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Electrocatalytic oxidation of some biologically important compounds at conducting polymer electrodes modified by metal complexes

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Abstract Conducting poly(3-methylthiophene) electrodes were electrochemically prepared. The resulting polymer films were modified with an inorganic complex, ferrocene. The incorporation of the ferrocene/ferrocenium moiety into the polymer film resulted in enhanced charge transfer towards the oxidation of some organic molecules of biological interest. The electrochemical response of the complex-containing polymer electrode was compared to that of the unmodified polymer electrode and that of the substrate. Apparent diffusion coefficients of the redox species were estimated from the cyclic voltammetric data for different biological molecules at the ferrocene-containing polymer electrode. Infra-red spectroscopic measurements for the “as-grown” films revealed the presence of the inorganic complex within the polymer. The modified polymer electrode showed noticeable enhancement for the charge transfer across the film interface and can be used as an electrochemical sensor for biological compounds.

Key words Electrocatalysis · Conducting polymers · Modified electrodes · Biosensors · Voltammetry

Introduction

The deliberate chemical modification of the electrode surface with a suitable reagent results in the control of the rates and selectivities of electrochemical reactions at the solid/liquid interface. The concept of electrode modification originated early in the 1970s with the work

of several research groups [1, 2]. Current research based on chemical modification of the electrode surface could be categorized into five major groups: electrocatalysis, preconcentration, membrane barriers, electroreleasing, and microstructures [3]. Different reagents were attached to the surface of the electrode, for example the chemisorption of quinone-bearing olefins on platinum [1] and of a dicobalt cofacial porphyrin electrocatalyst on pyrolytic carbon surfaces [4]. Adsorption of reagents containing mercaptide groups at mercury surfaces has also been exploited [5]. Chemical functionalization of the electrode surface to provide anchoring groups to attach reagents by definable covalent bonds was introduced by Murray and coworkers [2]. This approach was extensively developed for attaching monomolecular and multimolecular layers of electroactive substances to semiconductors, metal oxides and carbon electrodes [6–11]. Recently, electroactive polymeric films have acquired wide popularity since it is easier to generate these at the surface of the electrode than to use the monolayer approach [7]. Moreover, the relatively increased number of active sites through the polymer film rendered the electrochemical processes at its surface more pronounced than those at a monolayer-modified surface. Electroactive polymers could be divided into three classes: redox, electronically/ionically conductive and ion exchange polymers. Some examples of electronically/ionically conducting polymers are: poly(pyrrole), poly(thiophene), poly(*p*-phenylene), poly(aniline), and their derivatives. The aforementioned polymers are easily formed by electrochemical polymerization [12], and they can be used to entrap electrocatalysts such as phthalocyanines [13] and enzymes [14], as in the case of poly(pyrrole). However, the incorporation of metal complexes into conducting polymers has been demonstrated mainly for redox-type polymers in a limited number of publications [15–18]. Ferrocene- and phenothiazine-based and pyrene end-capped redox-active polymers were also prepared and characterized [19–22].

On the other hand, during the course of development in the area of electrochemical sensors, the desire for

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improvements in the stability, selectivity, and scope of such sensors followed from the real challenges of achieving the “successful” analysis of clinical and environmental samples [23]. Electronically/ionically conducting polymers were used successfully as new tools for biomolecular determination; refer for example to the review work of Mark et al. [24] and Wallace et al. [25]. To the knowledge of the author, however, the fabrication of a conducting poly(3-methylthiophene) containing metal complexes and its application for the electrocatalytic oxidation of some biological molecules have not been previously mentioned in the literature.

In this work, we assess the benefit of the important feature of the incorporation of the ions of the supporting electrolyte into the polymer film during its formation. The electrical and electrochemical properties of the polymer film are affected by the nature of the electrolyte employed [26]. Thus, we incorporated ferrocene moieties into the polymer film and studied its electrochemical properties and structural characterization [27]. This paper shows that the ferrocenium incorporated into the conducting poly(3-methylthiophene) mediates the electron transfer reaction of the oxidation of some biological molecules. The electrochemical response of the polymer electrode “modified” with ferrocene (PMT/Fc) towards the biological molecules is compared to that of the unmodified one and to the Pt and glassy carbon (GC) electrodes. The results are explained in terms of the increase in the electrocatalytic properties of the polymer film caused by the incorporation of the ferrocenium moieties into its composition.

Experimental

Chemicals and materials

All chemicals used were reagent grade. 3-Methylthiophene was used as the monomer, ferrocenecarboxaldehyde (FcCHO), tetrabutylammonium tetrafluoroborate (TBATFB), ferrocenium hexafluorophosphate (FcPF), potassium ferricyanide, and HPLC grade acetonitrile (AcN) were purchased from Aldrich (Milwaukee, Wis., USA). Other chemicals used in this work were obtained from Fisher Scientific (USA) and were used without further purification. Distilled deionized water was used to prepare aqueous solutions. Acetonitrile was stored over 4-Å molecular sieves for 24 h before use.

A platinum disk electrode (apparent area 0.03 cm²) obtained from Bioanalytical Systems, (West Lafayette, USA) was used for electropolymerizing the film using a conventional three-electrode cell. The auxiliary electrode was a platinum flag (2 × 2 cm²) and all potentials were recorded versus a saturated Ag/AgCl reference. All electrochemical measurements were performed in a conventional one-compartment three-electrode cell. Electrochemical experiments were performed using a CMS 100 electrochemical system (Gamry Instruments, USA). The CMS 100 system was connected to a PC where data were collected, processed and analyzed using the CMS 100-system data analysis software. Electron spectroscopy for chemical analysis (ESCA) was performed using the Perkin-Elmer ESCA-5300 Spectrometer with a pass energy of about 25 eV ($\Delta E = 0.5$ eV). IR experiments were performed using a Nicolet Impact 400 FTIR instrument (Nicolet, USA). A Burleigh

Instruments scanning tunneling microscope was used along with “True Image” software to produce surface morphological images. All film conductivities were measured using a four-point probe unit.

Electrode preparation

Films of poly(methylthiophene) modified with ferrocene moieties (PMT/Fc) were formed using the cyclic voltammetric technique. The electrode was polished with 3- and 1- μ m diamond paste to a mirror-like finish. The solvent/electrolyte was purged with N₂ for 15 min before use. The working Pt electrode was then subjected to repeated cycles between -0.5 V and 1.8 V vs Ag/AgCl. The thickness of the film formed was determined from the charge passed during the cyclic voltammetric experiments. The electrode was then held at a negative potential of -0.5 V in a monomer-free electrolyte containing ferrocenium hexafluorophosphate. The electrode was then removed from the applied potential control when its current reached the background level. A typical electrolytic medium used for the electropolymerization consisted of 0.08 M each of 3MT and FcPF and 0.1 M TBAHFP in AcN. The polymer thus formed was rinsed thoroughly with water and dried in air for further use. Polymer films were prepared for surface characterization according to the above-mentioned procedure using a special holder which contained a 1-cm² Pt electrode sheet. The film was dried for 24 h under Ar prior to further experiments. All electrochemical experiments were carried out under a purified N₂ atmosphere.

Results and discussion

Cyclic voltammograms of the ferrocenium-containing polymer electrode

Hydroquinone was used as a probe to determine whether the ferrocenium-containing polymer electrode (PMT/Fc) possessed an electronic conducting property, and to compare its electrochemical response to those of the poly(3-methylthiophene) (PMT), glassy carbon (GC), and platinum (Pt) electrodes. The cyclic voltammogram obtained at a bare Pt electrode in 0.5 mM hydroquinone and phosphate buffer (pH 6.7) shows no oxidation or reduction peaks for this concentration (see Fig. 1 curve a). Figure 1 (curve b) shows the electrochemical response of the PMT electrode; the oxidation and reduction peaks appeared at +0.47 and +0.40 V, respectively, which gives an $E^{\circ'}$ of +0.435 V and $\Delta E_p = 0.07$ V. It is important to notice that the redox potential for hydroquinone is not within the potential window in which the poly(3-methylthiophene) is conducting [27, 28]. This is in contrast to many electronically conducting polymers such as poly(aniline) [29]. However, the redox potential for hydroquinone is sufficiently positive of the Fc⁺/Fc redox couple so that the mediation by the ferrocenyl moiety can be evaluated. Thus, Fig. 1 (curve c) shows the cyclic voltammogram of hydroquinone in phosphate buffer at the PMT/Fc electrode, and the following conclusions are drawn: (1) oxidation and reduction peaks are observed at +0.46 and +0.40, respectively, (2) $E^{\circ'}$ and ΔE_p are +0.430 and 0.06 V, respectively, and (3) two distinct redox

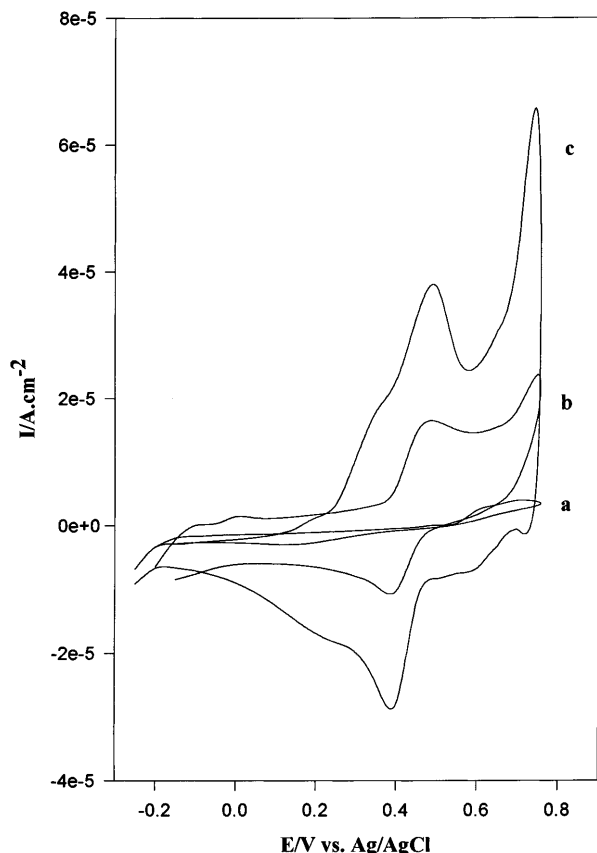


Fig. 1 Cyclic voltammograms of 5.00×10^{-4} M hydroquinone in phosphate buffer (pH = 6.7). Scan rate = 50 mV/s, vs Ag/AgCl. (a) Pt, (b) PMT, and (c) PMT/Fc electrodes

shoulders are observed at +0.2 and +0.3 V, respectively. The later redox peaks are assigned to the Fc^+/Fc redox couple in the PMT film, while the second wave is due to the hydroquinone oxidation. The catalytic effect of the ferrocenyl moiety on the mediation of the charge transfer is shown by comparing the peak current density for hydroquinone oxidation at the PMT and the PMT/Fc electrodes (curves b and c), which are 1.5×10^{-5} and 4.0×10^{-5} A cm^{-2} , respectively. The electrochemical behavior of the PMT/Fc electrode in the absence of the redox species in solution has been described [27].

The electrochemical response of the three electrodes, Pt, PMT, and PMT/Fc was also compared for the oxidation of 5×10^{-4} M ascorbic acid in phosphate buffer (pH 6.7), as shown in Fig. 2 (curves a, b, and c, respectively). In Fig. 2 it can be seen that: (1) the electrochemical response due to the oxidation of ascorbic acid at the platinum electrode at this concentration is not observed, (2) one oxidation peak appeared at the PMT electrode at +0.35 V, (3) two oxidation peaks appeared at the PMT/Fc electrode, the first at -0.05 V due to the redox couple of Fc^+/Fc and the second at +0.15 V due to the oxidation of ascorbic acid, and (4) the anodic peak currents I_{pa} corresponding to the oxidation of ascorbic acid are 2.00×10^{-6} and 3.00×10^{-6} A cm^{-2} at

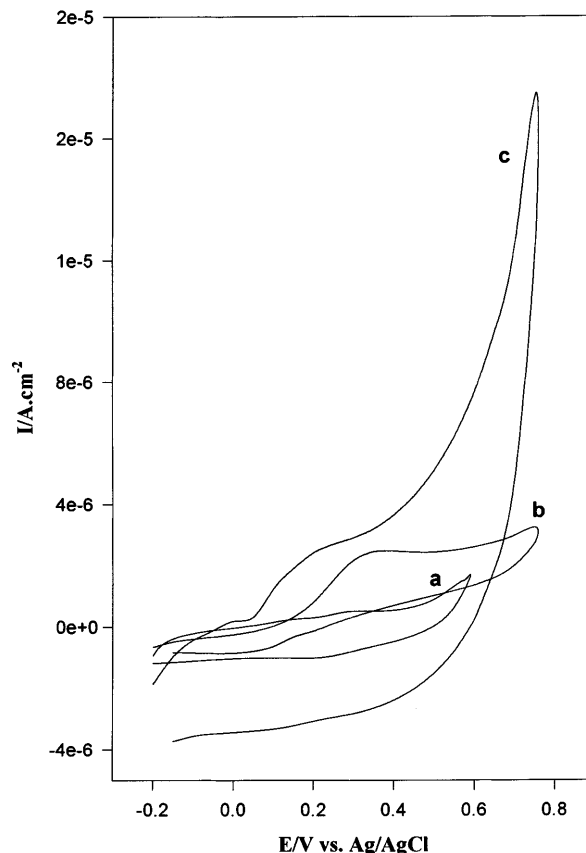


Fig. 2 Cyclic voltammograms of 5.00×10^{-4} M ascorbic acid in phosphate buffer (pH = 6.7). Scan rate = 50 mV/s, vs Ag/AgCl. (a) Pt, (b) PMT, and (c) PMT/Fc electrodes

the PMT and PMT/Fc electrodes, respectively. Two important conclusions could be drawn, (1) the PMT/Fc electrode displayed the highest value of oxidation current density I_{pa} when compared to the Pt and PMT electrodes, and (2) the position of the oxidation potential for the Fc^+/Fc couple changes with the type of supporting electrolyte employed.

Table 1 summarizes the electrochemical data for the oxidation of some molecules of biological interest. The data were collected from the cyclic voltammograms at Pt, GC, PMT, and PMT/Fc electrodes for the compounds indicated. The scan rate is 50 mV/s, and the analyte concentration is 5 mM in 0.1 M H_2SO_4 for the electrodes studied. Except for ascorbic acid, all test substances displayed reversible behavior in 0.1 M H_2SO_4 electrolyte (as well as in phosphate buffer, pH 6.7). From the biosensor point of view, the oxidation peak potential values, E_{pa} , for these substances as well as their corresponding oxidation peak current values, I_{pa} , are more important than their reversible behavior. Thus, all compounds shows significant decrease in the E_{pa} values in the following order: E_{pa} values at PMT/Fc < PMT < Pt < GC, respectively. Moreover, the I_{pa} increased in the following order: I_{pa} values at PMT/Fc > PMT > Pt > GC, respectively.

Table 1 Electrochemical data of some biological compounds at different electrodes. All compounds are 5.00×10^{-3} M in phosphate buffer (pH 6.7). Scan rate 50 mV/s

Compound	Electrode							
	Pt		GC		PMT		PMT/Fc	
	$E_{pa}(mV)$	$I_{pa}(A\ cm^{-2})$	$E_{pa}(mV)$	$I_{pa}(A\ cm^{-2})$	$E_{pa}(mV)$	$I_{pa}(A\ cm^{-2})$	$E_{pa}(mV)$	$I_{pa}(A\ cm^{-2})$
Acetaminophen	610	2.70×10^{-6}	910	3.00×10^{-6}	490	3.00×10^{-5}	480	3.60×10^{-5}
p-Aminophenol	625	2.80×10^{-6}	870	3.10×10^{-6}	465	2.90×10^{-5}	445	3.70×10^{-5}
Ascorbic acid	598	3.30×10^{-6}	985	3.50×10^{-6}	320	2.70×10^{-5}	175	3.90×10^{-5}
Catechol	690	3.50×10^{-6}	860	3.90×10^{-6}	525	3.30×10^{-5}	504	4.30×10^{-5}
Dopamine	685	2.90×10^{-6}	840	3.80×10^{-6}	515	3.20×10^{-5}	510	4.00×10^{-5}
Epinephrine	730	3.10×10^{-6}	930	4.20×10^{-6}	435	1.90×10^{-5}	415	5.10×10^{-5}
Hydroquinone	690	4.00×10^{-6}	740	5.60×10^{-6}	490	2.00×10^{-5}	465	4.50×10^{-5}
Fe^{3+}/Fe^{2+}	437	3.20×10^{-6}	560	4.80×10^{-6}	310	1.70×10^{-5}	305	6.20×10^{-5}

Origin of the electrocatalytic property of the PMT/Fc electrode

Glassy carbon (GC) electrodes are preferred for the oxidative analysis of biological molecules because of their relative resistance to the surface fouling caused by the adsorption of the oxidation products [30]. However, as can be seen from Table 1, the anodic peak potentials of all compounds were much higher than those obtained at the PMT electrode. These results are in good agreement with those obtained by Mark et al. [31]. On the other hand, the PMT/Fc displayed less positive oxidation potential values and higher corresponding oxidation peak currents than those for the PMT electrode. The superior catalytic effect of the PMT/Fc electrode towards the electrooxidation of the studied compounds could be explained on the following basis:

The redox process at the electrode surface can be expressed in the following way:



We should also indicate that the redox process of the analyte takes place at the PMT/Fc electrode within a potential window, ca. -0.2 V and 0.8 V, the polymer electrode being partially reduced and oxidized. The charge transfer, therefore, takes place through the polymer film at potentials well negative of its "fully" doped (oxidized) state, where the film becomes highly conducting [28]. Similar observations were reported earlier in the literature [24, 32]. In our discussion, however, we are assuming that the poly(3-methylthiophene) film is conducting or partially conducting at the positive potential limit, and the polymer film is not porous and can be reversibly oxidized and reduced.

The incorporation of a redox mediator system such as Fc/Fc^+ within the polymer film will result in an increase in the rate of charge transfer at its surface. An explanation of this observation is that the rate-determining step, which is due to the charge migration or hopping between the redox sites [33, 34], is affected by the presence of the Fc/Fc^+ couples within the polymer film. The total current, I_T , is given by:

$$I_T = I_{Red/Ox} + I_{CAT} + I_{Red/Ox}^{POL} + I_{dl} \quad (3)$$

Where: $I_{Red/Ox}$ is the charge exchange at the Pt substrate, I_{CAT} is the catalytic current component due to the charge transfer between the Red/Ox couple and the polymer oxidized states, $I_{Red/Ox}^{POL}$ is the current due to the redox process of polymer film, and I_{dl} is the charging/discharging component of the electrical double layer at the polymer/substrate and polymer/solution interfaces.

Two additional components which will enhance the catalytic effect of the electrode are added when the Fc/Fc^+ couple is incorporated to the polymer film. The total current, in this case, is given by:

$$I_T = I_{Red/Ox} + I_{CAT} + I_{Red/Ox}^{POL} + I_{dl} + I_{CAT}^{Fc} + I_{Red/Ox}^{POL/Fc} \quad (4)$$

Where: I_{CAT}^{Fc} is the catalytic current due to the charge transfer between the Red/Ox couple and the oxidized states of the polymer-containing Fc , and $I_{Red/Ox}^{POL/Fc}$ is the current component due to the reversible redox reaction of the PMT/Fc film (cf. equilibrium 1). Details of the conduction mechanism and equilibria involved are given in the literature [27].

The later distinct increase in the catalytic current at the PMT/Fc electrode is illustrated in Fig. 3A and B. The effect of increasing the concentration of dopamine in phosphate buffer (pH 6.7) at the PMT and PMT/Fc electrodes is given in Fig. 3A and Fig. 3B, respectively. Two important conclusions could be drawn from the results depicted in Fig. 3A and B: (1) The position of the potential oxidation peaks is almost identical for all concentrations studied at the PMT/Fc electrode, while slight shifts were observed at the corresponding PMT electrode as the concentration changed, and (2) the current sensitivity for the relatively low concentrations of dopamine at the PMT/Fc electrode is seen to be superior to that at the PMT electrode. The calibration curves obtained from the cyclic voltammetric data for different concentrations of dopamine in phosphate buffer at the PMT/Fc and the PMT electrodes is shown in Fig. 4A and B, respectively. Again, the higher sensi-

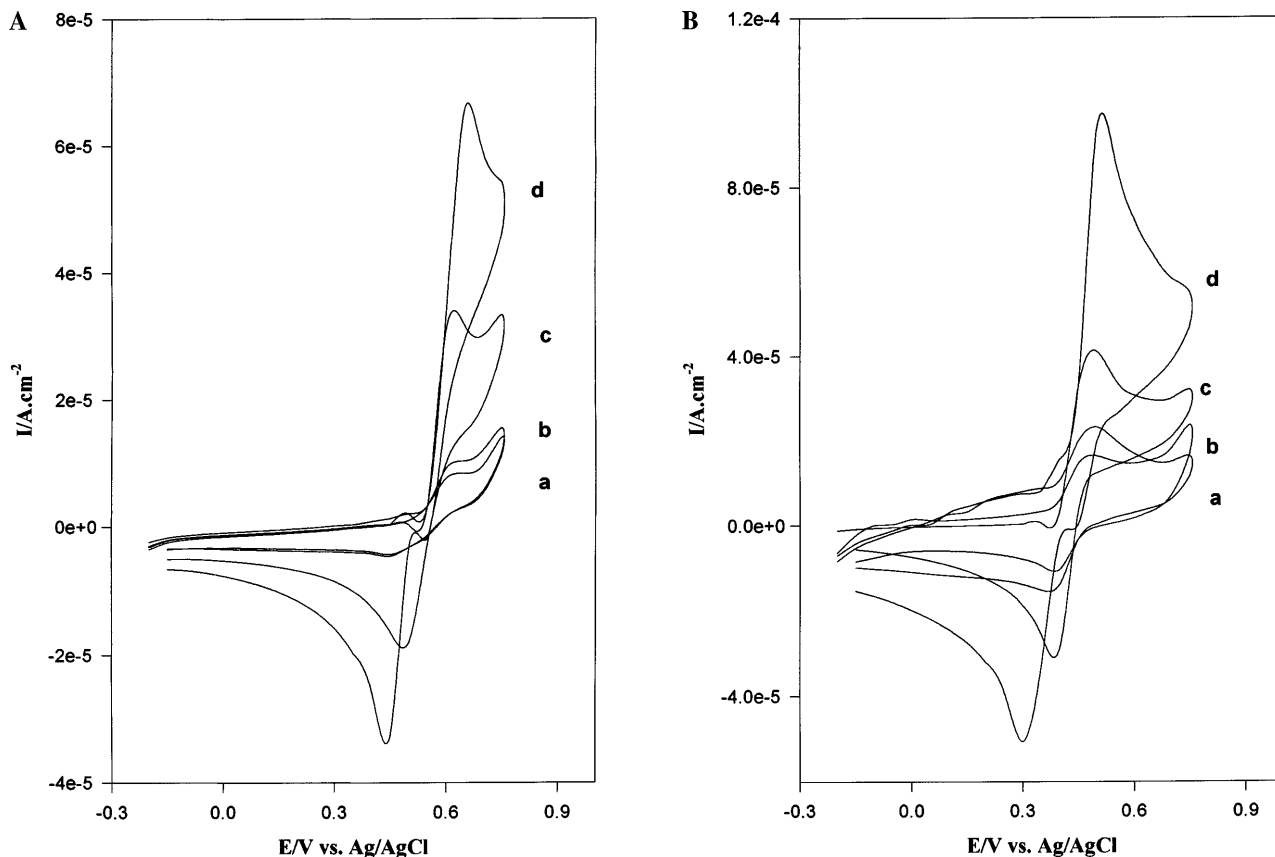


Fig. 3A,B The effect of increasing the concentration of dopamine in phosphate buffer (pH = 6.7) at (A) PMT, and PMT/Fc (B) electrodes. Scan rate = 50 mV/s, vs Ag/AgCl

tivity of the current response at the PMT/Fc electrode is apparent from the higher sensitivity of the calibration curve. As indicated above, the electrocatalytic current observed at the PMT/Fc electrode surface is higher than that of the PMT electrode and is attributed to the presence of the ferrocenium in the polymer film.

Apparent diffusion coefficients

The presence of the polymer film on the substrate surface complicates the approach used to calculate the diffusion coefficient. For clarification, we will consider two assumptions: (1) a competition exists between the transport of the oxidized species of the analyte through the polymer film, which is relatively slow, and the relatively fast electron-transfer reaction with the polymer, and (2) the rate of oxidation (or the redox reaction) depends on the concentration of the polymeric sites at which this reaction takes place. Two consequences arise from these two assumptions: (1) the concentration of the redox species in the polymer film will reach equilibrium only after a relatively long time period, and (2) the presence of Fc/Fc⁺ couple in the film will change the concentration of the active sites within the polymer. The transport of the charges through the PMT polymer film was also described previously in the literature as a “hopping”

process [35]. The apparent diffusion coefficients were found to be in the order of 1.00×10^{-10} to 1.00×10^{-15} cm² s⁻¹ [36]. The latter values are much smaller than those reported for redox species in solution [37].

In this section, we compare the estimated apparent diffusion coefficients D_{app} of the PMT and PMT/Fc electrodes from the dependence of the anodic peak current densities on the scan rate. The D_{app} values were calculated according to Eq. 5 [38]:

$$I_{ap} = 2.69 \times 10^5 n^{3/2} A D_{app}^{1/2} c^0 v^{1/2} \quad (5)$$

where I_{ap} is the anodic peak current density (A cm⁻²), n is the number of electrons transferred, at $T = 298$ K, A is the geometrical electrode area (0.031 cm²), c^0 is the analyte concentration (5.00×10^{-3} mol cm⁻³), and v is the scan rate (V s⁻¹). It is important to note that the apparent surface area used in the calculations did not take into account the surface roughness, which is an inherent characteristic of all polymer films formed using the electrochemical technique. Thus, for a diffusion-controlled process, a plot of the anodic peak current values versus the square root of the scan rate results in a straight-line relationship. The slope of these lines should result in an estimation of the value of D_{app} according to Eq. 1. Figure 5 shows a comparison of the square root of the scan rate versus I_{ap} plots of dopamine

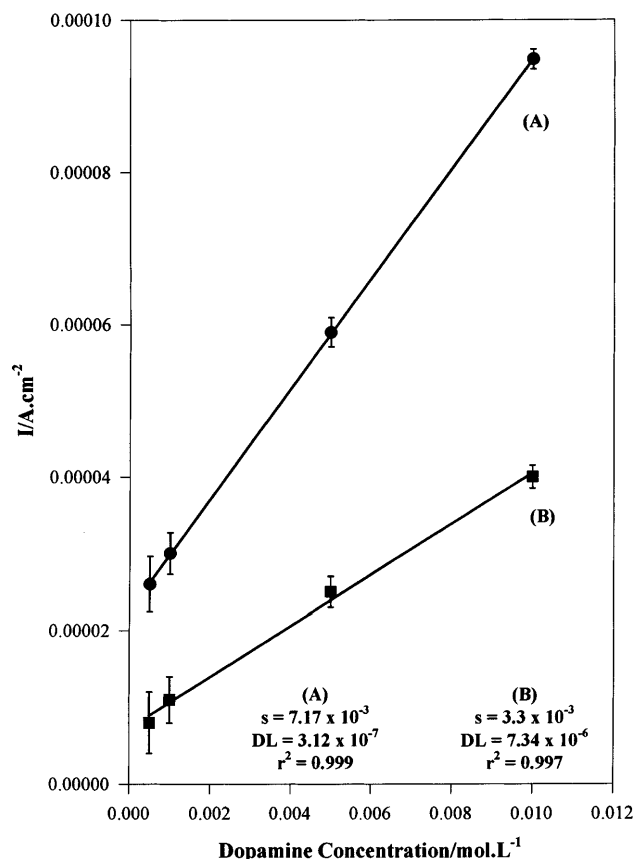


Fig. 4 Calibration curve for different concentrations of dopamine in phosphate buffer. Data obtained from cyclic voltammetric experiments at PMT/Fc (A) and PMT (B) electrodes

at PMT and PMT/Fc electrodes, respectively. The values calculated for the D_{app} from Fig. 5 are 2.29×10^{-10} and $5.68 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ at the PMT/Fc and PMT electrodes, respectively. The relatively high value of D_{app} for the PMT/Fc electrode compared with that of the PMT electrode indicates that the electron transfer step of the electrocatalytic reaction takes place faster at the former electrode surface. Similar results were reported earlier in the literature [40], indicating the electrocatalytic charge transfer at the conducting polymer electrode surface. Moreover, it also shows that the reaction occurs at the solution/polymer interface. Table 2 lists typical values for different biological molecules calculated at both electrodes.

Table 2 Apparent diffusion coefficients at PMT and PMT/Fc electrodes. Data estimated from cyclic voltammetric measurements

Species	Apparent diffusion coefficients D_{app} ($\text{cm}^2 \text{ s}^{-1}$)	
	PMT	PMT/Fc
Ascorbic Acid	1.13×10^{-11}	3.11×10^{-12}
Catechol	4.57×10^{-11}	1.13×10^{-12}
Dopamine	2.29×10^{-10}	5.68×10^{-11}
Epinephrine	6.88×10^{-11}	4.62×10^{-12}
Hydroquinone	1.18×10^{-12}	2.34×10^{-13}

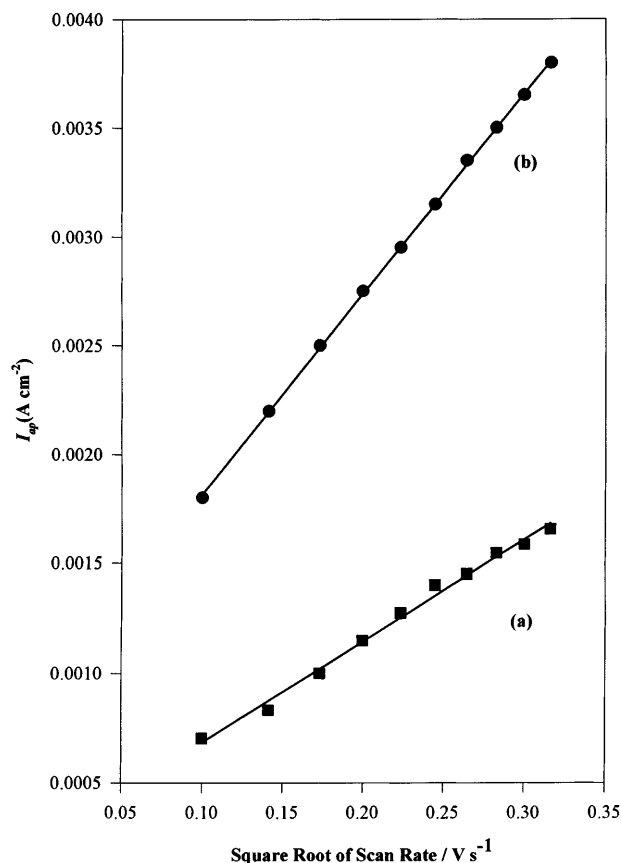
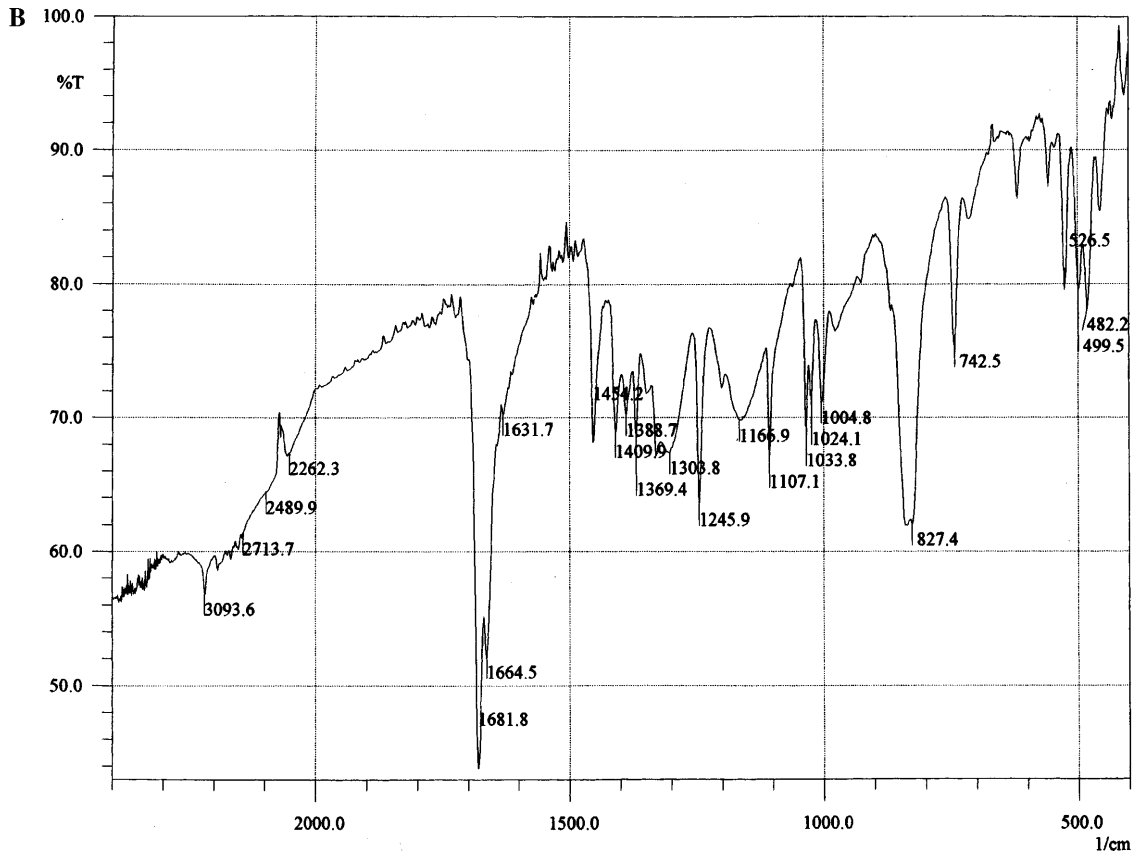
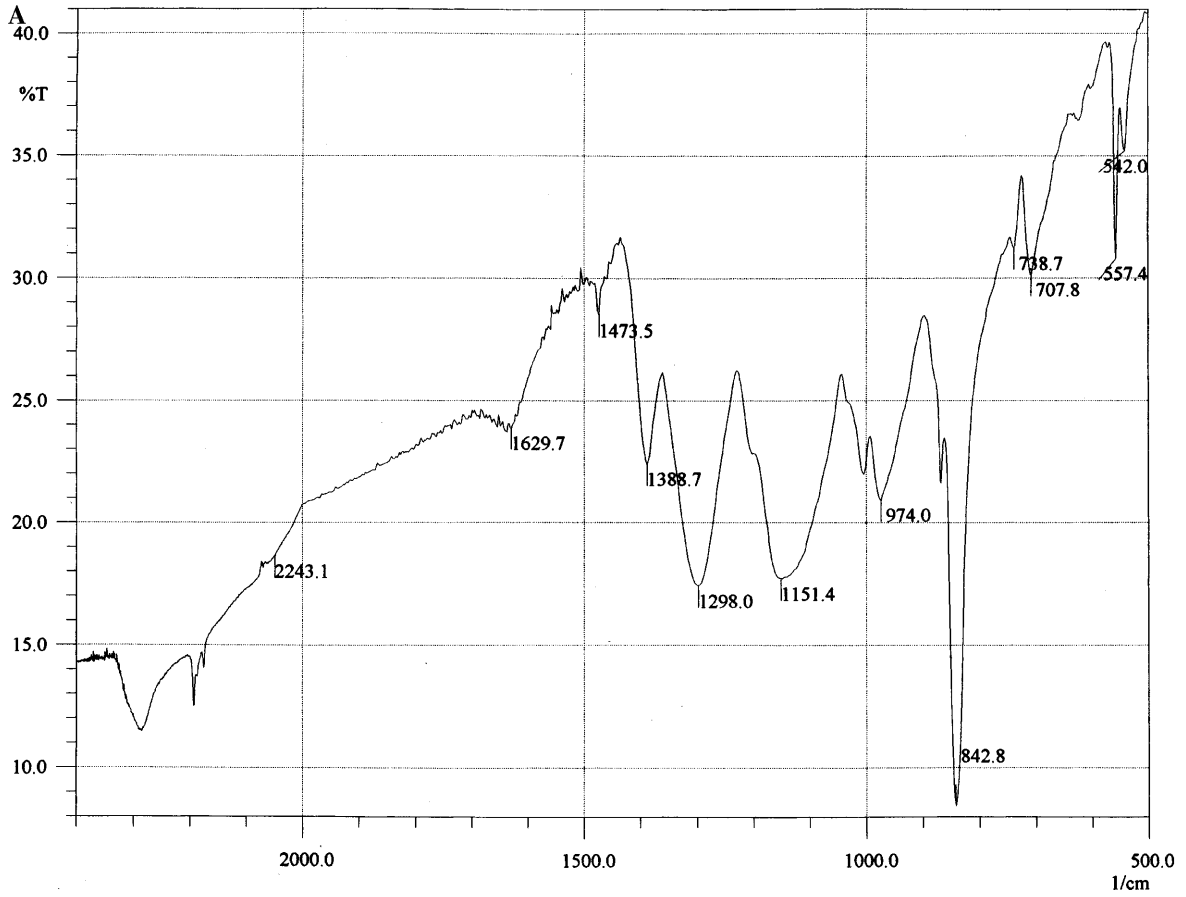


Fig. 5 Comparison of the square root of the scan rate vs I_{ap} plots of dopamine at PMT (a), and PMT/Fc (b) electrodes

IR spectroscopic analyses of the polymer film

The FTIR spectrum of a KBr pressed pellet of poly(3-methylthiophene) grown under a constant applied potential of 1.65 V is shown in Fig. 6A. The number of scans collected at a resolution of 2 cm^{-1} and with an accuracy of 0.004 cm^{-1} was 16 for all samples. The following results are in good agreement with that published earlier [39]. The assignments of the principal absorption bands are: the bands between 856 and 633 cm^{-1} are characteristics of the C-H out-of-plane vibrations, the sharp absorption band at 842 cm^{-1} is attributed to the ring C-H out-of-plane bending vibration, which is specific for the 2,5-disubstituted thiophene rings, the peak appearing at 1473 cm^{-1} is attributed to the stretching vibration of the 2,3,5-trisubstituted thiophene rings, and the band at 1388 cm^{-1} can be attributed to the deformation vibration of the methyl group. Figure 6B shows the FTIR spectrum of the P3MT/Fc film grown with the incorporation of

Fig. 6 A FTIR spectrum of KBr pressed pellet of PMT grown potentiostatically, $E_{ap} = 1.65 \text{ V}$ vs Ag/AgCl. B FTIR spectrum of KBr pressed pellet of PMT/Fc grown potentiostatically, $E_{ap} = 1.65 \text{ V}$ vs Ag/AgCl



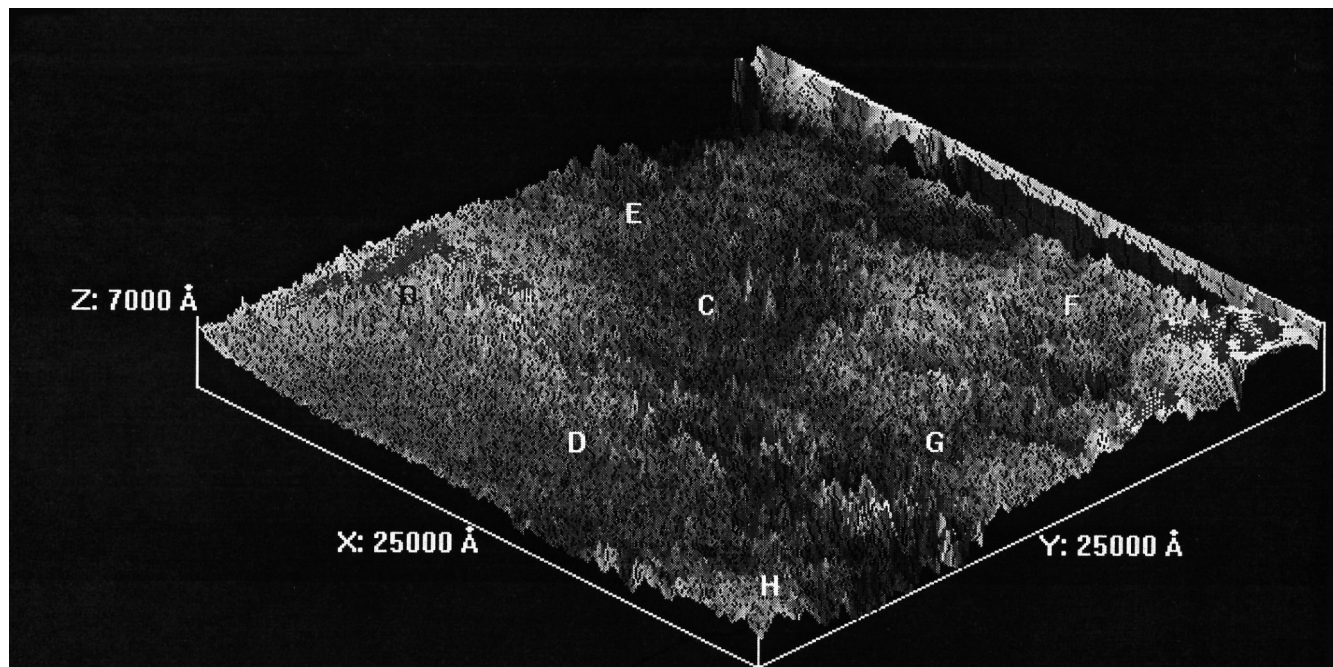


Fig. 7 Scanning tunneling micrograph of PMT/Fc grown on Pt substrate under potentiostatic conditions

ferrocene carboxaldehyde. The spectrum of Fig. 6B reveals the appearance of two peaks at 1664 and 1681 cm^{-1} , respectively. These peaks indicate the presence of the aldehydic group due to the incorporation of the ferrocenium moiety within the film.

Surface analyses of the PMT/Fc electrodes showed that the polymer film contained a sulfur atom bound to a heavy metal center [40]. The chemical shift for the sulfur spectra suggests that the sulfur atom is interacting with the iron of the ferrocenium moiety.

A scanning tunneling micrograph of the PMT/Fc film is shown in Fig. 7. The surface roughness appearing in the image of this film is identical to that obtained from scanning electron micrographs of the PMT films [41]. However, no indication was found of the formation of a porous film of PMT/Fc on the Pt substrate.

The conductivity measurements on the "as-grown" PMT/Fc films showed no appreciable differences when compared to the PMT films. In this case, the concentration of the ferrocenium moieties is not high enough to produce an increase in the conduction of the film.

Conclusions

Poly(3-methylthiophene) films were modified by the incorporation of an inorganic complex containing iron. The polymer films were grown onto platinum substrates and used for the determination of the electrochemical behavior of some organic molecules of biological interest. The electrochemical response of these electrodes showed higher currents for oxidation and reduction when compared to that of the "unmodified" polymer electrodes. Moreover, this work showed that the in-

corporation of an inorganic mediator into the conducting polymer film is possible using electrochemical means. The spectroscopic characterization of the polymer film proved the incorporation of the complex into the polymer matrix.

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