layer of polymer.[2-15] If the polymer contains electroactive groups or can sequester electroactive species from solution, the electrode acquires some very unusual properties.

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(1) Murray, R. W. *Acc. Chem. Res.* **1980**, *13*, 135.

(2) (a) Van De Mark, M. R.; Miller, L. L. *J. Am. Chem. Soc.* **1978**, *100*, 3223. (b) Miller, L. L.; Van De Mark, M. R. *Ibid.* **1978**, *100*, 639; Miller, L. L.; Van De Mark, M. R. *J. Electroanal. Chem.* **1978**, *88*, 437. (d) Kerr, J. B.; Miller, L. L.; Van De Mark, M. R. *J. Am. Chem. Soc.* **1980**, *102*, 3383.

(3) (a) Degrand, C.; Miller, L. L. *J. Am. Chem. Soc.* **1980**, *102*, 5728. (b) Degrand, C.; Miller, L. L. *J. Electroanal. Chem.* **1981**, *117*, 267. (c) Degrand, C.; Laviron, E. *Ibid.* **1981**, *117*, 283. (d) Degrand, C.; Miller, L. L. *Ibid.*, in press.

(4) (a) Kaufman, F. B.; Schroeder, A. H.; Engler, E. M.; Kramer, S. R.; Chambers, J. Q. *J. Am. Chem. Soc.* **1980**, *102*, 483. (b) Kaufman, F. B.; Schroeder, A. H.; Engler, E. M.; Patel, V. V. *Appl. Phys. Lett.* **1980**, *36*, 422. (c) Schroeder, A. H.; Kaufman, F. B.; Patel, V. V.; Engler, E. M. *J. Electroanal. Chem.* **1980**, *113*, 193. (d) Schroeder, A. H.; Kaufman, F. B. *Ibid.* **1980**, *113*, 209. (e) Kaufman, F. B.; Engler, E. M. *J. Am. Chem. Soc.* **1979**, *101*, 547.

(5) (a) Oyama, N.; Anson, F. C. *J. Am. Chem. Soc.* **1979** *101*, 739, 3450. (b) Oyama, N.; Anson, F. C. *J. Electrochem. Soc.* **1980**, *127*, 247, 640. (c) Oyama, N.; Anson, F. C. *Anal. Chem.* **1980**, *52*, 1192. (d) Scott, N. S.; Oyama, N.; Anson, F. C. *J. Electroanal. Chem.* **1980**, *110*, 303. (e) Oyama, N.; Shimomura, T.; Shigehara, K.; Anson, F. C. *Ibid.* **1980**, *112*, 271. (f) Oyama, N.; Sato, K.; Matsuda, H. *Ibid.* **1980**, *115*, 149. (g) Shigehara, K.; Oyama, N.; Anson, F. C. *J. Am. Chem. Soc.* **1981**, *103*, 2552.

(6) (a) Itaya, K.; Bard, A. J. *Anal. Chem.* **1978**, *50*, 1487. (b) Merz, A.; Bard, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 3222. (c) Peerce, P. J.; Bard, A. J. *J. Electroanal. Chem.* **1980**, *108*, 121. (d) Rubinstein, I.; Bard, A. J. *J. Am. Chem. Soc.* **1980**, *102*, 6641. (e) Henning, T. P.; White, H. S.; Bard, A. J. *Ibid.* **1981**, *103*, 3937.

(7) (a) Nowak, R.; Schultz, F. A.; Umana, M.; Abruna, H.; Murray, R. W. *J. Electroanal. Chem.* **1978**, *94*, 219. (b) Daum, P.; Murray, R. W. *Ibid.* **1979**, *103*, 289. (c) Nowak, R. J.; Schultz, F. A.; Umana, M.; Lam, R.; Murray, R. W. *Anal. Chem.* **1980**, *52*, 315. (d) Daum, P.; Lenhard, J. R.; Rolison, D.; Murray, R. W. *J. Am. Chem. Soc.* **1980**, *102*, 4649. (e) Abruna, H. D.; Denisevich, P.; Umana, M.; Meyer, T. J.; Murray, R. W. *Ibid.* **1981**, *103*, 1.

0002-7863/82/1504-0028$01.25/0

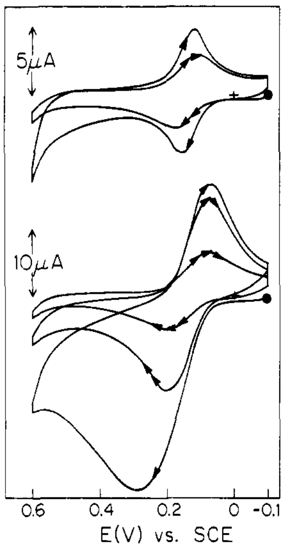


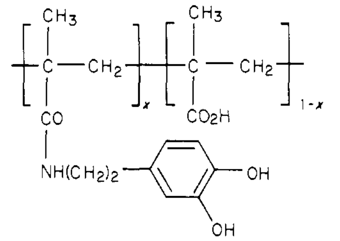
Figure 1. Top: Cyclic voltammograms using electrode **2a** (Γ_i = 0.16 nmol cm^{-2}) cycle 1 (<) and 24 (<<); Bottom: **2c** (Γ_i 16-nmol cm^{-2}) cycle 1 (<), 2 (<<), 24 (<<<). ν = 50 mV·s^{-1}, anodic current displayed down.

Particular attention has been given to the kinetics and mechanisms for charge transport within these polymer layers. This information is of intrinsic interest, but also promises to be important for the development of applications. One particular type of application involves electrocatalysis in which the electroactive, molecular species on the surface are charged and in turn perform redox reactions on compounds in solution. Thus, although polymer films tend to impede incoming reactants from reaching the underlying conductor, electroactive films can serve to relay the charge from conductor to reactant. Most importantly, the surface redox reagents can be designed to perform specific chemical transformations on the incoming reactant.

Theoretical treatments for the kinetics of reactions on polymer-coated electrodes have been developed.[7d,16-18] The kinetics of layer charging is modeled by dividing the polymer layer into sublayers.[16,17] The innermost sublayer (near the conductor surface) is charged by a heterogeneous redox process with rate k_1. The other sublayers are then sequentially charged by redox reactions between the first (innermost) and second sublayer; the second and third sublayer, etc. Each of these processes is modeled to have a rate k_2.

Since the first reports on polymer-modified electrodes in 1978 many experimental observations have been made on the kinetics of polymer-layer charging. Most of the available information concerns electroactive groups which are expected to react by fast, one-electron transfer. Quantitative studies generally show that "thin" layers can be rapidly charged and discharged on the time scale of milliseconds, if the layer is swollen with solvent–electrolyte. Thick layers often show kinetic limitations to the charging rate. One qualitative characteristic which has often been observed is that the cyclic voltammetric peaks attain a shape associated with diffusing species. It has, therefore, been proposed that some diffusional phenomenon is involved and, indeed, quantitative studies have reinforced this view. Understanding these results is complicated because polymer motion, diffusion of electrolyte, electron-transfer reactions, and changes in layer structure with charging must be considered.

We have been interested in even more complicated cases involving hydroquinone–quinone polymers.[3a,b,d] These electrodes are of particular interest as electrocatalysts because quinones can act as selective chemical oxidants. The present study is an outgrowth of previous work[3a] in which electrodes (**1**) were prepared by dip-coating vitreous carbon disks with a polymer I which was



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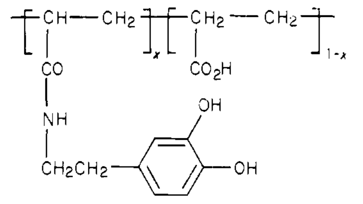

II

41% loaded with hydroquinone units. Cyclic voltammetry using aqueous solutions indicated that the hydroquinone units could be oxidized to quinones. The apparent surface concentration Γ_{coul} obtained from cyclic voltammetry for electrodes **1** prepared from dip-coating solutions of varying concentration varied from 0.05 to 0.75 nmol cm^{-2}. These electrodes catalyzed NADH oxidation. On a cleaned carbon surface NADH showed $E_p \sim 0.6$ V vs. SCE. Electrode **1** oxidized NADH at 0.2 V, because the surface quinone units generated at that potential reacted very rapidly with incoming NADH molecules. Study of the catalytic efficiency showed that maximum efficiency was obtained for Γ_{coul} = 0.2 nmol cm^{-2}. "Thicker" or "thinner" layers were less effective. These data raised several questions concerning layer charging which are retrospectively addressed here. We also report some unexpected ways of catalyzing the charging process.

Results and Discussion

Polymer I was resynthesized and analogue II was also prepared with various loading levels. These materials were characterized by UV, IR, and elemental analysis. Vitreous carbon electrodes were coated either by dipping the electrode into a solution of I or II in pyridine, or by applying a known volume of a solution of polymer II in methanol to an electrode and allowing the methanol to evaporate. The latter method provided a surface holding a known amount of polymer. This amount is characterized as Γ_i, the initial surface concentration of hydroquinone units.

Nonpropagation of Polymer Layer Oxidation. The results of cyclic voltammetric studies using dip-coated electrodes **1** (from polymer I) in aqueous, pH 7, buffered solutions have been described.[3a] Consider now electrodes **2** (from II, 37% loaded with hydroquinone units). Cyclic voltammograms at a sweep rate ν = 200 or 50 mV s^{-1} were very similar to those for electrodes **1**. Only the data at ν = 50 mV s^{-1} are reported, since the faster sweep rate gave no additional insight. Of particular interest here are the integrated currents, and very similar values were obtained at either sweep rate. Two typical voltammograms are shown in

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(8) (a) Doblhofer, K.; Nolte, D.; Ulstrup, J. *Ber. Bunsenges. Phys. Chem.* **1978**, *82*, 403. (b) Doblhofer, K.; Durr, W. *J. Electrochem. Soc.* **1980**, *127*, 1041.

(9) (a) Bruno, F.; Pham, M. C.; Dubois, J. E. *Electrochim. Acta* **1980**, *22*, 451. (b) Tourillon, G.; Lacaze, P. C.; Dubois, J. E. *J. Electroanal. Chem.* **1979**, *100*, 247. (c) Pham, M. C.; Dubois, J. E.; Lacaze, P. C. *Ibid.* **1979**, *99*, 331; **1978**, *86*, 147. (d) Pham, M. C.; Tourillon, G.; Lacaze, P. C.; Dubois, J. E. *Ibid.* **1980**, *111*, 385. (e) Dubois, J. E.; Lacaze, P. C.; Pham, M. C. *Ibid.* **1981**, *117*, 233.

(10) Dautartas, M. F.; Evans, J. F. *J. Electroanal. Chem.* **1980**, *109*, 301.

(11) Diaz, A. F.; Kanazawa, K. K. *J. Chem. Soc., Chem. Commun.* **1979**, 635.

(12) Bolts, J. M.; Bocarsly, A. B.; Palazotto, M. C.; Walton, E. G.; Lewis, N. S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 1378.

(13) Samuelson, G. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 307.

(14) Haas, D.; Vos, J. G. *J. Electroanal. Chem.* **1980**, *113*, 139.

(15) Heineman, W. R.; Wieck, H. J.; Yacynych, A. M. *Anal. Chem.* **1980**, *52*, 345.

(16) (a) Laviron, E. *J. Electroanal. Chem.* **1980**, *112*, 1. (b) Laviron, E.; Roullier, L.; Degrand, C. *Ibid.* **1980**, *112*, 11. (c) Laviron, E.; Roullier, L. *Ibid.* **1980**, *115*, 65.

(17) Andrieux, C. P.; Saveant, J. M. *J. Electroanal. Chem.* **1980**, *111*, 377.

(18) Peerce, P. J.; Bard, A. J. *J. Electroanal. Chem.* **1980**, *114*, 89.

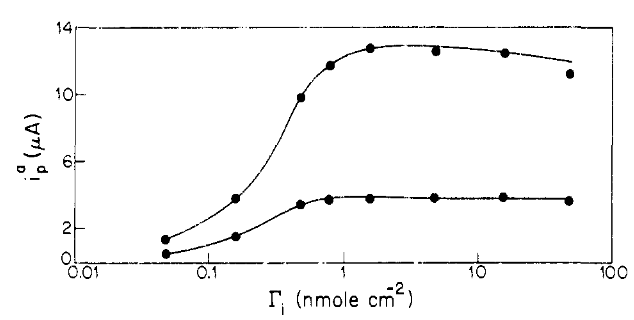

Figure 2. Anodic peak currents for electrodes **2**; ν = 50 mV s^{-1} (cycles 2 and 24).

Figure 1. Electrode **2a** was prepared initially holding 0.053 μg cm^{-2} (ignoring roughness) of II. Thus Γ_i was 0.16 nmol cm^{-2}. Integration of the first- or second-sweep, background subtracted, voltammogram gave Γ_{coul} = 0.11 nmol cm^{-2}. Thus, it is clear that with this low surface concentration most of the hydroquinone units can be oxidized. This is not surprising since they must be quite near the carbon surface. A close-packed monolayer of 4-methyl-1,2-dihydroxybenzenes lying flat ("π-complexed") on a perfectly flat carbon surface corresponds to about 0.6 nmol cm^{-2}.

Electrode **2b** was prepared by adding 0.26 μg cm^{-2} of polymer II to this cleaned carbon disk. Again, a reasonable correspondence of Γ_i = 0.78 nmol cm^{-2} and Γ_{coul} = 0.53 nmol cm^{-2} from voltammetry was observed. Electrode **2c** was prepared by adding 20 times as much polymer to the same, cleaned electrode. In this case (Figure 1), the first sweep voltammogram was distorted in shape and only the reproducible second-sweep data are used. Now, Γ_i = 16 nmol cm^{-2}, but Γ_{coul} increased only to 0.64 nmol cm^{-2}. Thus, it is suggested that after the first sweep only the innermost sublayer is electroactive on this (ν = 50 mV s^{-1}) time scale. Figure 2 shows a plot of i_p^a, the anodic peak current, against the Γ_i, which provides further data in accord with this conclusion. The structure of this "innermost sublayer" or "first equivalent monolayer" is not known, and because of unknown surface roughness and the necessity of assuming that the polymer molecules which are actually adsorbed have the average (37%) loading, Γ is not interpretable in terms of the surface area occupied by each monomer unit. It is reasonable to conclude, however, that one equivalent monolayer is about 0.6 nmol cm^{-2} of geometric area.

As previously indicated for electrode **1**, Γ_{coul} for **2** decreases with continued cycling. The extent of decay after 24 cycles is shown in Figure 2. The i_p^a/Γ_i curve has the same shape after many cycles even though the i_p^a values were decreased (Figure 1). Surprisingly, having a large number of groups available (large Γ_i) does not serve to replenish those units which are destroyed. If the "extra" hydroquinones on the large Γ_i electrodes, like **2c**, were useful, **2c** would not show a Γ_{coul} which decreases with time at the same rate as Γ_{coul} for **2b**. Since we believe (see below) that even after several sweeps **2c** still holds most of its original polymer layer, it is proposed that the initially active hydroquinone–quinone couples are inactivated. *o*-Quinones are extremely labile to nucleophilic attack and this provides one explanation for the slow degradation. Potentiostating the electrode **2c** at −0.1 V had no deleterious effect on Γ_{coul}. Potentiostating at 0.6 V, however, did serve to lower Γ_{coul}. Clearly, it is the oxidized form which is unstable.

In terms of the theoretical models which have been proposed, these electrodes have k_1 for charging the inner layer which is comparable to the electrochemistry of *N*-acetyldopamine (III) in solution (see below). In analogy to the results previously reported for electrode **1**, the peak separation, ΔE_p, increases with increasing sweep rate, indicating that k_1 is not large on this time scale. At a constant sweep rate ΔE_p also changes slightly as Γ_i changes. As shown in Figure 3 this change takes place as Γ_i increases from 0.3 to 2 equivalent monolayers. Above or below this range, ΔE_p remains constant. Thus, it is clear that the rate depends to a small extent on the packing of dopamine units near the surface, but that the addition of many outer layers does not affect the rate of charging the inner layer.

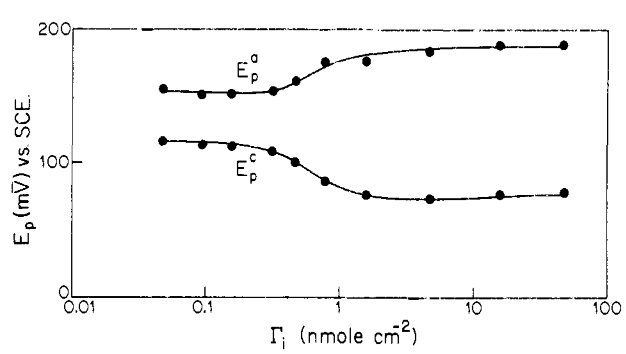

Figure 3. Peak potentials for electrodes **2** as Γ_i changes. ν = 50 mV s^{-1}.

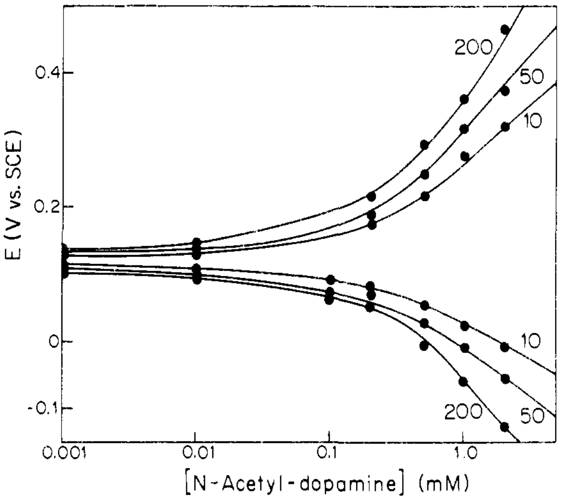

Figure 4. Peak potentials E_p^a and E_p^c for *N*-acetyldopamine on cleaned carbon. Curves are numbered according to ν = 10, 50, and 200 mV s^{-1}.

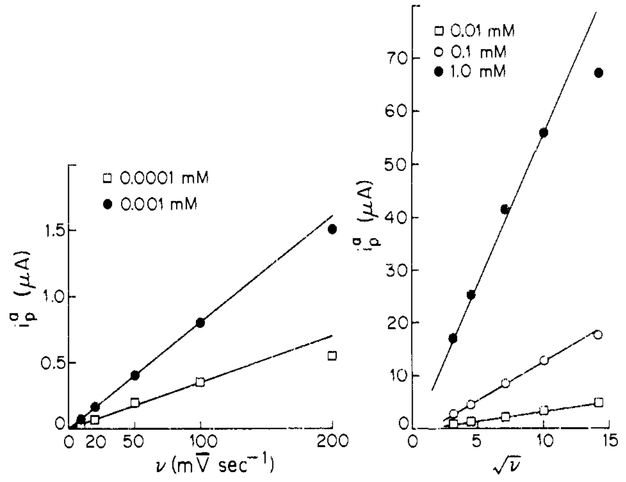

Figure 5. Peak currents for *N*-acetyldopamine as concentration and sweep rate change.

The rate of propagation of the oxidation from one sublayer to another (k_2) is very small. This requires that (a) the oxidation of hydroquinone units in the second layer by quinone units in the inner layer is slow on this time scale and (b) physical replacement of a quinone in the inner layer with a hydroquinone unit from the second layer is slow. Point a is supported by solution-phase kinetic studies of the oxidation of a hydroquinone by a quinone. At neutral pH or in nonaqueous solution these reactions are rather slow. Indeed, unsymmetrical quinhydrones (the charge-transfer complexes) can be crystallized from solution.[19] Point b refers

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[19] Desiraju, G. R.; Curtin, D. Y.; Paul, I. C. *J. Org. Chem.* **1977**, *42*, 4071. Bothner-By, A. A. *J. Am. Chem. Soc.* **1953**, *75*, 728. Carter, S.; Murrell, J. N.; Rosch, E. J.; Trinajstic, N.; Wyatt, P. A. H. *J. Chem. Soc. B* **1967**, 477.

to the physical exchange of positions via polymer motion. No direct data on this rate are available, but we note that quinone adsorption on the surface or cross-linking by quinhydrone formation could severely slow the mixing of the inner layers. We have demonstrated[3b,d] that an anthraquinone polymer electrode behaves in a qualitatively similar fashion to electrodes **1** and **2**.

Because of the unusual observations made for electrodes **1** and **2** it became of interest to study the cyclic voltammograms of *N*-acetyldopamine (III). Figures 4 and 5 provide E_p and i_p results, respectively. At low concentrations (<0.01 mM), ΔE_p is less than the theoretical 30 mV for a two-electron couple, the currents are higher than expected for this low concentration, and a plot of i_p^a vs. ν is linear. These data and the peak shape demonstrate that this voltammogram results from adsorbed III and its still adsorbed quinone counterpart. The increasing ΔE_p as ν increases shows that the reaction is not fast even on the time scale of these rather slow sweep rates. The results are comparable to those reported for adsorbed phenanthraquinone.[20]

At higher concentrations (>0.1 mM) of III the voltammograms assume the shape expected for a diffusionally controlled process and i_p^a now plots linearly vs. $\nu^{1/2}$. Not unexpectedly ΔE_p at any concentration increases with increasing ν. Most interestingly, however, ΔE_p is a sensitive function of concentration (Figure 4). The reaction becomes much slower at high concentration. At 5 mM (ν = 200 mV s^{-1}) the peak separation, ΔE_p, is 786 mV. This behavior is indicative of an electrode reaction which is less than first order in III. A classical interpretation is that the reaction is inhibited by an adsorbed product or intermediate.

Indeed, this behavior can be compared to the results obtained on the classic 1,4-benzoquinone/hydroquinone couple. In that case it has been shown using various electrode materials that there is a strong inhibition of hydroquinone oxidation at high concentrations.[21] On platinum with hydroquinone concentrations less than 10^{-2} M, linear Tafel plots could be obtained.[19a] These plots demonstrated that even at low concentrations, oxidation was apparently 0.62 order in hydroquinone. The reduction was apparently 0.65 order in quinone. These non-first-order results imply some inhibition due to association reactions on the surface. It is proposed that the oxidation of III is similar and that surface phenomena which inhibit the reaction occur at high concentrations of III. The surface structure responsible for this inhibition is not known.

The slow oxidation of III may be closely related to the slowness of charging the bulk of the polymer layer for electrodes **1** and **2**. Specifically, it should be realized that *the polymer layer corresponds to a solution which is very concentrated in dopamine units and by analogy the oxidation of that layer is expected to be slow.*

Electrodes 1 and 2 in the Presence of Electroactive Solutes. According to the above model and previous observations, a thick layer of polymer I or II should inhibit the electrochemistry of solution species by slowing their transport to the carbon surface and by blocking the surface. We have, indeed, observed this in several cases. Specifically, a layer of I was prepared by dip-coating from a 0.1% solution in pyridine. Its cyclic voltammogram in the presence of 0.3 m*M* *N*-acetyldopamine (III) was identical with that in the absence of III even though on a cleaned carbon disk the peak current from 0.2 mM III was roughly twice as large as that from the polymer layer charging. Similar behavior was observed for 10 m*M* *p*-phenylenediamine (E_p^a = 0.18 V on cleaned carbon).

More interesting results were found when one-electron couples were used. Consider first the unexpected result obtained when electrode **2** was used in the presence of bis(hydroxymethyl)ferrocene (IV). This compound (0.2 mM in aqueous pH 7 solution) on the cleaned carbon electrode gave a reversible couple of E_p^a = 0.26 V, i_p^a = 10 μA, and E_p^c = 0.19 V at ν = 50 mV s^{-1}. When an electrode was coated with 47 μg cm^{-2} of II ($\sim$180 equivalent monolayers) giving **2d** and used in the absence of IV, i_p^a at 0.19 V was 8.1 μA. Thus **2d** and IV together were expected to produce from 8 to 18 μA of peak current. Instead i_p^a = 152 μA! Not only did the polymer layer not inhibit the oxidation of IV, but the current from IV plus polymer was some eight times higher than the sum of the separate currents. This could have arisen from the fact that either (a) the layer sequestered a large amount of IV from the aqueous solution or (b) the IV/IV$^{+\cdot}$ couple catalyzed oxidation of the polymer layer; i.e., IV$^{+\cdot}$ propagates the oxidation out from the inner sublayer.

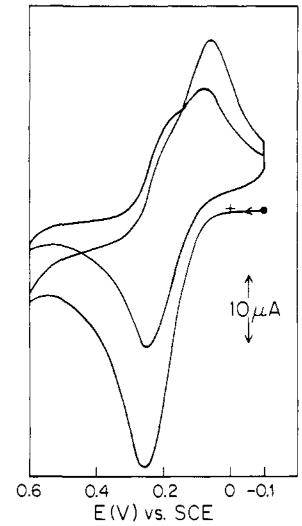

Figure 6. Cyclic voltammogram using **2c** and 0.2 mM bis(hydroxymethyl)ferrocene (IV) (cycles 1 and 20).

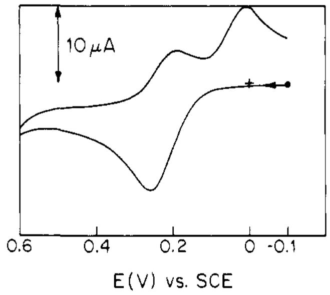

Figure 7. Cyclic voltammogram using 0.1 mM *N*-acetyldopamine (III) and 0.08 mM bis(hydroxymethyl)ferrocene (IV).

A more careful analysis can be made from the typical voltammogram (ν = 50 mV s^{-1}) shown in Figure 6. This result is for an electrode **2c** ($\sim$20 equivalent monolayers of II) in the presence of 0.2 mM IV. It will be seen that there is a single, merged anodic peak. There are two cathodic peaks on the return half-cycle. The cathodic peak at 0.19 V corresponds to the reduction of IV$^{+\cdot}$, while the second cathodic peak near 0.07 V corresponds to the reduction of the polymeric quinone of electrode **2**. This assignment was confirmed when thicker layers were used because the anodic peak and the second cathodic peak grew, but the first cathodic peak at 0.19 V did not increase. As expected from the electrochemistry of III alone, the larger the current, the greater was the difference in E_p between the anodic peak and the second cathodic peak. This increasing ΔE_p explains why the ferrocene and polymer anodic peaks merge into one. Thus, the data demonstrate that the IV/IV$^{+\cdot}$ couple mediates (catalyzes) the oxidation of the outer sublayers and rules out the possibility of enhanced currents from sequestering IV into the layer.

In agreement with this hypothesis is the voltammogram for *N*-acetyldopamine (III) in the presence of the ferrocene IV. As shown in Figure 7, the shape of the voltammogram is identical with that for electrode **2** plus ferrocene IV: one merged anodic peak at potentials positive to that for III alone and two cathodic peaks, one due to IV$^{+\cdot}$ reduction and one due to reduction of the quinone from III. This latter peak is at more negative potentials than for an equivalent concentration of III alone.

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(20) Brown, A. P.; Anson, F. C. *J. Electroanal. Chem.* **1978**, *92*, 133.

(21) (a) Lu-An, Y.; Vasil'ev, Yu. B.; Bagotskii, V. S. *Electrokhimiya* **1965**, *1*, 141. (b) Vetter, K. J. *Z. Elektrochem.* **1952**, *56*, 797. (c) Zeigerson, E.; Gileadi, E. *J. Electroanal. Chem.* **1970**, *28*, 421.

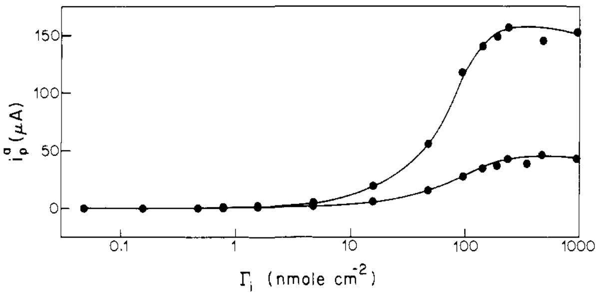

Figure 8.

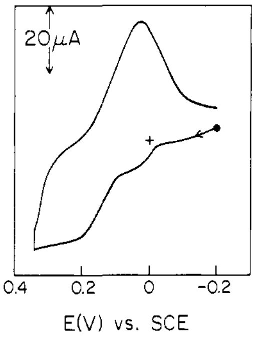

Figure 9.

The relationship between the initial surface hydroquinone concentration (Γ_i) and the current in the presence of IV was of obvious interest. When electrode **2** and compound IV were used together, the current decreased considerably with repetitive scans making comparisons difficult. Therefore, a series of electrodes was prepared. With each electrode four voltammetric cycles were recorded in the absence of IV. This was followed by 20 cycles in a 0.2 mM solution of IV and again one cycle in the absence of IV. The sweep rate was always 50 mV s^{-1}. This procedure allowed a measure of current enhancement before and after the 20 sweeps. The data (Figure 8) show that for electrodes **2** holding less than one equivalent monolayer the observed i_p^a for **2** with IV (cycle 5) is simply the sum of the i_p^a for **2** alone (cycle 4) plus i_p^a for IV on cleaned carbon. There is no inhibition or enhancement. For **2** holding more than one equivalent monolayer, the i_p^a of cycle 5 is larger than expected. The enhancement is progressively larger for electrodes holding up to 200 equivalent monolayers. Above that thickness, the enhancement is relatively constant. A similar comparison using i_p^a from the last cycle in the presence of IV (cycle 24) and cycle 25 gave similar results (Figure 8).

These results are in agreement with a model in which IV diffuses to the carbon surface (even though 500 equivalent monolayers); IV is then oxidized to IV$^{+\cdot}$ which catalyzes the oxidation of hydroquinone units in sublayers 2 to 200. There is no need for catalysis in sublayer 1 and the rate is still slow enough so that sublayers outside the 200th are still inactive. As before, the quinone form of the polymer is not too stable so that the currents decrease during successive cycles.

Data were also taken using a more concentrated (0.8 mM) solution of IV. As expected, even larger catalyzed currents were observed. Using a faster sweep and 0.2 mM IV also gave slightly greater enhancements in current for relatively thick layers. For example, a layer corresponding to 120 equivalent monolayers gave i_p^a = 270 μA at 200 mV s^{-1} compared with 130 μA at 50 mV s^{-1}. Quantitative interpretation of this result is not possible.

These unexpected results led us to study briefly two other one-electron reversible couples as catalysts. One, *N,N,N′,N′*-tetramethylphenylenediamine (V), has on cleaned carbon E_p^a = 0.07 V; i.e., E_p^a is less positive than E_p^a for the polymer layer. Using compound V (0.23 mM) with electrode **2** showed strong anodic and cathodic peak current enhancements (Figure 9). On the anodic side there were generally two peaks visible: one at 0.07 V due to V and a second at potentials greater than 0.2 V due to the polymer. On the return half-cycle there was one merged peak.

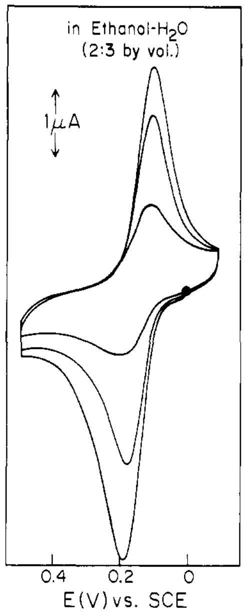

Figure 10.

E_p^c depended upon the layer thickness. Thicker layers gave larger cathodic currents at more negative potentials, as expected.

Ferrocenedicarboxylic acid (VI) has a reversible couple at potentials positive to that of the polymer film. Using electrode **2c** (20 equivalent monolayers) some anodic current enhancement was observed when VI was present, but the peaks were quite distorted. No cathodic peak current increase was noted. Thus, all three one-electron couples give anodic current enhancement, but only in cases of IV and V are the enhancements large and the voltammograms well defined.

A clearer conception of the normally slow charging of the layer and the catalysis by IV or VI can be obtained from chronocoulometry. Consider a set of three experiments in which the charges accumulated after 1 min were compared: electrode **2d**, 120 μC; 0.2 mM IV on a cleaned carbon electrode, 160 μC; and **2d** + 0.2 mM IV, 1260 μC. Compound VI was less efficient. Stepping the potential to 0.5 V the values were: **2d**, 150 μC; **2d** + 0.8 mM VI, 410 μC.

It is clear that the reversible one-electron couples, but not the quasi-reversible two-electron couples, are capable of propagating the oxidation process through thick films. It is proposed that this is due to chemical redox reactions which catalyze reaction of the outer sublayers. The details of this mechanism are not obvious and will remain unclear until the slow electrochemistry of concentrated solutions of *N*-acetyldopamine is understood.

Effect of Organic Cosolvents. The use of mixed organic–aqueous solvents also had large effects on the dynamics of charge propagation through this quinoid film. In these experiments polymer I, 40% loaded with hydroquinone units, was employed. The polymer was dip-coated from 0.02% solution in pyridine onto vitreous carbon. Used in aqueous solution, this electrode (**1b**) gave a first sweep Γ_{coul} = 0.31 nmol cm^{-2}. This current decayed to an almost constant value on continuing cycling of 0.19 nmol cm^{-2}. The electrode was cleaned and reprepared identically, then used in a solution of 40% ethanol/60% pH 7 aqueous buffer. The first sweep voltammogram anodic peak, gave Γ_{coul} = 0.83 nmol cm^{-2} (Figure 10). This decayed rapidly to give after 12 cycles a steady-state value of 0.18 nmol cm^{-2}. It is thus clear that the organic cosolvent allows much of the layer to be oxidized. This oxidation is, however, destructive and only about one equivalent monolayer of electroactive material can be retained. It is suggested that this destruction of the layer is due to desorption as well as reaction of the quinone units. Most important is the clear implication that ethanol acts to accelerate polymer motion at the carbon–polymer interface.

As discussed above, one mechanism for propagating the oxidation through the layer is to physically interchange quinone units

Table I. Solvent Effect on Γ_{coul} for Electrode 1a

	surface concentration (Γ_{coul}/nmol·cm^{-2})			
	first cycle		steady cycle[b]	
ethanol[a] (vol %)	*Q* anodic	*Q* cathodic	*Q* anodic	*Q* cathodic
0	0.31	0.32	0.19	0.21
4	0.36	0.40	0.16	0.20
10	0.45	0.40	0.15	0.18
20	0.62	0.52	0.18	0.23
40	0.88	0.56	0.18	0.21
60	0.85	0.50	0.17	0.23

[a] Solvent, e.g., 4% ethanol, 96% pH 7.0 phosphate buffer containing 0.1 M sodium perchlorate. [b] Γ_{coul} decreases with continued potential cycling. After the 15–20th cycle, this change becomes negligibly small.

in the inner sublayer with hydroquinone units in sublayer two. Ethanol should swell the hydrophobic polymer layer and desorb the quinone and hydroquinone units. An alternative explanation in which organic cosolvent accelerated the redox reaction between quinone and hydroquinone is less likely since such reactions are more rapid in aqueous than in nonaqueous media. This is, of course, what is expected since proton transfers are involved.

It is emphasized that these large Γ_{coul} values cannot be taken to represent Γ. As shown in Figure 10, the trace does not return to background during the anodic half-cycle, indicating that there is still unoxidized material present. Using a slower sweep rate did not give larger Γ_{coul} values. This was presumably due to a less favorable competition between destruction and complete oxidation.

A more thorough study of this solvent effect is described by the data in Table I. There it can be seen that ethanol is, indeed, acting as a solvent, not a reagent, since at ~1 M concentration it has a very small effect. Note also that 40% ethanol or 60% ethanol solutions gave very similar results. When a variety of organic cosolvents was used in place of ethanol (all 40% organic/60% water), they all gave voltammograms with similar shapes and Γ_{coul} values which were within ±15%. Thus, we conclude that 40% dioxane, acetone, acetonitrile, or *N*,*N*-dimethylformamide are all sufficiently effective "swellers" to give the same charging rate. In all cases when the outer sublayers are oxidized, they are eventually destroyed or desorbed.

Summary

Electrodes **1** and **2** in aqueous solution are unusual in that the inner sublayer of polymer is readily oxidized, but the outer sublayers are oxidized only very slowly. This behavior is closely analogous to that of concentrated solutions of *N*-acetyldopamine. The outer sublayers can be charged in mixed organic/aqueous media because polymer chain motion becomes more rapid, the inner quinone layer desorbs, and the other (originally inert) hydroquinone units can reach the carbon surface. More surprisingly, some oxidation of the outer sublayers can be catalyzed by suitable redox couples like bis(hydroxymethyl)ferrocene (IV) in solution.

The results correlate with observations made for an anthraquinone polymer electrode[3c] and make clear the reason for our previous observations concerning NADH catalysis.[3a] In particular, it was observed that the maximum catalytic current using **1** was obtained for $\Gamma_{\text{coul}} = 0.2$ nmol cm^{-2}. This can be understood since less than 0.2 nmol cm^{-2} was less than a monolayer and fewer catalytic sites gave lower catalytic currents. Larger dip-coating concentrations gave thick layers, but increased Γ_{coul} only slightly. These electrodes were less efficient because only the innermost sublayer was oxidized and the outer layers acted to impede the diffusion of NADH. Because of the NADH size and low diffusion coefficient, this was a critical factor.

It is of further interest to point out that one equivalent monolayer of quinone is a very effective catalyst for NADH electrooxidation. The theory derived for "redox catalysis"[17] indicates that this is not possible. There is, however, no contradiction because quinones do not catalyze by a simple electron transfer scheme. This quinone case, indeed, is representative of the central idea of using modified electrodes for electrocatalysis in that the molecular surface structure gives a chemical oxidation with specificity and rapid rates which are otherwise unavailable at an electrode.

Experimental Section

Cyclic voltammetry was performed by using a PAR Model 173 potentiostat in conjunction with a PAR 175 universal programmer. The current integral was measured by the "copy, cut, and weigh" method after background subtraction. All potentials were measured and are reported with reference to a saturated calomel electrode. The electrolyte solution was aqueous pH 7.0 phosphate buffer (0.05 M) containing 0.1 M sodium perchlorate (experiments with electrode **1**), sodium chloride (electrode **2**), or sodium nitrate (*N*-acetyldopamine).

Vitreous carbon electrodes (Ultracarbon) were used in two ways. One utilized a carbon rod sealed into glass so that a 7.1-mm^2 disk was exposed. This was used for dip-coating from pyridine solution. In a second method a known volume of a methanol solution of polymer was syringed onto the upright surface of an 11-mm^2 vitreous carbon rod. The droplet spread over the surface and the solvent was allowed to evaporate. The electrode was then placed into an adapter (Ace Glass, "Acethred" Adapter ₮ 14/20) and screwed into place so that only the modified disk surface was exposed to the solution. The outside of the disk was pressing against an O-ring so that only a 7-mm diameter was exposed. The reproducibility of the procedure and apparatus as judged by Γ_{coul} was ±10%. There is, however, also some (±10%) inaccuracy in measuring the area actually exposed to the solution. This apparatus was used because the electrode could be removed easily for cleaning and coating and it could be accurately repositioned. Because the disk was not surrounded by glass all the polymer added was retained on the carbon surface. The electrodes were cleaned by polishing on Gamal polishing cloth No. 12-282 (Fisher Scientific) with alumina (Magomet Polishing Compound No. 40-6440 AB from Buehler Ltd.), washing with distilled water and air-drying.

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Registry No. Acryloyl chloride, 814-68-6; methacryloyl chloride, 920-46-7; dopamine, 51-61-6.