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Electrochemistry and detection of some organic and biological molecules at conducting poly(3-methylthiophene) electrodes

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Abstract: Electrodes modified by the electrodeposition of poly(3-methylthiophene) were used as chemical sensors for some organic and biological molecules of industrial and medicinal interest. The electrochemical behaviors of ferri/ferrocyanide, catechol, ascorbic acid, hydroquinone, dopamine epinephrine, acetaminophen, *p*-aminophenol and NADH were examined by cyclic voltammetry. The results showed that the proposed modified surface catalyzes the oxidation of these compounds. Differential pulse and square wave techniques were used for the analysis of binary mixture of ascorbic acid with catechol, NADH, dopamine and *p*-aminophenol. Voltammetric peak resolution was also demonstrated for a ternary mixture of ascorbic acid, catechol and *p*-aminophenol. Polymer coated electrode was also used in an amperometric detector for flow injection analysis of most of the aforementioned compounds. The responses of the polymer electrode were 4–10 times larger as compared to those of platinum. The modified electrode displayed excellent response stability for successive injections and detection limits were 10 ppb for catechol, dopamine, epinephrine, NADH and *p*-aminophenol, 1 ppb for acetaminophen and 100 ppb for ascorbic acid. Voltammetric peak positions were affected by the nature of the electrolyte and its pH. Also, film thicknesses were shown to be a factor affecting both the current magnitudes and oxidation peak potential of NADH.

Keywords: acetaminophen, ascorbic acid, catechol, conducting polymers, dopamine, electrocatalysis, electrolyte, epinephrine, flow injection analysis, hydroquinone, modified electrode, NADH, *p*-aminophenol, poly(3-methylthiophene), voltammetry.

INTRODUCTION

The concept of the modified electrode is certainly one of the exciting developments of the last two decades and worldwide interest can be readily measured by the large number of publications in this field. The underlying motivations for electrode surface modifications stem from the desire for the improved electrocatalysis and freedom from surface fouling effects. Alternatively, electrodes can be modified to prevent undesirable reactions from competing kinetically with the desired

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electrode processes (Murray, 1980, 1984; Murray *et al.*, 1987; Redepenning, 1987).

The most widely adapted scheme for the electrocatalysis is to use soluble or surface immobilized electron transfer mediators, so that oxidation or reduction of the desired substrate occurs at a potential nearer to its expected thermodynamic potential, e.g. the activation potential that exists at unmodified (bare) electrode is overcome. However, this scheme can only be useful if the formal potentials of mediator catalyst and substrate are similar. In other words, electron exchange via redox mediators is limited by the redox potential of the mediator, which generally provides only a very narrow useful potential window.

There is a multitude of polymeric coatings for wide variety of electrode applications in electrochemistry (Murray, 1984; Hillman, 1987). Electrically conducting polymers, which constitute one group of a larger family of polymers (redox polymers, ion exchange polymers, conducting polymers and inert neutral polymers) appear to have a distinct advantage over redox mediators for catalysis. This advantage is inherent in the fact that conduction, and therefore interfacial electron transfer, can take place over a broad potential window.

Poly(3-methylthiophene), PMeT, is an electronically conducting polymer which is easily deposited onto electrodes by electrooxidation of its monomer. Its applications have been discussed and emphasized in terms of electrochromic effects and energy storage and conversion (Tourillion, 1986). In the field of catalysis its use was customarily considered in conjunction with metallic aggregates or clusters embodied into the polymer matrix to achieve high electrocatalytic activity for hydrogen generation (Tourillion & Garnier, 1984).

We have been using electrodes coated with poly(3-methylthiophene) in a thin layer amperometric cell for the determination of inorganic anions with flow injection analysis (Russell *et al.*, 1989). The principle of this type of detection is based on the incorporation of anions (counter-anions) into the positively held PMeT. A similar scheme has been adapted earlier by using other conducting polymers such as polypyrrole (Ikariyama & Heineman, 1986) and polyaniline (Ye & Baldwin, 1988).

The use of conducting polymers for electrochemical determination of some biologically important compounds has been demonstrated in a very limited number of works. For instance, Saraceno *et al.* (1986) used a polypyrrole-coated glassy carbon electrode for resolving voltammetric waves of ascorbic acid and dopamine. They concluded that the current observed was mass-transport limited and not limited by permeation into or through the polymer film. PMeT-coated electrodes were used by Wang and Li (1989) to eliminate the passivation problems, otherwise occurring at glassy carbon electrodes, in voltammetric measurements of phenolic compounds. They also observed significantly larger oxidation peaks for acetaminophen. In a different study Wang *et al.* (1989) showed that conducting polymers (polyaniline, polypyrrole and polyphenol) could be used for controlling the size-exclusion selectivity. The smaller the molecules, the more facile was their transport through the polymer film. Thus, bare electrode (platinum) responses were always larger than those obtained at the coated electrodes. However, these studies concerning the use of conducting polymers for non-mediated electron transfer were limited to a small number of compounds. Also, no observations were made regarding the effects of film thickness and electrolyte properties on the electrocatalytic ability of the conducting polymer electrodes.

In this paper we examine the electrochemical behavior of a large number of biologically important compounds at a PMeT modified electrode. Although limited, the effects of the nature and pH of the base electrolyte and film thickness were also studied. Electrocatalysis effect of PMeT film is clearly demonstrated and selective voltammetric determination of even ternary mixtures was shown to be possible. Additionally, the PMeT-coated electrodes were also used for sensitive determinations in a flow injection analysis–amperometric detection regime.

EXPERIMENTAL

Reagents

NADH, dopamine, epinephrine (Sigma), ascorbic acid, acetaminophen (Aldrich), *p*-aminophenol, catechol, hydroquinone and potassium ferricyanide (Fisher) were used as received. 3-Methylthiophene and tetrabutylammonium tetrafluoroborate were received from Aldrich and were not

further purified. Redistilled acetonitrile (UV grade, Aldrich) was used as solvent for electrochemical polymerization. Sörensen buffer, which was used as electrolyte in square wave and differential pulse voltammetric studies and also as mobile phase in flow injection analysis was prepared as follows: 60 ml Na_2HPO_4 (9·47 g/liter) + 40 ml NaH_2PO_4 (9·208 g/liter) + 0·460 g NaCl. The measured pH of this buffer was 6·9.

Procedure and apparatus

Electrochemical polymerization was carried out in a one compartment cell containing deaerated acetonitrile, 0·1 M tetrabutylammonium tetrafluoroborate and 0·05 M 3-methylthiophene. Either a potentiostatic or a galvanostatic mode was adapted for film growth. Cyclic voltammetry was done with films grown at a constant potential of 1·80 V for 45 s. In all other cases, films were grown under galvanostatic mode with a current density of 10 mA/cm^2 for 25 s. After the polymerization, all films were kept at −0·20 V for 10 min to undope BF_4^- (original electrolyte anion).

A platinum (MF2013, Bioanalytical Systems, Inc. (BAS), West Lafayette, Indiana, USA) or a glassy carbon (MF2012, BAS) electrode, coated or otherwise, was used for the voltammetric (cyclic, differential pulse or square wave) measurements. These measurements were conducted with a BAS-100 electrochemical analyzer and voltammograms were recorded with a DMP-40 digital plotter from Houston Instrument. Analyte concentrations stated for voltammetric analysis were obtained by directly adding a carefully weighed analyte(s) into the electrolyte solution(s).

A thin layer detector cell with dual Pt-Pt electrodes (MF1012, BAS) was used for flow injection-amperometric detection of analytes. Mobile phase was driven by an Altex model 100 double reciprocating pump with a flow rate of 1·0 ml/min. A 20 μl sample injection loop was used throughout the experiment. The electrode potential was controlled by a BAS model CV-1B cyclic voltammetry unit and signals were recorded with a Fisher Series 5000 recorder. Analyte solutions with desired concentrations were prepared through serial dilution of 1000 ppm stock solutions. Mobile phase buffer was used as a solvent for the preparation of stock solutions and for other dilution procedures. All potential values were expressed versus Ag/AgCl (3 M NaCl) (MF2020, BAS).

RESULTS AND DISCUSSION

Oxidation kinetics at poly(3-methylthiophene) electrode

Figure 1 shows the cyclic voltammetric behaviors of ascorbic acid, catechol, dopamine and *p*-aminophenol at PMeT electrodes. Except for ascorbic acid, these and other test substances (ferri/ferrocyanide, hydroquinone, acetamidophenol and NADH) all displayed reversible behavior in 0·1 M H_2SO_4 electrolyte. From the biochemical sensor application point of view, oxidation peak potential positions of these substances are more important than their reversibility characteristics. In this respect, all compounds demonstrate dramatically improved electrode kinetics at PMeT-coated platinum electrodes. The enhanced electron transfer ability of the PMeT-coated electrodes are presented in Table 1 by tabulating the anodic peak potentials of test substances at three different electrodes (PMeT, platinum and glassy carbon).

Glassy carbon (GC) electrodes are often preferred for the analysis of biological systems owing to their relative resistance to surface fouling effects (Ewing *et al.*, 1981). However, as can be seen from Table 1, the anodic peak potentials of all the compounds were always much higher than those obtained at platinum electrodes in the electrolyte chosen for this study (0·1 M H_2SO_4). Table 1 clearly demonstrates the electrocatalytic ability of the PMeT electrodes.

One other characteristic of the voltammograms in Fig. 1 is that they all display large current envelopes. This kind of marked increase in the shapes of voltammograms which is also observed for analyte free electrolytes, appears to be an inherent property of conducting polymers. It seems that the large surface area provided by the three-dimensional porous structure of the coating greatly increases both faradaic and nonfaradaic residual currents. This phenomenon, which is observed by other workers with polypyrrole (Saraceno *et al.*, 1986) and with PMeT (Wang & Li, 1989), greatly impairs the peak resolution for a given binary mixture, although the data in Table 1 otherwise indicate large differences in anodic peak potentials. For instance, the difference in anodic peak potentials for ascorbic acid and dopamine is 510 − 296 = 214 mV. However, because of the general increase in the entire envelope of the voltammograms, the peak

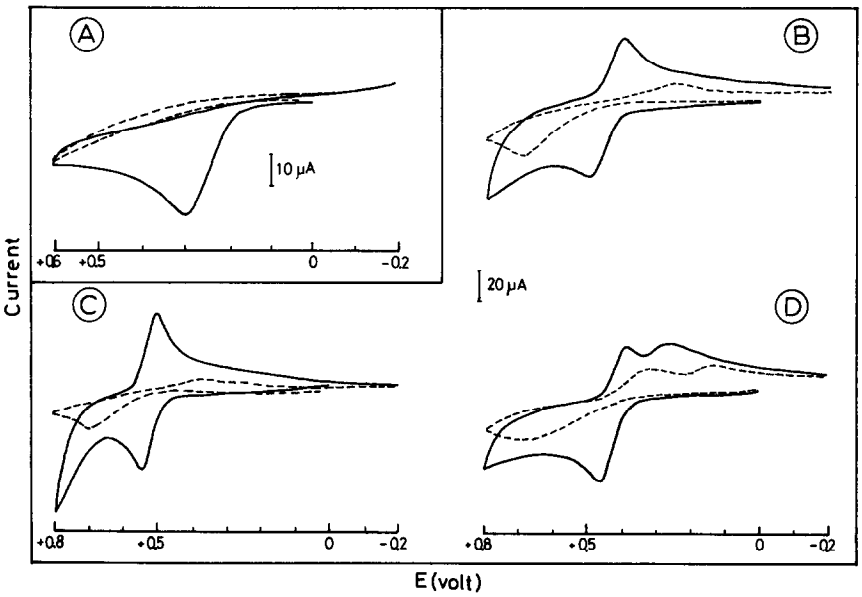

Fig. 1. Cyclic voltammograms for 5 × 10^{-3} M ascorbic acid (A), dopamine (B), catechol (C) and p-aminophenol (D) at PMeT-coated (solid curves) and bare platinum (broken curves) electrodes. Scan rate, 50 mV/s; electrolyte, 0·1 M H_2SO_4.

TABLE 1
Oxidation peak potentials of some biological compounds at three different electrodes[a]

Compound	*Ep(a) (mV)*		
	PMeT	*Pt*	*GC*
Acetaminophen	492	600	904
p-Aminophenol	471	620	900
Ascorbic acid	296	—[b]	981
Catechol	520	689	849
Dopamine	510	690	831
Epinephrine	440	735	940
Hydroquinone	492	567	729
Fe^{3+}/Fe^{2+}	317	437	568

[a]Values are obtained from the positive scan of first cycle electrolyte: 0·1 M H_2SO_4; analyte concentration 5 mM. Scan rate: 50 mV/s.
[b]No peak was observed up to 1250 mV.

resolution is obscured to such an extent that their simultaneous observation by cyclic voltammetry is almost impossible.

Square wave voltammetric study of mixtures

Analytical advantages of the PMeT electrodes especially for the analysis of mixtures can be realized by voltammetric techniques such as differential pulse or square wave voltammetry, which compensate for the charging currents that account for large current envelopes in cyclic voltammograms. For instance, the ascorbic acid and dopamine separation problem experienced in cyclic voltammetric mode can be alleviated if the square wave technique is used. In fact, Fig. 2 gives four examples of simultaneous voltammetric detection with square wave technique.

Differential electrocatalysis of ascorbic acid (which is an interferent) and other biological compounds, especially the neurotransmitter dopamine is of great importance in bioanalytical chemistry. Classically, this problem was dealt with using nafion-coated electrodes (Nagy *et al.*, 1985). Ascorbic acid is an anion whereas dopamine is a cation at physiological pH. Therefore, ascorbic acid, being a counter ion of charged nafionic film is largely excluded and gives no electrochemical response. It is suggested (Saraceno *et al.*, 1986) that differential electrocatalysis of ascorbic acid in the presence of dopamine at polypyrrole electrodes was achieved due to favorable interaction between an anion (ascorbate) and a polymer containing fixed positive charges. Although the dopamine peak position is not changed at polypyrrole with regard to bare glassy carbon electrode, ascorbic acid shifts to more negative values and a separation is thus rendered.

One peculiar occurrence has to be noted with regard to the peak position of ascorbic acid in

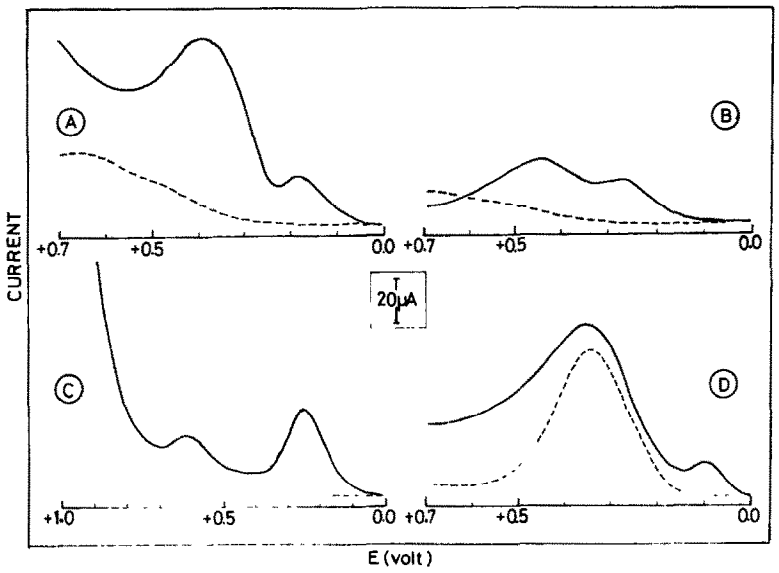

Fig. 2. Square wave voltammograms of binary mixtures (5×10^{-3} M of each) of ascorbic acid with catechol (A), dopamine (B), NADH (C) and p*-aminophenol (D) at PMeT-coated (solid curves) and bare platinum (broken curves) electrodes. Amplitude, 25 mV; frequency, 15 Hz; step, 4 mV; electrolyte, Sörensen buffer (pH = 6·9). The peaks which appear at less positive potentials belong to ascorbic acid.*

Fig. 2. It is apparent that the peak position of this solute at the PMeT electrode shows variation with the type of the second analyte in the mixture. This phenomenon is not confined to ascorbic acid; it was observed that peak positions of individual solute types were not necessarily the same when they were mixed. Although not extensively studied, a synergistic effect might be in question.

As stated earlier, glassy carbon is the choice of electrode material for most of the protocols published in the field of electroanalysis of biological compounds. Although much work is done using the platinum as the substrate coated with the PMeT, the authors also wanted to demonstrate the use and advantages of PMeT-coated glassy carbon electrodes. Differential pulse voltammetry at a glassy carbon electrode of an equimolar ternary mixture of ascorbic acid, *p*-aminophenol and catechol produces, as expected, a single overlapped peak (Fig. 3(A)). However, the separation is easily achieved at PMeT-coated glassy carbon (Fig. 3(B)). This example, illustrating the separation of ascorbic acid, *p*-aminophenol and catechol has not yet been demonstrated at any surface to the best of our knowledge and on its own, deserves special attention.

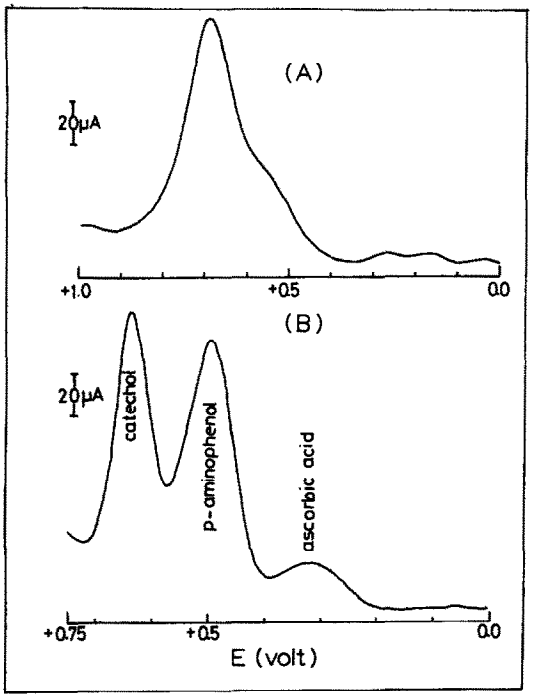

Fig. 3. Differential pulse voltammogram of a ternary mixture (5×10^{-3} M of each) of ascorbic acid, p*-aminophenol and catechol at glassy carbon (A) and PMeT (B) electrodes. Scan rate, 4 mV/s; amplitude, 25 mV; electrolyte, Sörensen buffer (pH = 6·9).*

TABLE 2
Electrolyte effect on the cyclic voltammetric peak potentials for catechol[a]

Electrolyte[a]	*PMeT*		*Pt*	
	Ep(a) (mV)	*ΔE (mV)*[b]	*Ep(a) (mV)*	*ΔE (mV)*[b]
Sulfuric acid	560	69	702	364
Sodium sulfate	544	238	628	455
Hydrochloric acid	559	77	634	251
Sodium chloride	590	250	610	376
Nitric acid	559	79	658	278
Sodium nitrate	556	225	641	408
Phosphoric acid	585	165	777	424
Sodium phosphate	513	231	616	558

[a]Catechol and electrolyte concentrations were 5 and 100 mM, respectively. Scan rate = 100 mV/s.
[b]ΔE = Peak potential difference between anodic and cathodic peaks.

Effect of electrolyte type and its pH and film thickness on responses

Earlier works involving the use of conducting polymer coated electrodes (Saraceno *et al.*, 1986, Wang & Li, 1989; Wang *et al.*, 1989) employed only one type of base electrolyte with a defined pH value to examine the behavior of a certain class of compounds. It has been the authors' experience that the background electrolyte itself has a marked effect on the peak positions and anodic and cathodic peak separation values. This was first noticed in the case of NADH, which displayed a relatively higher oxidation potential with $NaNO_3$ than with other electrolytes (Na_2SO_4, H_2SO_4 and NaCl) (Nada *et al.*, 1991). Although extensive studies have not yet been conducted on the effect of background electrolyte for the test substances examined in this work, electrolyte effect will only be demonstrated for the case of catechol. The peak potential values shown in Table 2 represent those obtained on the first cyclic voltammetric scans. The data in Table 2 clearly demonstrate that acids improve the reversible behavior of catechol when compared to their sodium salts at both PMeT and platinum electrodes. However, this improvement is of dramatic size at the PMeT electrodes and mainly accrues from large shifts of cathodic peak potentials toward less negative values.

Also, film thickness had an effect, not only on the peak potentials, but also on the peak current magnitudes. Figure 4 depicts the effect of film thickness on the anodic peak potential of NADH in cyclic voltammetric mode. As the film thickness increases (estimated from charge consumed during polymerization by assuming a value of 50 g-equivalent for 3-methylthiophene and 1 g/cm^3 for the film density) anodic peak potential shifts to more positive potentials until a limiting value is obtained for thickness around 1800 Å. Although not shown here, peak potential currents pass through a maximum, indicating a film thickness region of 250–700 Å for optimum current responses for the NADH.

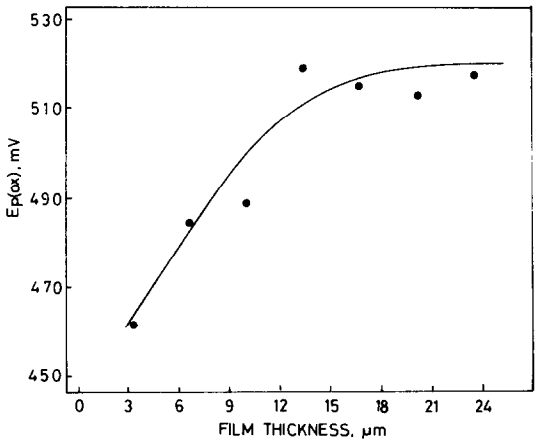

Fig. 4. Effect of film (PMeT) thickness on the anodic peak potential of 1 mM NADH. Electrolyte, 10 mM Na_2SO_4; scan rate, 50 mV/s.

Although not extensive, the aforementioned observations manifest the importance of electrolytes and film conditions upon the acquired data.

Judicious control of the film polymerization conditions seems to be essential for the repeatability of results. On the other hand, electrocatalytic effects of conducting polymers need to be discussed and reported in relation to the electrolyte properties.

Amperometric detection/flow injection analysis of test substances

Amperometric measurements under flow injections or liquid chromatographic conditions are particularly beneficial since the fouling problems are not as severe as in batch experiments, because of the small amount of product that is generated. This is especially true for works at low concentrations.

Flow injection analyses of catechol, ascorbic acid, dopamine, epinephrine, NADH, p-aminophenol and acetaminophen were performed using Sörensen buffer as mobile phase, 20 μl of each test substance having concentration levels of 1–100 ppm with 10 ppm increments were injected and current signals were measured from the recorded peak heights. Working electrode potential for each substance was set at a value that was slightly above the anodic peak potentials of each compound shown for the PMeT electrode in Table 1. Figure 5 shows the calibration curves for catechol and ascorbic acid obtained on PMeT and platinum electrodes. Current responses at the PMeT electrode were 4–10 times higher (depending on analyte type) than those obtained on platinum, and excellent linearity was observed for all of the substances for the concentration range studied. For the estimation of detection limits 1, 10 and 100 ppb solutions of respective test substances were injected and the concentration, which produced a current signal with a magnitude at least 2·5 times as high as the signal that is caused by the injection of buffer itself is accepted as a practical limit for detectability. Detection limits estimated from the procedure described above were 10 ppb for catechol, dopamine, epinephrine, NADH and *p*-aminophenol; 1 ppb for acetaminophen and 100 ppb for ascorbic acid.

Also, the signal stability was tested for 100 repetitive injections of 5 mM NADH. Coefficient of variation was found to be 8·1%. This implies that PMeT electrode is not subject to surface fouling by the oxidation product(s) of NADH, which is notorious for its surface fouling effects. It should be stated, however, that no attempt was made at this point for the selective determination of mixtures of compounds by FIA.

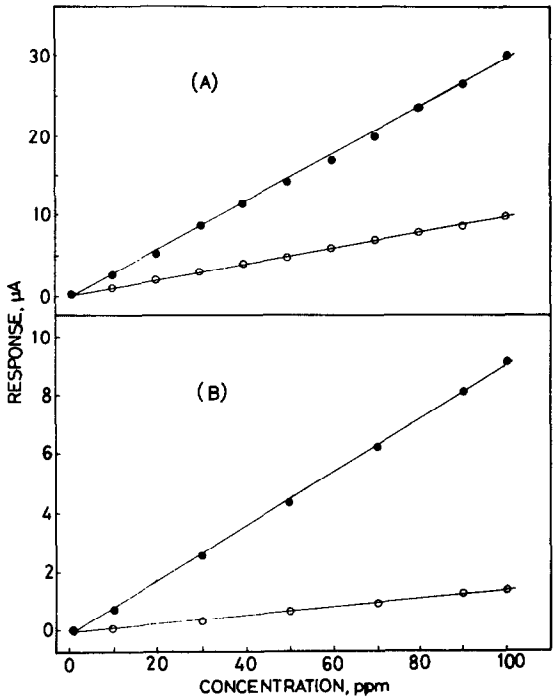

Fig. 5. Flow injection–amperometric detection calibration curves for catechol (A) and ascorbic acid (B) at PMeT (●) and Pt (○) electrodes. Sample size, 20 µl; mobile phase, Sörensen buffer (pH = 6·9); flow rate, 1·0 ml/min. Working electrode potential, 0·500 V.

CONCLUSION

It is shown that electrode reactions of some biologically important compounds are catalyzed over the poly(3-methylthiophene) conducting polymer electrodes. These improved reaction kinetics can be advantageously used for voltammetric analysis of multicomponent mixtures, and the use of poly(3-methylthiophene) as an amperometric detector electrode material provides higher sensitivities than those achieved at bare electrodes. Reaction kinetics appear to be dependent not only on the type of analyte but also on the nature of electrolyte. However, nothing much can be spoken of at this time regarding the correlation between electrolyte type and electrochemical behavior of analytes.

However, overall performance of PMeT or any other conducting polymer electrode as analytical sensor needs to be carefully studied from the

(a)

(b)

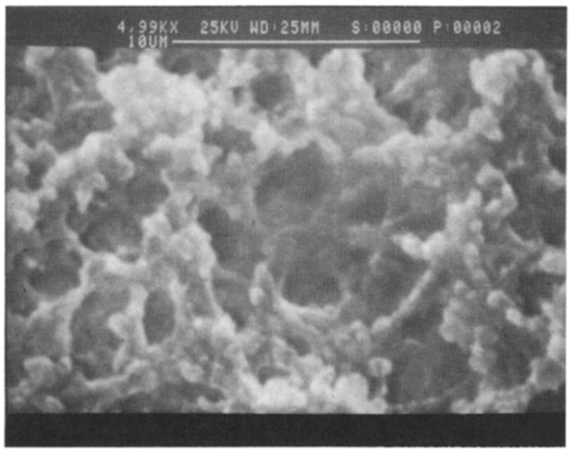

Fig. 6. Scanning electron micrographs of PMeT-coated electrode before (a) and after (b) exposure to 0·1 M NADH at 0·5 V for 2 h.

precision, repeatability and reproducibility points of view. Electrocatalysis effects and current signal magnitudes might be affected by several factors, such as: film growth conditions, film pretreatment procedures and the history of film electrode before the analysis of a given compound. It would be interesting to demonstrate the behavior of a PMeT electrode toward some analytes after the electrode was exposed previously to another kind of substance(s). Prolonged exposure may cause a change in film morphology and the response of this film in proceeding analyses might be totally different than freshly prepared ones. For example, SEMs in Fig. 6 illustrate a dramatic deformation on the surface of a PMeT film which was exposed to 0·1 M NADH solution for extended periods. After such long exposures, one may not expect that the behavior of this film will be the same as before, although no significant fouling effect was observed with this particular sample type in FIA. The points raised and suggestions made above are currently being studied in our laboratory.

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