



# Poly(3-methylthiophene)/palladium sub-micro-modified sensor electrode. Part II: Voltammetric and EIS studies, and analysis of catecholamine neurotransmitters, ascorbic acid and acetaminophen

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## ABSTRACT

Promising voltammetric sensors based on the modification of Pt and poly(3-methylthiophene) (PMT) electrodes with Pd nanoparticles were achieved for the determination of catecholamine neurotransmitters, ascorbic acid and acetaminophen. Electrochemistry of the indicated compounds was studied at these electrodes and interesting electrocatalytic effects were found. Furthermore, simple, easily prepared one electrochemical step Pd-modified Pt electrode (Pt/Pd) is reported for the first time. Cyclic voltammetry (CV) and chronocoulometry (CC) were used for the determination of the apparent diffusion coefficients in different electrolytes at these electrodes and the values are in the range from  $10^{-4}$  to  $10^{-5}$   $\text{cm}^2 \text{s}^{-1}$ . Furthermore, it was found that the method of polymer formation had a substantial effect on the synergism between the polymer film and the loaded metal particles towards the oxidation of dopamine (DA) in different supporting electrolytes. This was confirmed by the CV, CC and EIS (electrochemical impedance spectroscopy) as well as SEM (Scanning Electron Microscopy) results. Pt and PMT electrodes modified with Pd nanoparticles showed excellent results for the simultaneous determination of tertiary and quaternary mixtures of the studied compounds.

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## 1. Introduction

Conducting polymers (CPs) are widely employed as coatings conferring the electrode systems antifouling properties and possibly activating electrocatalytic redox processes [1,2]. Among different CPs, PMT showed unusual characteristics towards the determination of catecholamine neurotransmitters compared to commonly used electrodes such as Pt, Au, glassy carbon, and chemically modified electrodes [3,4]. A step forward with respect to 'simple' modification with pristine CPs consist of the inclusion of metal functionalities inside the polymeric matrix, in order to further increase the performances of the resulting composite material. In particular, inclusion of noble metal nanoparticles (NPs), whose catalytic properties are well known [5], constitutes one of the most interesting possibilities. Similar composites based on polypyrrole and polyaniline have been recently reported [6–10]. Polythiophenes/NPs composites are even less studied [11–13]. Among polythiophenes, poly(3,4-ethylenedioxythiophene) (PEDOT) is presumably the most studied one but few recent papers are reported on PMT/NPs composites [14–16] in spite of its interesting properties. Among the reported conducting polymer–metal composites,

platinum (Pt) is probably the most studied one. The fabrication and the subsequent characterization of palladium (Pd)-modified CP nanocomposites are not extensively reported in the literature [16,17]. On the other hand, the rate of charge or mass transport associated with redox reactions in modified films is commonly studied by determining the apparent diffusion coefficient ( $D_{\text{app}}$ ) [18].

The development of voltammetric sensors for the determination of catecholamine neurotransmitters and specially dopamine (DA) has received considerable interest during the last few years [15]. They include dopamine (DA), epinephrine (E), and norepinephrine (NE). They play important roles in various biological, pharmacological and physical processes [19]. Recently, attention has been paid to develop a new generation of modified electrodes involving monolayers, conducting polymers and nanoparticles able to solve efficiently the problems encountered in the conventional unmodified electrodes.

Electrochemical impedance spectroscopy (EIS) is an effective technique for probing the features of chemically modified electrodes and for understanding electrochemical reaction rates [20,21]. EIS was used to characterize Pt-modified polyaniline (PAN) film in  $\text{H}_2\text{SO}_4$  solution [22]. The results showed that compared with the pure polyaniline film/ $\text{H}_2\text{SO}_4$  solution interface, the deposition of platinum in the polyaniline matrix greatly reduces the electrochemical charge transfer resistance ( $R_{\text{ct}}$ ) in the platinum-modified polyaniline film/ $\text{H}_2\text{SO}_4$  solution interface.

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In the first part of this work, we have reported the modification of PMT polymer films with Pd particles [16]. In this paper, the electrochemistry of dopamine and other catecholamine neurotransmitters as well as ascorbic acid, acetaminophen and some organic compounds at the Pd nanoparticles modified PMT electrode are considered. Different methods were used for the formation of PMT films and the deposition of Pd nanoparticles. The effect of supporting electrolyte on the electrochemistry of these compounds is addressed as well. CV and CC are used for the determination of the apparent diffusion coefficient values for these compounds at different electrodes and electrolytes as it gives some information about the kinetics of charge transfer during the redox reactions of these compounds. The effect of the method of polymer film formation on the synergism between the polymer film and the subsequently loaded Pd particles is thoroughly studied. CV, CC, SEM and EIS measurements were used to address this point. EIS was used to study the capacitance and resistance of the metal modified polymer composites. Finally, this novel modified sensor electrode is used for the simultaneous detection of tertiary and quaternary mixtures of these compounds.

## 2. Experimental

### 2.1. Chemicals and reagents

All chemicals were used as received without further purification. 3-Methylthiophene (distilled under rotary evaporation prior to use) tetrabutyl ammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ ), acetonitrile (HPLC grade), hydroquinone, catechol, dopamine, epinephrine, norepinephrine, methyl-L-DOPA, p-aminophenol, acetaminophen, ascorbic acid, sulfuric acid, nitric acid, hydrochloric acid, phosphoric acid, perchloric acid, sodium sulfate, sodium nitrate, sodium chloride, and sodium phosphate were supplied by Aldrich Chem. Co. (Milwaukee, WI, USA). Palladium (II) chloride was supplied by Schering Kaul Paum AG, Berlin, Germany. Aqueous solutions were prepared using double distilled water.

### 2.2. Electrochemical cells and equipments

Electrochemical polymerization and characterization were carried out with a three-electrode/one-compartment glass cell. Experimental details can be found elsewhere [16]. All experiments were performed at 25 °C.

Electrochemical impedance spectroscopy was performed using a Gamry-750 system and a lock-in-amplifier that are connected to a personal computer. The data analysis software was provided

with the instrument and applied non-linear least square fitting with Levenberg-Marquardt algorithm. All impedance experiments were recorded between 0.1 Hz and 100 kHz with an excitation signal of 10 mV amplitude.

### 2.3. Electrodeposition of the polymer film on Pt electrode and further modification with Pd particles

Two electrochemical methods were employed for the deposition of the polymer film from a solution of 0.05 M 3-methylthiophene and 0.05 M  $\text{Bu}_4\text{NPF}_6$  in acetonitrile. In the first method (BE method) the potential applied between the platinum disc working electrode and the reference ( $\text{Ag}/\text{AgCl}$ ) is held constant at +1.8 V for 30 s (the electrode is indicated Pt/PMT(BE)). The second alternative (CV method) is to vary the potential with time, namely  $50 \text{ mV s}^{-1}$ , between two potential limits, ca.  $E_i = -0.1 \text{ V}$  and  $E_f = +1.8 \text{ V}$  for 15 cycles (the electrode is indicated Pt/PMT(CV)).

Further modification with Pd particles involves the following: a polymer film is prepared and washed with doubly distilled water. This was followed by the electrochemical deposition of Pd particles from a solution of 2.5 mM  $\text{PdCl}_2$  in 0.1 M  $\text{HClO}_4$  by applying a double potential step (BE) or cyclic voltammetric program (CV) to the polymer. The double potential step conditions are ( $E_i = -0.05 \text{ V}$ ,  $\Delta t_i = 30 \text{ s}$ ,  $E_f = +0.01 \text{ V}$ ,  $\Delta t_f = 300 \text{ s}$ ). In the cyclic voltammetric (CV) method, on the other hand, the electrode is cycled between  $-0.25 \text{ V}$  and  $+0.65 \text{ V}$  at a scan rate of  $50 \text{ mV s}^{-1}$  for 25 cycles [16]. Moreover, Pd particles were also deposited directly over Pt electrode.

## 3. Results and discussion

### 3.1. Electrochemistry of DA at Pt/PMT/Pd-modified electrodes

Initial studies of the voltammetric behavior of DA were performed using cyclic voltammetry. Fig. 1(A) compares typical cyclic voltammograms of  $5 \text{ mmol L}^{-1}$  dopamine in  $0.1 \text{ mol L}^{-1}$   $\text{H}_2\text{SO}_4$  recorded at four different working electrodes (i.e. bare Pt, Pt/PMT(BE), Pt/PMT(BE)/Pd(BE), and Pt/PMT(BE)/Pd(CV) electrodes). At bare Pt electrode, a poorly defined oxidation peak was observed at 664 mV whereas at Pt/PMT(BE) electrode the potential shifts negatively to 543 mV. Further, an increase in peak current is also observed due to the improvements in the reversibility of the electron transfer processes and the larger real surface area of the polymer film. The porous structure of conducting polymer allows dispersing the metal particles into the polymer matrix and generates additional electrocatalytic sites [23–25]. The electrodeposition of Pd particles on the polymer film causes a remarkable

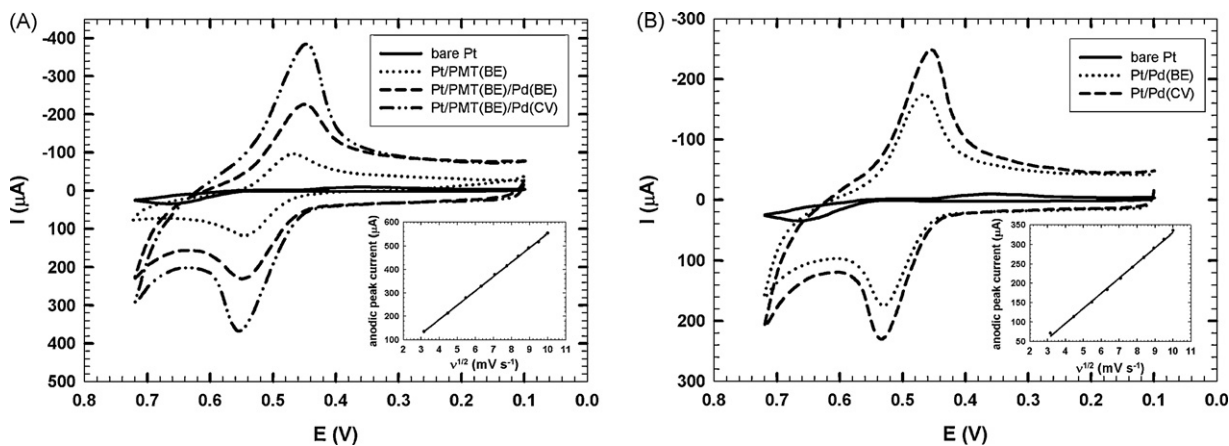


Fig. 1. Cyclic voltammetric behavior of  $5 \text{ mmol L}^{-1}$  DA/ $0.1 \text{ mol L}^{-1}$   $\text{H}_2\text{SO}_4$  at: (A) bare Pt, Pt/PMT(BE), Pt/PMT(BE)/Pd(BE), and Pt/PMT(BE)/Pd(CV) electrodes. (B) Bare Pt, Pt/Pd(BE) and Pt/Pd(CV) electrodes. Scan rate =  $50 \text{ mV s}^{-1}$ . (Inset: relationship between the square root of scan rate and anodic peak current.)

**Table 1**Summary of the cyclic voltammetry results obtained at Pt/PMT(BE), Pt/PMT(CV), Pt/PMT(BE)/Pd(BE), and Pt/PMT(BE)/Pd(CV) in 5 mmol L<sup>-1</sup> analyte/0.1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>.

Compound	Pt/PMT				Pt/PMT(BE)/Pd			
	BE <sup>a</sup>		CV <sup>a</sup>		BE <sup>b</sup>		CV <sup>b</sup>	
	<i>E</i> <sub>pa</sub> (mV)	<i>I</i> <sub>pa</sub> (μA cm <sup>-2</sup> )	<i>E</i> <sub>pa</sub> (mV)	<i>I</i> <sub>pa</sub> (μA cm <sup>-2</sup> )	<i>E</i> <sub>pa</sub> (mV)	<i>I</i> <sub>pa</sub> (μA cm <sup>-2</sup> )	<i>E</i> <sub>pa</sub> (mV)	<i>I</i> <sub>pa</sub> (μA cm <sup>-2</sup> )
Hydroquinone	446	103.2	473	80.3	443	164.1	455	262.2
Catechol	551	120.4	591	105.2	555	188.8	553	289.3
Dopamine	543	110.3	572	89.5	549	193.7	556	321.5
Methyl-L-DOPA	565	125.1	594	90.1	566	188.6	579	292.4
Epinephrine	574	99.6	596	79.9	561	144.4	561	249.2
Norepinephrine	573	110.9	593	80.2	556	134.2	556	215.1
p-Aminophenol	532	119.5	551	82.3	528	153.1	556	330.8
Acetaminophen	693	135.3	718	121.4	696	213.5	692	361.7
Ascorbic acid	360	58.5	362	47.4	311	128.6	314	197.6

<sup>a</sup> The method of formation of the polymer film.<sup>b</sup> The method of deposition of Pd particles.

increase in peak currents. Thus, the deposition of the polymer film on Pt electrode decreases the potential of oxidation substantially (i.e. thermodynamically feasible reaction). Further, the electrodeposition of Pd particles over PMT film enhances the redox current effectively indicating an improvement in the electrode kinetics by the presence of Pd particles. The remarkable enhancement in current response followed by a drop in peak potential provides clear evidence of the catalytic effect of the Pd-modified PMT electrodes that acts as a promoter to enhance the electrochemical reaction, considerably accelerating the rate of electron transfer.

Now, what about the catalytic effect of Pd particles when Pd is deposited directly to Pt electrode? CVs of 5 mmol L<sup>-1</sup> DA were recorded at Pt/Pd(BE) and Pt/Pd(CV) electrodes in 0.1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, Fig. 1(B). DA exhibits well-defined redox peaks at the Pd-modified electrodes with the oxidation potential shifted negatively to 466 and 456 mV at Pt/Pd(BE) and Pt/Pd(CV) electrodes, respectively. A substantial increase in the peak currents is also observed but it is still less than the corresponding values at Pt/PMT/Pd electrodes. The aforementioned results confirm the key role played by Pd particles on the catalytic oxidation of DA.

Further, the linear relationship between the peak current and square root of scan rate (Fig. 1, insets) in the scan rate range from 10 to 100 mV s<sup>-1</sup> points to the diffusion-controlled nature of DA oxidation on Pt/Pd and Pt/PMT/Pd electrodes.

### 3.2. Electrochemistry of catecholamine neurotransmitters, acetaminophen, and ascorbic acid

Initial studies of the voltammetric behavior of all compounds were performed using cyclic voltammetry. Tables 1 and 2 summarize the electrochemical data for the oxidation of some molecules of biological interest, namely, dihydroxy compounds (hydro-

quinone, catechol), catecholamine neurotransmitters (dopamine, epinephrine, and norepinephrine), methyl-L-DOPA, as well as p-aminophenol, acetaminophen and ascorbic acid. The data were collected from the cyclic voltammograms at Pt/PMT(BE), Pt/PMT(CV), Pt/PMT(BE)/Pd(BE), Pt/PMT(BE)/Pd(CV) and Pt, Pt/Pd(BE), Pt/Pd(CV) electrodes for the compounds indicated (BE refers to formation using bulk electrolysis and CV refers to formation using cyclic voltammetry of the corresponding interface). The scan rate is 50 mV s<sup>-1</sup>, and the analyte concentration is 5 mmol L<sup>-1</sup> in 0.1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> for the electrodes studied. Except for ascorbic acid and acetaminophen (undergo irreversible oxidation) all test substances displayed reversible behavior in 0.1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> electrolyte. From the biosensor point of view, the oxidation peak potential values, *E*<sub>pa</sub>, for these substances as well as their corresponding oxidation peak current values, *I*<sub>pa</sub>, are more important than their reversible behavior. Thus, all compounds show significant decrease in the *E*<sub>pa</sub> values at the Pd-modified electrodes. Moreover, the *I*<sub>pa</sub> increased in the following order: *I*<sub>pa</sub> values at Pt < Pt/PMT(BE) < Pt/PMT(BE)/Pd(BE) < Pt/PMT(BE)/Pd(CV) and Pt < Pt/Pd(BE) < Pt/Pd(CV). The electrodeposition of Pd over bare Pt- or PMT-modified electrode effectively enhances its electrocatalytic activity towards the oxidation of the indicated compounds. Furthermore, Pd-modified electrodes show excellent stability of the redox signal in the repeated cyclic voltammograms in solutions containing the compounds of study up to 50 cycles.

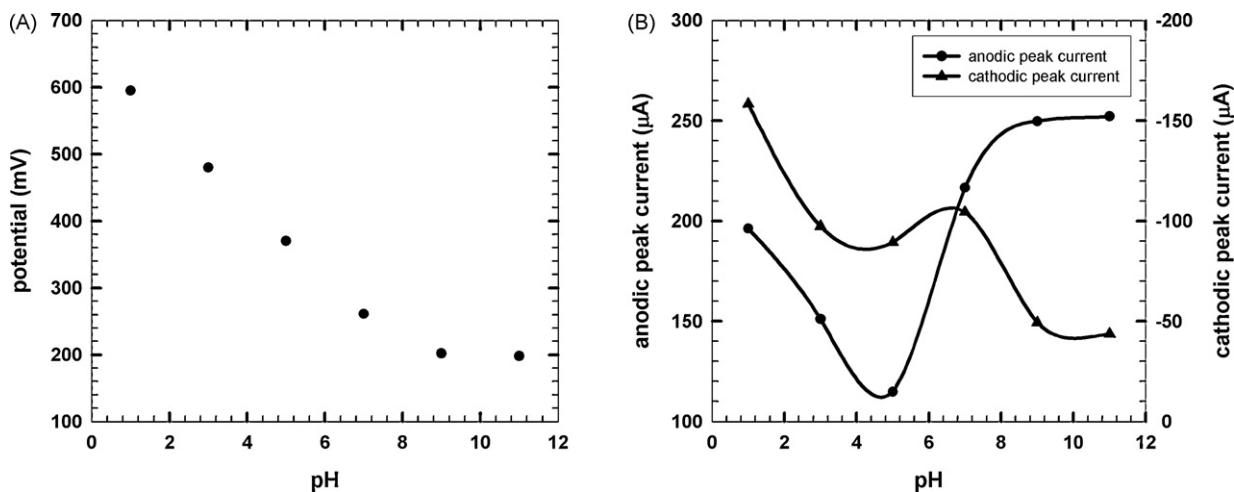
### 3.3. Effect of solution pH

The redox system should be affected by changes in pH because of the involvement of protons in the overall electrode reaction. The effect of changing the pH of the medium on the response of

**Table 2**Summary of the cyclic voltammetry results obtained at Pt, Pt/Pd(BE), and Pt/Pd(CV) electrodes in 5 mmol L<sup>-1</sup> analyte/0.1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>.

Compound	Pt		Pt/Pd			
			BE <sup>a</sup>		CV <sup>a</sup>	
	<i>E</i> <sub>pa</sub> (mV)	<i>I</i> <sub>pa</sub> (μA cm <sup>-2</sup> )	<i>E</i> <sub>pa</sub> (mV)	<i>I</i> <sub>pa</sub> (μA cm <sup>-2</sup> )	<i>E</i> <sub>pa</sub> (mV)	<i>I</i> <sub>pa</sub> (μA cm <sup>-2</sup> )
Hydroquinone	562	42.4	429	99.5	431	156.4
Catechol	686	32.9	536	120.1	538	177.2
Dopamine	664	34.7	530	160.2	534	214.1
Methyl-L-DOPA	689	31.2	543	80.5	558	165.9
Epinephrine	737	29.8	537	78.6	555	148.1
Norepinephrine	756	32.2	538	75.1	545	145.5
p-Aminophenol	617	25.1	523	109.8	532	160.4
Acetaminophen	728	38.8	695	173.6	694	226.9
Ascorbic acid	– <sup>b</sup>	– <sup>b</sup>	296	55.2	294	90.5

<sup>a</sup> The method of deposition of Pd particles.<sup>b</sup> No value was observed up to 1.2 V.



**Fig. 2.** Effect of solution pH on the electrochemical behavior of Pt/PMT(BE)/Pd(CV) electrode. (A) Dependence of the anodic peak potential of dopamine oxidation on solution pH. (B) Dependence of the anodic peak current of dopamine oxidation on solution pH. Results were taken from cyclic voltammograms carried out in 5 mmol L<sup>-1</sup> dopamine/0.1 mol L<sup>-1</sup> phosphate buffer of different pH values at a scan rate of 50 mV s<sup>-1</sup>.

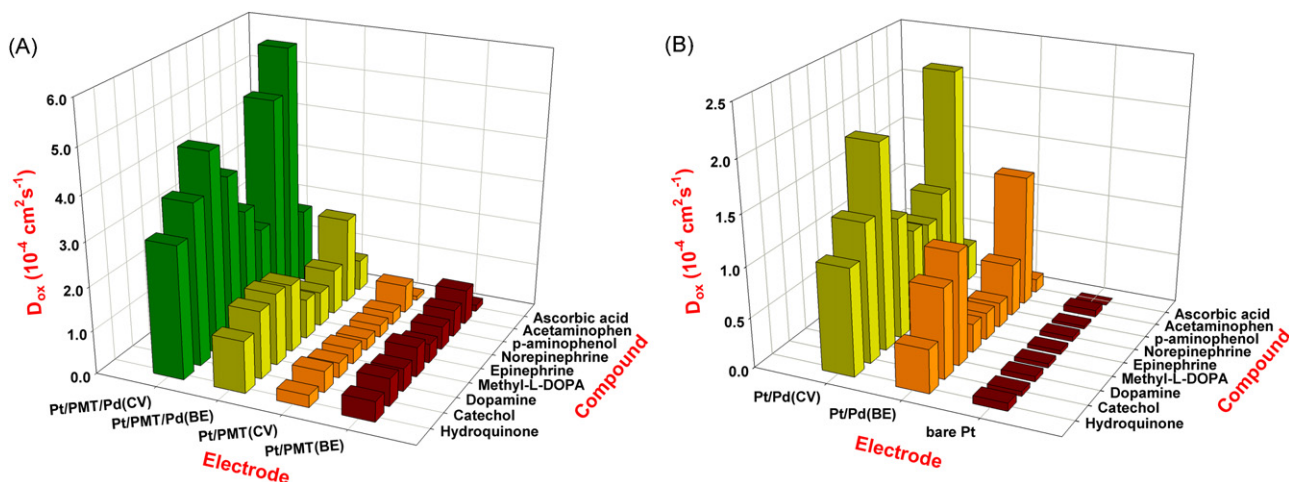
electrodes was examined in phosphate buffers. As illustrated in Fig. 2(A), the anodic peak potential shifts linearly to more negative values as pH increases over a range from 1 to 7. The slope is  $-55.6$  mV/pH unit for Pt/PMT(BE)/Pd(CV) electrode. The nearly Nernstian slope obtained here suggests two-proton, two-electron process for dopamine oxidation [26–28]. According to the Nernst equation, the slope of  $-55.6$  mV/pH reveals that the proportion of the electron and proton involved in the reactions is 1:1. As the dopamine oxidation is a two-electron process, the number of protons involved is also predicted to be two. In solution, the  $pK_a$ 's of dopamine are 8.9 ( $pK_{a1}$ ) and 10.6 ( $pK_{a2}$ ) [29]. A linear behavior was observed for pH values in the range from 1 to 7 and just a little deviation was obtained at pH 9. This indicates the deprotonation of dopamine at pH 9 so that it is no longer a two-proton, two-electron process at this point and other equilibria should be taken into account. At pH 11 the redox reaction of DA is no longer pH dependent as dopamine is completely deprotonated at this pH.

Fig. 2(B) shows that from pH 1 to 5 the anodic peak current decreases with increasing solution pH value. Dopamine exists in the protonated form at low pH values. The current of oxidation increases abruptly as the pH increases from 5 to 7. Further, beyond pH 7 the current increases with pH but at a lower rate.

### 3.4. Apparent diffusion coefficients of the studied compounds

The presence of the polymer film on the surface of an electrode tends to complicate the mathematical treatment required for the diffusion coefficient calculation [30]. It has been assumed, by many researchers, that the polymer film is another layer that the analyte or a counter anion has to penetrate in order for the electron to move through the film for a redox reaction to be observed. This movement of the charges through the polymer layer is known as the “electron hopping process” [31]. Effective diffusion coefficients for redox reactions at various polymer films were, as expected, much lower ( $10^{-10}$  to  $10^{-15}$  cm<sup>2</sup> s<sup>-1</sup> [32]) than those typically found in aqueous solution (ca.  $10^{-5}$  cm<sup>2</sup> s<sup>-1</sup> [33]). Furthermore, the effective diffusion coefficient values for different polymers can vary by several orders of magnitudes for the same analyte [34].

In this study, the dependence of the anodic peak current density on the scan rate has been used for the estimation of the “apparent” diffusion coefficient,  $D_{app}$ , of various organic species. 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



**Fig. 3.** Apparent diffusion coefficient values for all studied compounds as calculated from the oxidation segment of the corresponding CVs at: (A) bare Pt, Pt/Pd(BE), and Pt/Pd(CV) electrodes. (B) Pt/PMT(BE), Pt/PMT(CV), Pt/PMT(BE)/Pd(BE), and Pt/PMT(BE)/Pd(CV) electrodes.

of the value of  $D_{app}$  according to Randles Sevcik equation [35]:

$$i_p = 2.69 \times 10^5 n^{3/2} A C^0 D^{1/2} \nu^{1/2} \quad (1)$$

where  $i_p$  is the peak current density ( $A\text{cm}^{-2}$ ),  $n$  is the number of electrons transferred, at  $T=298\text{K}$ ,  $A$  is the geometrical electrode area ( $0.0176\text{cm}^2$ ),  $C^0$  is the analyte concentration ( $5 \times 10^{-6}\text{mol cm}^{-3}$ ),  $D$  is the diffusion coefficient of the electroactive species ( $\text{cm}^2\text{s}^{-1}$ ), and  $\nu$  is the scan rate ( $\text{Vs}^{-1}$ ). It is important to notice that the apparent surface area used in the calculations did not take into account the surface roughness, which is an inherent characteristics for all polymer films formed using the electrochemical technique. Fig. 3 shows  $D_{app}$  values at different electrodes for the studied compounds.

The calculated  $D_{app}$  values are between  $10^{-4}$  and  $10^{-7}\text{cm}^2\text{s}^{-1}$ . Those values were observed for the following electrodes: PMT-modified electrodes (Pt/PMT(BE), Pt/PMT(CV)), Pd-modified PMT electrodes (Pt/PMT(BE)/Pd(BE), Pt/PMT(BE)/Pd(CV)), bare Pt-, Pd-modified Pt electrodes (Pt/Pd(BE), and Pt/Pd(CV)).  $D_{app}$  values are higher than those reported earlier in the literature [36,37]. This is possibly due to the quick mass transfer of the analyte molecules towards electrode surface from bulk solutions and/or fast electron transfer process of electrochemical oxidation of the analyte molecule at the interface of the electrode surface and the solutions [38,39]. These results are consistent with recent publications [40–42]. Furthermore, it also shows that the redox reaction of the analyte species takes place at the surface of the electrode under the control of the diffusion of the molecules from solution to the electrode surface and not within the polymer and polymer/Pd matrices. From the data of Fig. 3 the following trends can be noticed:

- $D_{app}$  values for bare Pt and Pt electrodes modified with Pd increase in the following order: Pt < Pt/Pd(BE) < Pt/Pd(CV) which confirms the role of Pd particles in improving the electron transfer kinetics at the electrode/solution interface.
- $D_{app}$  values for PMT-modified Pt electrodes increases in the following order: Pt/PMT(CV) < Pt/PMT(BE) for all analytes studied. SEM micrographs show that Pt/PMT(BE) is more compact than Pt/PMT(CV), which seems to be more porous [16]. The compact structure of Pt/PMT(BE) enhances the diffusion of molecules at the electrode/solution interface. The diffusional current and the diffusion coefficients are therefore higher at the relatively more homogeneous Pt/PMT(BE) electrode.
- $D_{app}$  values for PMT electrodes modified with Pd particles using different methods increase in the following order: Pt/PMT(BE)/Pd(BE) < Pt/PMT(BE)/Pd(CV) for all analytes. SEM micrographs [16] show that the Pd particles are smaller and homogeneously distributed in the case of Pt/PMT(BE)/Pd(CV) electrode, while larger Pd particles with dendritic shape are observed in the case of Pt/PMT(BE)/Pd(BE) electrode. This confirms that the size and homogeneity of the deposited particles affect the electroactivity of these modified electrodes [43].

- $D_{app}$  values at the polymer modified electrodes increase in the following order: Pt/PMT(CV) < Pt/PMT(BE) < Pt/PMT(BE)/Pd(BE), Pt/PMT(BE)/Pd(CV) which is in agreement with the cyclic voltammetry results of Section 3.2.

### 3.5. Effect of the supporting electrolyte

In this section a study of the effect of different supporting electrolytes on the electrochemical behavior of different electrodes and the calculated diffusion coefficient values of dopamine at the studied electrodes are presented. It was reported that both redox potential and current depend on the kind of electrolyte used [4]. The supporting electrolytes used were acids ( $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{HClO}_4$ ,  $\text{HCl}$ , and  $\text{H}_3\text{PO}_4$ ) and their corresponding sodium salts ( $\text{Na}_2\text{SO}_4$ ,  $\text{NaNO}_3$ ,  $\text{NaCl}$ , and  $\text{Na}_3\text{PO}_4$ ). Furthermore, the effect of the method of polymerization on the synergistic electrocatalytic effect between the polymer film and the loaded metal particles towards the oxidation of DA in different supporting electrolytes is considered. For this reason, a comparison is made between the behavior of Pt/PMT(BE)/Pd and Pt/PMT(CV)/Pd, where Pd was deposited by the CV method.

The anodic peak potentials,  $E_{pa}$ , of DA for all the modified electrodes are much less positive than those obtained at the conventional Pt bare electrode in all electrolytes, Table 3. This confirms the catalytic effect of the modified surfaces over conventional electrodes. It is also important to notice that for Pt/PMT/Pd electrodes, where PMT is deposited by BE and CV methods,  $E_{pa}$  values are always lower at this electrode for which PMT is formed by BE method in all electrolytes. This suggests the higher catalytic activity of the PMT/Pd composite in which PMT is formed by BE method over that with CV method. In addition, this difference increases when the sodium salts were used as electrolytes. Moreover, the anodic peak currents,  $I_{pa}$  (Table 3) obtained at these electrodes increases in the following order irrespective of the electrolyte type Pt < Pt/PMT(BE) < Pt/Pd < Pt/PMT(BE)/Pd. This result agrees with the cyclic voltammetry data (Fig. 1) and it also shows that the relative electrocatalytic behavior of these electrodes is constant in all electrolytes.

#### 3.5.1. Diffusion coefficients of dopamine in different electrolytes

The diffusion coefficients,  $D_{app}$ , of DA in different electrolytes were calculated from cyclic voltammetry (CV), chronocoulometry (CC) experiments and the results were compared.  $D_{app}$  values were calculated from CV as in Section 3.4, while CC data were used to calculate the value of  $D_{app}$  according to the formula given by Anson [44]:

$$Q = \frac{2nFACD^{1/2}t^{1/2}}{\pi^{1/2}} \quad (2)$$

From the slope of the linear relationship between  $Q$  and  $t^{1/2}$ ,  $D$  can be determined if  $C$  (concentration,  $\text{mol cm}^{-3}$ ),  $A$  (surface area of the electrode,  $\text{cm}^2$ ), and  $n$  (electron transfer number) are known. Chronocoulometric experiments were performed in the solution

**Table 3**

Summary of the cyclic voltammetry results obtained at Pt, Pt/PMT(BE), Pt/Pd(CV), Pt/PMT(CV)/Pd, and Pt/PMT(BE)/Pd in  $5\text{mmol L}^{-1}$  DA/ $0.1\text{mol L}^{-1}$  electrolyte.

Electrolyte	Pt		Pt/PMT(BE)		Pt/Pd		Pt/PMT(CV)/Pd		Pt/PMT(BE)/Pd	
	$E_{pa}$ (mV)	$I_{pa}$ ( $\mu\text{A cm}^{-2}$ )	$E_{pa}$ (mV)	$I_{pa}$ ( $\mu\text{A cm}^{-2}$ )	$E_{pa}$ (mV)	$I_{pa}$ ( $\mu\text{A cm}^{-2}$ )	$E_{pa}$ (mV)	$I_{pa}$ ( $\mu\text{A cm}^{-2}$ )	$E_{pa}$ (mV)	$I_{pa}$ ( $\mu\text{A cm}^{-2}$ )
$\text{H}_2\text{SO}_4$	664	34.7	543	109.2	536	207.9	583	193.2	556	321.1
$\text{HNO}_3$	688	29.4	540	117.7	540	194.9	613	220.4	566	324.5
$\text{HClO}_4$	686	32.2	545	132.0	537	193.2	582	216.7	562	287.9
$\text{H}_3\text{PO}_4$	734	28.2	545	69.3	543	153.1	623	139.1	573	215.1
$\text{HCl}$	675	34.5	541	77.4	545	223.0	585	35.8	575	253.7
$\text{Na}_2\text{SO}_4$	605	22.56	466	49.2	451	118.9	580	73.7	493	184.2
$\text{NaNO}_3$	636	24.1	500	32.5	490	113.8	620	35.6	533	176.0
$\text{NaCl}$	671	23.5	530	45.4	496	110.1	601	32.6	539	163.2
$\text{Na}_3\text{PO}_4$	−72	12.1	−87	57.1	−88	99.7	−80	36.1	−85	148.4

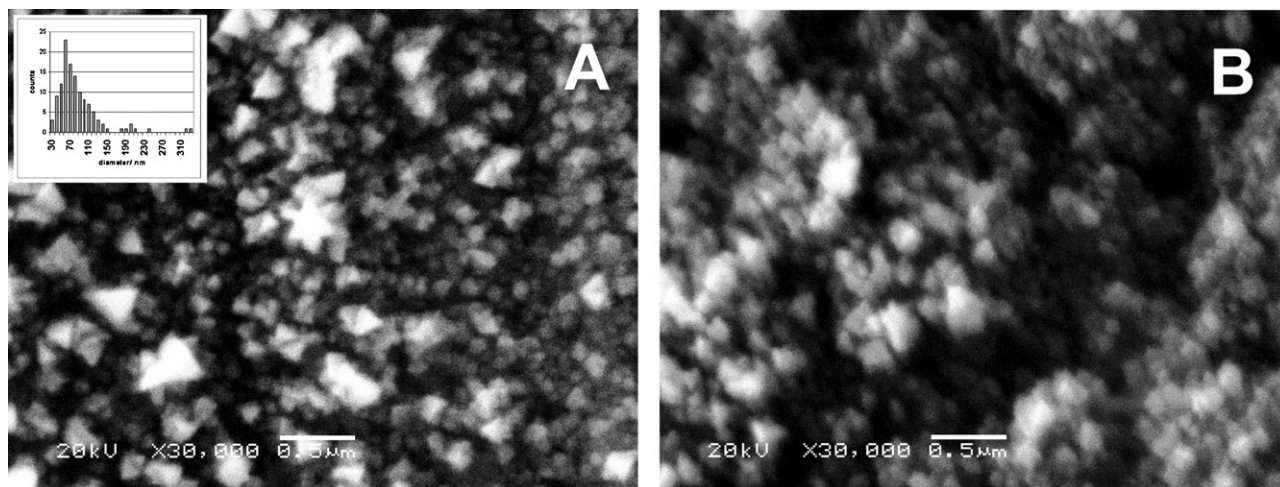


Fig. 4. SEM for (A) Pt/PMT(BE)/Pd(CV) and (B) Pt/PMT(CV)/Pd(CV). The inset: a histogram showing the particle size distribution.

containing dopamine and then the slope of the Anson plot is subtracted from the slope of the Anson plot of the same experiment carried out in the supporting electrolyte without the electroactive species. The resulting slope was then used to calculate  $D_{app}$  from the Anson equation shown above.  $D_{app}$  values obtained from CC were in close agreement with those calculated from CV measurements.  $D_{app}$  values range from  $10^{-7}$  to  $10^{-4}$   $\text{cm}^2 \text{s}^{-1}$ . These values are close to the values of  $D_{app}$  in solution. Again, this is possibly due to the fast mass transfer of the analyte molecules towards electrode surface from bulk solutions and/or fast electron transfer process of electrochemical oxidation of the analyte molecule at the interface of the electrode surface and the solutions [38,39].

$D_{app}$  values of DA increase in the following order in all electrolytes Pt < Pt/PMT(BE) < Pt/Pd(CV) < Pt/PMT(BE)/Pd(CV). However, the diffusion coefficients at Pt/PMT(CV)/Pd(CV) electrode are always lower than Pt/PMT(BE)/Pd(CV). The difference between these two electrodes increases in neutral and alkaline media in which  $D_{app}$  values at Pt/PMT(CV)/Pd(CV) are even lower than the individual Pt/PMT and Pt/Pd electrodes. SEM analysis can be used to confirm the difference in morphology between Pt/PMT(CV)/Pd(CV) and Pt/PMT(BE)/Pd(CV) electrodes, Fig. 4. Thus, higher loading of Pd with smaller particle size is achieved at the latter electrode. The particle size distribution obtained at Pt/PMT(BE)/Pd(CV) indicates that the most frequent particle size is around 60 nm. Thus, the amount of Pd, particle size, better distribution as well as the different morphologies of the polymer substrate and the difference in the doping level of the polymer films [16] may be the reason for the difference between these two electrodes.

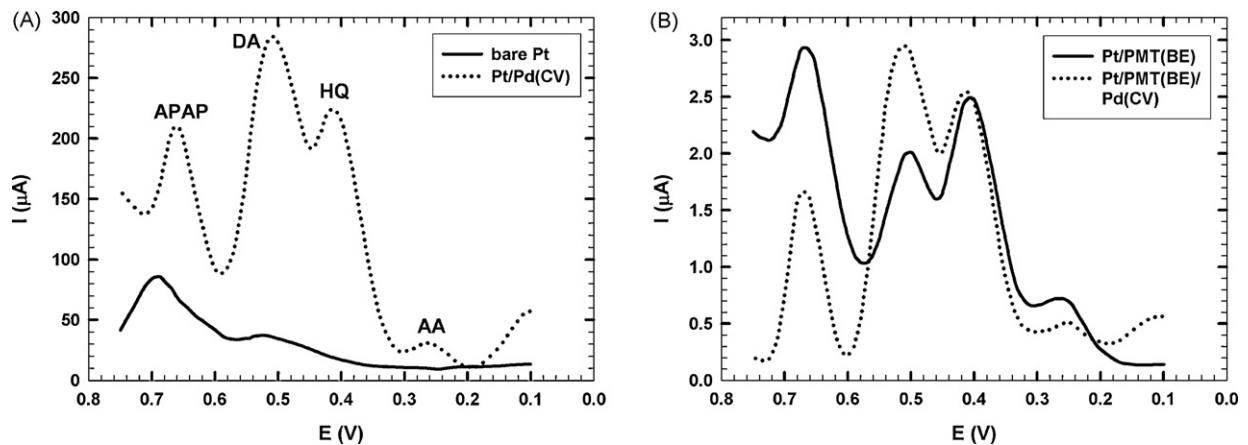
### 3.6. Analysis of mixtures

The determination of catecholamines in biological samples is crucial for the diagnosis of many diseases [45]. However, electrochemical oxidation of catecholamines especially dopamine (DA) at conventional electrodes is found difficult because of (a) fouling of the electrode surface due to the adsorption of oxidation products, (b) interference due to the co-existence of interfering compounds such as ascorbic acid (AA) and others in the biological fluids, which also undergoes oxidation more or less at the same potential [46].

Acetaminophen (paracetamol), APAP, is also likely to interfere with DA and AA determination [47]. To our knowledge, only one report was published for the analysis of AA, DA, and APAP mixture [41]. The differential pulse voltammograms (DPV) for the analysis of a tertiary mixture of  $5 \text{ mmol L}^{-1}$  AA,  $5 \text{ mmol L}^{-1}$  DA, and  $5 \text{ mmol L}^{-1}$

APAP in  $0.1 \text{ mol L}^{-1}$   $\text{H}_2\text{SO}_4$  over bare Pt and Pt/Pd (CV) electrodes was measured. An unresolved oxidation peak was observed in the potential range from 0.1 to 0.75 V illustrating that the oxidation peaks of AA, DA, and APAP cannot be separated on the bare Pt. When the Pt/Pd(CV) electrode was used, three well-separated signals were obtained. The anodic peak potentials of AA, DA, and APAP oxidations on the Pt/Pd(CV) electrode were at approximately 256, 500, and 656 mV, respectively. DPVs for the analysis of the same mixture of AA, DA, and APAP, at Pt/PMT(BE) and Pt/PMT(BE)/Pd(CV) electrodes were also measured. Three oxidation peaks appeared on each electrode corresponding to AA, DA, and APAP. The oxidation potentials on Pt/PMT are observed at 268, 500, and 664 mV for AA, DA, and APAP, respectively. On the other hand, the oxidation peaks of AA, DA, and APAP on Pt/PMT(BE)/Pd(CV) electrode appeared at 260, 508, and 670 mV, respectively. Therefore, better separation of the signals was achieved on Pt/PMT(BE)/Pd(CV) electrode. Furthermore, Pt/PMT(BE)/Pd(CV) electrode has high selectivity for the determination of DA in the presence of AA and APAP. This can be checked by investigating the values of oxidation current on both electrodes. Lower oxidation current for AA and APAP, higher oxidation current for DA was achieved at Pt/PMT/Pd(CV) electrode with respect to Pt/PMT electrode. Hence, DA can be easily determined on Pt/PMT/Pd electrode even in the presence of higher concentration of AA and APAP (analysis of DPV results indicate that DA/AA current ratio = 19.1:1 on Pt/PMT/Pd(CV) and 2.98:1 on Pt/PMT). A comparison of the behavior of these electrodes with respect to the oxidation of DA and AA shows the synergism between the polymer matrix and the embedded Pd nanoparticles.

Fig. 5 shows the DPV results for the analysis of a quaternary mixture containing  $5 \text{ mmol L}^{-1}$  AA,  $5 \text{ mmol L}^{-1}$  hydroquinone (HQ),  $5 \text{ mmol L}^{-1}$  DA, and  $5 \text{ mmol L}^{-1}$  APAP in  $0.1 \text{ mol L}^{-1}$   $\text{H}_2\text{SO}_4$ . When this mixture is analyzed on bare Pt electrode (Fig. 5(A)), a rather broad oxidation peak was obtained and the peak potentials of the existing species were indistinguishable. It is therefore impossible to determine the individual concentrations of these compounds because of the merged voltammetric oxidation peak. However, modification of the Pt electrode with Pd particles resolved the merged voltammetric peak into four well-defined peaks at potentials around 264, 408, 504, and 656 mV for AA, HQ, DA, and APAP, respectively. Fig. 5(B) shows the same results as in Fig. 5(A) but on Pt/PMT(BE) and Pt/PMT(BE)/Pd (CV) electrodes. Again, better selectivity for the resolved determination of DA was achieved at Pt/PMT(BE)/Pd(CV) electrode as the current due to the interferences (AA and APAP) has been decreased while at the same time the current due to DA has been increased.



**Fig. 5.** DPVs for a quaternary mixture of 5 mmol L<sup>-1</sup> AA, 5 mmol L<sup>-1</sup> HQ, 5 mmol L<sup>-1</sup> DA and 5 mmol L<sup>-1</sup> APAP in 0.1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> at: (A) bare Pt and Pt/Pd(CV) electrodes and (B) Pt/PMT(BE) and Pt/PMT(BE)/Pd(CV) electrodes. DPV conditions: pulse amplitude = 50 mV, scan rate = 20 mV s<sup>-1</sup>, sample width = 17 ms, pulse width = 50 ms.

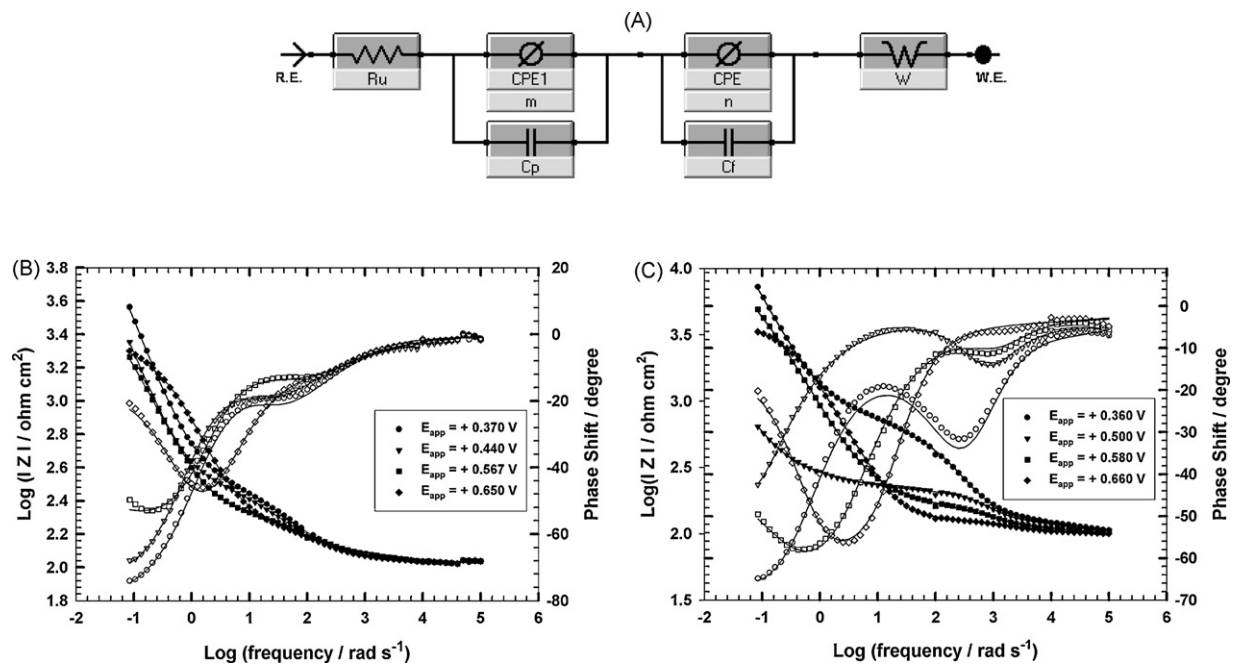
### 3.7. Electrochemical impedance spectroscopy (EIS) studies

EIS data were obtained for PMT modified with Pd particles at ac frequency varying between 0.1 Hz and 100 kHz with an applied potential in the region corresponding to the electrolytic oxidation of dopamine in 0.1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>. Effect of the method of formation of PMT on the synergistic effect between the polymer film and the loaded metal particles was studied. The data are presented as a relation between the impedance and the frequencies, the Bode plot. In all cases the experimental data will be compared to an “equivalent circuit” that uses some of the conventional circuit elements, namely: resistance, capacitance, diffusion and induction elements. Thus, it is anticipated that the changes in the conditions of the experiments, as will be described, are reflected on the electrochemical parameters. The equivalent circuit is shown in Fig. 6A. In this circuit,  $R_u$  is the solution resistance. Capacitors in EIS experiments often do not behave ideally; instead they act like a constant phase element (CPE). Therefore, CPE1 and CPE are constant phase elements and  $m$  and  $n$  are their corresponding exponents ( $m, n$  are less than

one).  $C_p$  and  $C_f$  represent the capacitance of the double layer. Diffusion can create an impedance known as the Warburg impedance,  $W$ .

Table 4 lists the best fitting values calculated from the equivalent circuit (Fig. 6A) for the impedance data of Fig. 6(B and C). The average error ( $\chi^2$ ) of the fits for the mean error of modulus was in the range:  $\chi^2 = (1.5\text{--}3.8) \times 10^{-2}$ . The following observations and conclusions could be drawn from Table 4:

- For PMT films formed by CV and relatively high applied potentials, the capacitive component of the film increases as expected and is in good agreement with the CVs that depicts a behavior similar to a capacitor with relatively large capacitance value [48,49]. On the other hand, PMT films formed by BE show relatively decreased values of the capacitive component indicating a more porous character of the films as confirmed by SEM pictures.
- It is important to notice that ionic species are solvated and their migration within the polymeric film depends on the pore size of the film. And since anionic species are the major components



**Fig. 6.** (A) Equivalent circuit used in the fit procedure of the impedance spectra. The results were analyzed using Levenberg–Marquardt/simplex algorithms based on a complex non-linear least squares procedure. The Bode plot of impedance spectra for (B) Pt/PMT(BE)/Pd(CV), (C) Pt/PMT(CV)/Pd(CV) all tested in 5 mmol L<sup>-1</sup>/0.1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>.

**Table 4**  
EIS fitting data corresponding to Fig. 6(B and C), where I = Pt/PMT(BE)/Pd(CV), II = Pt/PMT(CV)/Pd(CV).

Electrode	$E/V$	$R_u (\Omega \text{ cm}^2)$	$CPE1 (\text{F cm}^{-2})$	$m$	$C_p (\mu\text{F cm}^{-2})$	$CPE (\text{F cm}^{-2})$	$n$	$C_f \mu\text{F cm}^{-2}$	$W (\Omega \text{ s}^{-1/2})$
I	+0.370	110.5	13,990	0.700	509	383.7	0.227	11.29	101.7
	+0.440	110.6	16,230	0.199	996	431.9	0.269	7.789	10.0
	+0.567	109.2	246.3	0.219	8.29	2146	0.284	762.5	40.0
	+0.650	108.3	30.8	0.280	6.59	1371	0.131	239.3	60.0
II	+0.360	116.7	899	0.15	2.22	29,170	0.10	353	987.1
	+0.500	111.2	181	0.10	1.59	544	0.52	2780	40.0
	+0.580	104.7	56	0.05	3.17	4123	0.35	234	786.6
	+0.660	99.8	2796	0.17	0.978	200	0.26	1.69	60.0

compensating for the charge within the polymer film [48,50], contribution of solvent used that may catalytically decompose at the film/electrolyte interface is not expected except at relatively high applied potentials. Thus, polarization resistance appreciably decreases with increase in applied potential for films formed by CV or BE. The change in polarization resistance is more pronounced in the case of films prepared by BE. This could be attributed to a change in morphology that is mainly dictated by the porosity of the films. The shape and compactness of each film, namely those formed by two different synthetic methods, should also contribute to the rate and mechanism of charge transfer leading to the remarkable impedance characteristics of each film.

- Moreover, the impedance response of the films at the low-frequency domain should be controlled by the capacitive elements. However, the deposition of the film layer for instance leads to depreciated effect for applied potential for various polymer types and electrochemical method used for deposition.
- From the data indicated in Table 4, the value of solution resistance,  $R_u$ , is almost constant within the limits of the experimental errors. On the other hand, the ionic/electronic charge transfer resistance,  $CPE$ , shows gradual increase then decrease in value with the applied potential indicating that the migration of ionic species within the film pores is not the only mean of charge exchange at the polymer/electrolyte interface. This is also observed with the relative change in the value of the Warburg impedance,  $W$ , which changes accordingly with the charge transfer resistances. The last observation indicates the key role played by the morphology, film composition, and its thickness in the charge transfer. Another indication of this model is proved by the noticed increase in the capacitance values with applied potential and whether the film is formed by CV or BE methods.
- It is important to notice that for all films, the charge transfer shows relatively small changes before reaching full oxidized polymer films. This indicates that while the ionic conductance within the film is a function of potential and nature of the film, the electronic conductance is not affected with the same conditions. Therefore,  $CPE$  represents mainly electronic resistance while  $CPE1$  represents the predominant diffusion influence on the charge transfer process.

Although the general trend for all films indicate a gradual shift to lower impedance values with applied potential, it would be difficult within the scope of this study to clarify the relation between the pore size and the film morphology and their influence on the subsequent effect on the metal deposition.

#### 4. Conclusions

The electrochemistry of DA and other catecholamines as well as ascorbic acid and acetaminophen at Pt/PMT/Pd electrodes was studied. A remarkable enhancement in current response followed by a drop in peak potential was observed which provide clear evi-

dence of the catalytic effect of the Pd-modified PMT electrodes. What was interesting is the Pt electrodes modified with Pd particles (Pt/Pd) which resulted in well-defined redox peaks with low oxidation potential and high peak current values. This result puts this kind of metal modified Pt electrodes in the category of promising and highly electroactive modified electrodes. The apparent diffusion coefficients were also calculated at different electrodes and electrolytes for the compounds studied.  $D_{app}$  values indicate quick mass transfer of the analyte molecules towards electrode surface from bulk solutions and/or fast electron transfer process of electrochemical oxidation of the analyte molecule at the interface of the electrode surface and the solutions. Furthermore, it was found that the method of polymerization had a substantial effect on the synergism between the polymer film and the loaded metal particles towards the oxidation of DA in different supporting electrolytes. This was confirmed from the CV, CC, EIS and SEM results. Pt/PMT(BE)/Pd(CV) and Pt/Pd(CV) electrodes showed excellent results for the simultaneous determination of tertiary and quaternary mixtures of the studied compounds. EIS was used to study the capacitance and resistance of the metal modified polymer composites.

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