

Figure 2. Cyclic voltammograms of 1.33×10^{-3} M 9,10-diphenylanthracene in acetonitrile/0.1 M TBAP at a 0.07-cm^2 platinum disk (scan rate, 200 mV/s): ---, on blank platinum surface; —, after coating the electrode and reimmersing into the same solution.

species at the PVF-coated electrode. Both chemically reversible reduction and oxidation of DPA (Figure 2) and reduction of AQ could be observed at the modified surface in ACN-TBAP solutions. At slow scan rates, the observed peaks occurred at the same potentials and had identical peak current densities as those seen with an uncoated electrode of the same area (Figure 2); however, the peak-to-peak separations of the DPA and AQ waves showed a distinct and scan rate dependent increase on the coated electrode; e.g., at 50 V/s the ΔE_p values for the DPA/DPA⁺ and DPA/DPA⁻ couples were 196 and 600 mV, respectively.¹⁴ In these experiments, the polymer film again was highly stable. Upon continuous potential scanning between -0.3 and -2.5 V the polymer peaks were unchanged after 3 h. When the polymer peaks were included into these scans (+0.7 V to -2.5 V), these showed the same decay behavior as described above for the polymer alone. Again, when the potential range was extended to +1.3 V, which included the oxidation of DPA, the voltammetric response of the polymer film disappeared within 50 cycles. However, when the electrode potential is scanned only between +0.8 and +1.5 V, the film remains stable. Since electron transfer through the thick polymer film seems unlikely at potentials where PVF is not reduced, the reduction behavior of DPA and AQ suggests the possibility of pin holes, or channels, in the coating through which the solute species may diffuse to the metal surface. As long as the scan time was such that the diffusion layer thickness was large compared with the film thickness and the spacing between the holes, the voltammetric behavior at such an electrode for a dissolved species would resemble closely that of an uncoated electrode,¹⁵ while a pattern of large coated and uncoated areas on the surface should give rise to a decrease of peak currents which would reflect the reduced active area of the electrode. Oxidations taking place beyond the potential for ferrocene oxidation could occur via the polymer however. The surface of a platinum foil coated as described above was examined by ESCA spectroscopy. Besides the expected signals for carbon and iron the spectrum also showed platinum bands at 71, 74, 100, 314, and 333 eV. Although these were strongly attenuated as compared to blank platinum, this result is inconsistent with a uniform film of the calculated thickness. Further work is in progress to confirm the actual structure of the PVF coating.

In conclusion, a platinum surface coated by adsorption or precipitation of the polymer PVF behaves like a chemically modified electrode. The polymer films are sufficiently stable that the electrochemical behavior of the films and of solute species can be studied over a wide potential range and for an extended period of time. The preparation of our PVF coated

electrode is extremely simple and depends neither on a specific adsorption phenomenon nor on a special pretreatment of the electrode surface. In our case, the electroactive groups linked to the polymer chain provide a convenient monitor for studying the coverage by means of cyclic voltammetry, but their presence does not appear to be essential in the preparation of the film itself. Thus, a more general application of polymer coated electrodes may be envisaged with polymers of special design, e.g., for electrocatalytic properties,¹⁶ for provision of a chiral electrode environment,^{2,7} for protection of semiconductor electrodes,¹³ and in attaching or producing thin layers of dyes for photochemical or photoelectrochemical studies.¹⁷

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A Poly-*p*-nitrostyrene Electrode Surface. Potential Dependent Conductivity and Electrocatalytic Properties

Sir:

We have recently reported a general method for the preparation of organic electrode surfaces involving the strong adsorption of polymers on metals.¹ This approach recalls the results of Hubbard who chemisorbed alkenes on platinum.² Polymer adsorption is, however, relatively nonspecific and this should allow modification of virtually any electrode surface. It should also allow relatively large but controllable amounts of active material to be bound. Recent work has begun to verify this view.^{3,4} These materials are analogous to other chemically modified electrodes in which species are covalently bound to carbon⁵ or metal oxide surfaces⁶ but promise to have unique and especially useful properties. We report here on the electrochemistry of poly-*p*-nitrostyrene (I) adsorbed on platinum. The initial experiments revealed the following results. (1) An adsorbed layer of I could be conveniently prepared by dip

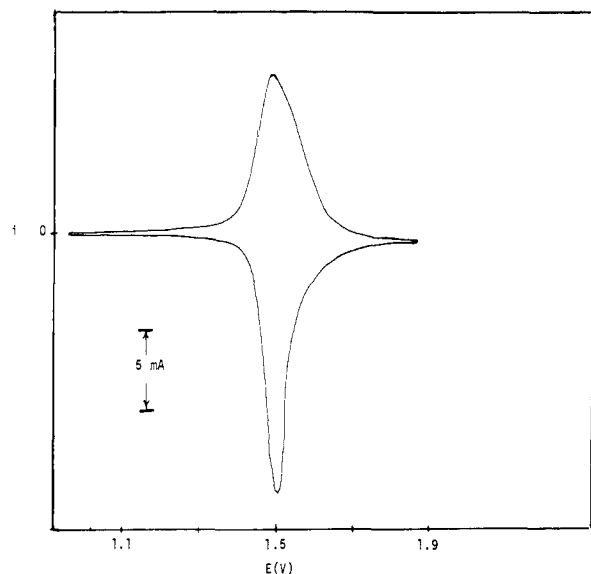


Figure 1. Cyclic voltammogram of Pt/I from 0.5% dip solution (sweep rate 1 V/s).

coating, analyzed by Auger electron spectroscopy (AES) and did not desorb under a variety of electrochemical conditions. (2) Cyclic voltammetry demonstrated that the adsorbed layer could be negatively charged by addition of electrons to the nitrotoluene moieties in a chemically reversible manner and that the amount of charge corresponded qualitatively to the film thickness. (3) The polymer is an insulator when uncharged but acts to reduce solution species when charged. Currents of 0.1 A/cm² can be supported. (4) This electrode is catalytic for the reduction of oxygen, shifting the oxygen reduction peak 200 mV positive of the E_p on clean platinum.

The coating was achieved by dipping platinum sheet into a *N,N*-dimethylformamide solution containing small amounts (0.5–5%) of poly-*p*-nitrostyrene.⁷ After 7.5 min the electrode was removed, quickly shaken to remove excess solution, and dried in air at 160 °C for 15 min. These samples were analyzed by AES, providing an elemental analysis of the surface.⁸ The C, N, O band intensity ratio 305:20:24 was near that predicted for the bulk polymer. The film from 0.2% solution diminished the intensity of the platinum 64-eV band to <10% and diminished the 1967-eV band to 30% of that on uncoated Pt.⁹

Platinum sheet/poly-*p*-nitrostyrene electrodes (2 cm²) prepared identically with those examined spectroscopically were used for electrochemistry. Cyclic voltammetric experiments were performed using triply distilled acetonitrile,¹³ 0.1 M tetraethylammonium bromide, and activated alumina¹⁴ as the solvent electrolyte. An Ag/AgNO₃ reference electrode was employed.¹³ The solvent was degassed with purified nitrogen for 1 h. Using an electrode prepared from a 0.5% solution and sweeping at 1 V/s, a reduction peak ($E_p^c = -1.5$ V, $i_p^c = 7$ mA, integrated charge = 2.4 mC) appeared, followed on the return sweep by an anodic peak at $E_p^a = -1.53$ V, $i_p^a = 10$ mA (Figure 1). Integration of the peaks demonstrated that the number of coulombs passed to charge the layer was recovered on the reverse sweep. The integrated current corresponds to about 12 monolayers of monomer. This curve can be reproduced on electrodes prepared identically and is stable for tens of cycles at 100 mV/s. The long-term stability is dependent on the dryness of the solvent. Since $E_p = -1.4$ V for nitrotoluene, it is proposed that the charging is due to reduction of nitrotoluene moieties along the polymer chain. It was also noted that at ~ 1.4 V the electrode becomes red which corresponds to the color of the nitrotoluene radical anion.

The shape of these cyclic voltammograms is of great interest but depends in a complex way on sweep rate and film thickness.

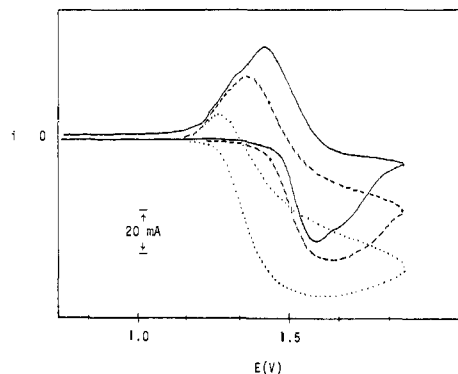


Figure 2. Cyclic voltammograms of Pt/I from 5% dip solution (sweep rate 1 V/s): —, no CCl₄; ---, 10 mM CCl₄; ···, 30 mM CCl₄.

A qualitative correlation between the integrated current or I_p and the film thickness is readily apparent. Thicker films also give a larger anodic–cathodic peak separation, e.g., for an electrode from a 5% dip solution; $I_p^c = 60$ mA, $\Delta E_p = 200$ mV at 1-V/s sweep rate. The sweep rate dependence is characterized by increasing ΔE_p , increasing i_p , and decreasing integrated currents at faster sweep rates. It seems clear that the rate of charging the layer is not fast on this time scale and this implies that the rate of charge transfer between nitrotoluene moieties is important.

The use of these electrodes for electrochemical reactions on solution species revealed that the uncharged layer acts as an insulator while the charged layer conducts. Thus, in agreement with previous studies on polystyrene and polyester,¹ the normally reversible electrochemistry of 1 mM ferrocene in 50% aqueous ethanol–lithium perchlorate was strongly inhibited by I. For electrodes from a 1% dip solution only 1% of the i_p achieved on clean platinum was observed. The reduction of CCl₄ gave more interesting results. Using an electrode coated from a 5% solution in a 10 mM acetonitrile solution of CCl₄, the cathodic surface peak at -1.5 V was enhanced and the reverse anodic peak diminished (Figure 2). Using 0.10 M CCl₄ the currents at E more negative than -1.4 V were very strongly increased amounting to 0.1 A at -1.6 V and the anodic wave was absent. Clearly the charged layer is reducing carbon tetrachloride. The layer is of limited stability under these conditions.

Ideally a catalytic electrode should have a long life and reduce the potential required for the redox process. We describe the reduction of oxygen by this platinum/poly-*p*-nitrostyrene electrode. On platinum in CH₃CN/0.1 M Et₄NBr, the oxygen reduction wave occurs at $E_p = -1.5$ V. On the polymer surface, oxygen shows a wave just positive of the surface charging wave ($E_p = -1.3$ V). No oxidation wave is seen on the reverse sweep. Thus, the overpotential for oxygen reduction is decreased. This is still, however, not at the reversible potential. When oxygen is continuously bubbled through the solution, a reduction wave is produced. At -1.4 V the current is some three times larger than on clean platinum. A total of 200 coulombs of charge was passed. The current due to surface charging after discontinuation of the oxygen supply indicated that the polymer could still be charged to 50% of its original capacity. This indicates that the catalyst turned over some 10⁵ times.

These results further indicate that the adsorption of polymers will provide a wide variety of stable materials with unique and useful properties. Numerous applications to catalysis, photoelectrochemistry, and selective synthesis are readily imagined.

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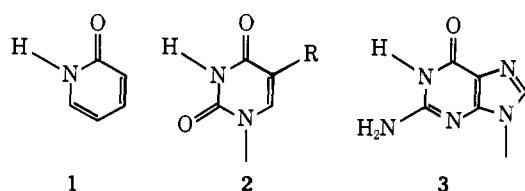
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Study of the Binding of *cis*- and *trans*-Dichlorodiammineplatinum(II) to Calf Thymus DNA by Extended X-Ray Absorption Fine Structure Spectroscopy

Sir:

The complex *cis*-dichlorodiammineplatinum(II) (DDP) is an active antitumor drug while the *trans*-DDP isomer is ineffective, a result that may reflect differences in their ability to bind DNA.¹⁻⁵ While various chemical and physical techniques have been used to explore the interactions of these platinum compounds with DNA, there appears to be no direct structural information about the resulting platinum-DNA complex. Recent crystallographic study^{5c} of the blue compound formed between *cis*-diammineplatinum and α -pyridone (**1**) suggested^{5b} that thymine (**2**, R = CH₃) and guanine (**3**) bases in DNA



might bridge two *cis*-diammineplatinum units using the deprotonated amide nitrogen and the exocyclic oxygen as donor atoms. The resulting complex would have a short Pt-Pt distance, 2.5-3.2 Å, depending upon the platinum oxidation state. To test this possibility and to provide information about the binding sites of DDP, samples of *cis*- and *trans*-[Pt(NH₃)₂Cl₂] bound to calf thymus DNA, **4** and **5**, respectively, were prepared and studied by extended x-ray absorption fine structure (EXAFS) spectroscopy.

The platinum-DNA samples were prepared in the following manner. Solid DDP complexes were suspended in buffered solutions (10 mM NaNO₃, 5 mM Tris·NO₃, pH 8) of calf thymus DNA and left to stir in the dark at room temperature for 5 days. The formal ratio (*r_f*) of *cis*-DDP (concentration 5.1 mM in 15 mL) to that of DNA phosphate (5.3 mM) was 0.96, a value also used for the *trans*-DDP (5.3 mM in 75 mL) with DNA (5.5 mM) binding experiment. Following the incubation, the opalescent solutions were centrifuged at 190 000 × g for 16-18 h, pelleting the platinum-DNA complex.⁶ The pellets were diluted with sucrose and a small amount of buffer to perform the measurements.

The raw data (Pt L₁ edge)^{7a} in the form of $\mu x = \ln I_0/I$ vs. E (where μx is the absorption factor, I_0 and I are the incident and transmitted light intensities, and E is the x-ray photon energy) of **4** and **5** were recorded at ambient (cf. Figures 1a and 1b) and liquid nitrogen (cf. Figure 1c) temperatures with the synchrotron radiation of EXAFS I at SLAC-SSRL.^{7b} After conversion of E into photoelectron wavevector k (where $k = [2m/\hbar^2(E - E_0)]^{1/2}$ and E_0 is chosen as 13 900 eV and varied in the subsequent curve fittings) and μx into $\chi(k) = (\mu - \mu_0)/\mu_0$,⁸ the data were multiplied by k^3 and the background was removed by a cubic spline technique (four sections with $\sim 4 \text{ \AA}^{-1}$ each).⁸ Fourier transforms of these data provide the radial distribution (RD) functions shown in Figure 1. To obtain interatomic distances from these Fourier transform functions, phase shift corrections must be acquired from other known systems and applied to the peak positions.⁹ Knowing the average Pt-N distance of 2.043 Å in [Pt(en)]₂²⁺ (en = H₂NCH₂CH₂NH₂),¹⁰ the phase shifts of 0.46 Å for Pt-N, at E_0 of 13 900 eV, were obtained. With the assumption that the phase shift for Pt-O can reasonably be assumed to be 0.46 Å, the average Pt-N (or -O) distance is 2.03 Å for both **4** and **5**.

The most definitive result that can be deduced from the radial distribution functions shown in Figure 1 is the lack of distinct Pt-Pt bonding¹¹ in the DNA complexes of both the *cis*- and *trans*-DDP. This conclusion is further supported by a detailed comparison of Figure 1 with the Fourier transforms of the EXAFS spectra of the structurally characterized¹² [(Pt(en)(Guo)₂]²⁺, Guo = guanosine, which does not contain any Pt-Pt bond, and of a series of *cis*-diammine- or *cis*-di-(alkylamine)platinum uridine blues which have been shown to contain Pt-Pt bonds of $\sim 2.9 \text{ \AA}$.¹³ Specifically, the RD curves of **4** (Figures 1a and 1c; except for the shoulder at 2.01 Å in the latter) and **5** (Figure 1b) are quite similar to that of [Pt(en)(Guo)₂]²⁺ (cf. Figure 1d of ref 13) but grossly different from that of the platinum blues (cf. Figures 1a and 1b of ref 13).¹³ This conclusion is reinforced by the observation that the amplitude of the Pt·X (X = C, N, O) peaks decreases with increasing distances and that for similar distances the Pt-Pt peaks are two to three times higher than the Pt·X peaks.^{13,14}

The number of nearest neighboring atoms and the corresponding Pt-N (or -O) distances can be obtained by Fourier filtering^{8a} the largest peak in Figure 1 with a smooth window of 1.0-2.4 Å (cutoff limits) and transforming it back into k space. The resulting EXAFS spectra can then be fitted (as shown in Figure 2)^{8b} with a "single-distance" model based on the amplitude and phase functions (chemical transferabilities