

# Preparation of Poly-N-Methylpyrrole - Coated Platinum Modified Electrode in Chloroform in the Presence of Various Supporting Electrolytes and Its Use for the Catalytic Oxidation of Ascorbic Acid and Hydroquinone

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**ABSTRACT:** *The electrochemical preparation of poly-N-methylpyrrole (PMPy) coated platinum electrode in chloroform in the presence of tetrabutylammonium Perchlorate, hexafluorophosphate, hydrogensulphate, Periodate and Iodide as supporting electrolytes was performed. The influence of electrosynthesis method, dopant anion type and operation temperature on electrochemical behavior of polymer were demonstrated. The electrocatalytic effect of the PMPy-coated electrode revealed by its oxidation of ascorbic acid and hydroquinone in water. The electrochemical data show the occurrence of a redox reaction at the film/solution interface. Results in comparison to the literature show that the electrocatalytic effect of PMPy prepared in chloroform is greater than the polypyrrole prepared in this solvent and also PMPy prepared in acetonitrile has greater electrocatalytic effect than PMPy prepared in chloroform. The calculated heterogeneous electron transfer rate constant ( $K^0$ ) at the PMPy-modified Pt electrode at 25° C was  $8 \times 10^{-4} \text{ cms}^{-1}$  which is 800-fold greater than the value ( $<10^{-6} \text{ cms}^{-1}$ ) reported for bare Pt electrode.*

**KEY WORDS:** *Electropolymerization, Electrocatalysis, Poly N-methylpyrrole, Ascorbic acid, Hydroquinone, Chloroform.*

## INTRODUCTION

Electrocatalysis of chemical reactions is one of the important applications of chemically modified electrodes, polypyrrole (PPy) and its derivatives have received much attention since 1979 when it was synthesized by Diaz *et al* [1]. The ability of the PPy and Poly-N-methylpyrrole (PMPy) in electrocatalysis of some electrochemical reaction have been reported [2-4]. investigations have shown the influence of solvent, supporting electrolyte, operation temperature, monomer concentra-

tion and the method of electropolymerization on the properties of these Polymers [5-7]. According to previous studies, the polymerization of N-methylpyrrole is performed in aprotic solvents and acetonitrile [7] as the most commonly used solvent. Previously, PMPy was prepared on a gold electrode in acetonitrile [2] and its electrocatalytic effects demonstrated.

The aim of the present work is the electrosynthesis of the PMPy on a Pt electrode in chloroform as a convenient

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aprotic solvent with low dielectric constant where in electropolymerization proceeds via a radical mechanism. We have demonstrated the influence the type of dopant anion, electropolymerization method and operation temperature. In this context we report the ability of the PMPy-coated Platinum modified electrode prepared in chloroform in catalysing some slow oxidation processes in aqueous and solution and compare it with the ability of the PMPy-coated platinum modified electrode prepared in acetonitrile [2] and the PPy-coated platinum electrode prepared in chloroform [4].

## EXPERIMENTAL

### Chemicals

The solvent used was reagent grade chloroform from E Merck (Darmstadt ,Germany). N-methylpyrrole was from Aldrich -Milwaukee , WI, U.S.A, (it was vacuum distilled twice and then stored under nitrogen), the supporting electrolytes were tetrabutylammonium perchlorate (TBAP), hexafluorophosphate (TBAHFP), hydrogensulphate (TBAHS), Iodide (TBAI) and periodate (TBAPI) were obtained from Fluka (Buchs , Switzerland). Other reagents were of analytical grade, water was deionized and distilled. All solutions were bubbled with  $N_2$  gas (99.999%) during the electrochemical experiments.

### Apparatus

All voltammograms were records with three electrode system using a Taccussel potentiostat/ galvanostat model PJI 35-2, Taccussel triangular-rectangular wave signal generator model GSTP4 (Taccussel Co., France) and Yokogawa X-Y recorder (3023, Yokogawa Co., Japan). A conventional three electrode cell, with calomel and a platinum disk electrode ( $A=0.145\text{ cm}^2$ ) as working electrode were used (Zu 628, Metrohm). A pH meter model 250 (Corning from England) was used to adjust of the pH of buffer solutions.

### Electropolymerization

The working electrode surface was polished using a thin layer of fine alumina powder ( $0.05\mu\text{m}$ ) then washed with water and acetone, respectively and used after drying. The PMPy films were prepared in 0.25 M solutions

of the different Supporting electrolytes and 0.05 M N-methylpyrrole in chloroform. In the potentiostatic method the applied potential was 0.15 V vs. the reference electrode. In the galvanostatic method, the current density was  $250\ \mu\text{A}$  ( $E=1.1\text{ V}$ ) and in the potentiodynamic method the potential was scanned between 0 and 1.2 V with a scan rate of  $50\text{ mVs}^{-1}$ . During the polymerization, the solution was thermostatted.

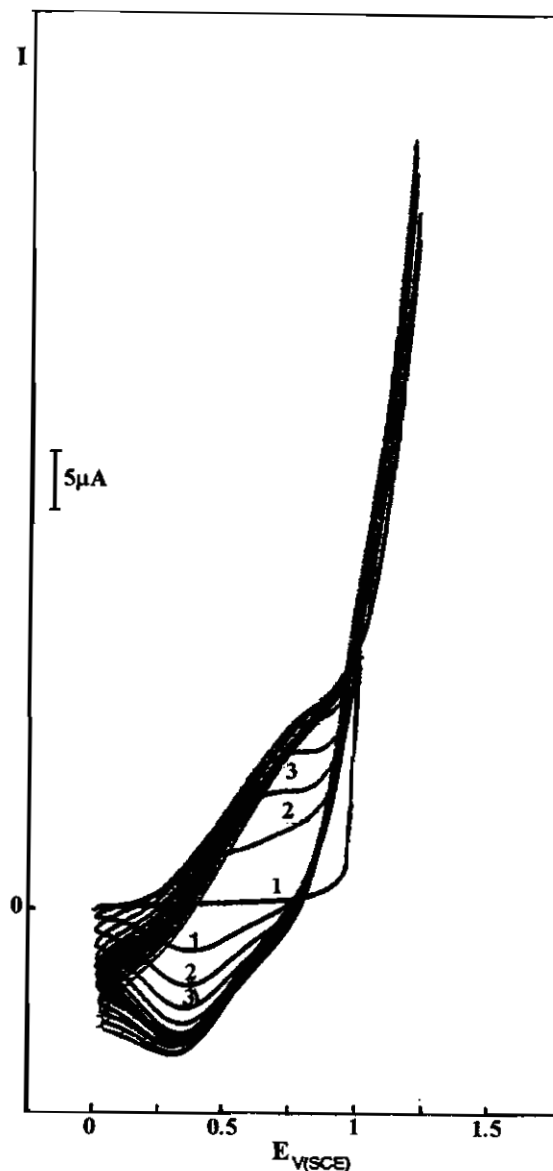


Fig. 1 : Cyclic voltammograms (CVs) of Pt electrode in chloroform solution containing 0.25 M N-methylpyrrole and 0.25 M TBAP, during the electropolymerization at consecutive cycles.  $v=50\text{ mVs}^{-1}$ .

## RESULTS AND DISCUSSION

### Electrochemical behavior of Polymer during the electropolymerization

Cyclic voltammograms (CVs) of bare Pt electrode were recorded in 0.25 M TBAP-chloroform solution in the presence of the monomer (Fig.1).

The potentials for the oxidation of N-methylpyrrole in chloroform and the peaks related to doping-undoping cycle of polymer synthesized during first scan and in the second scan of potentials were observed about 1.1 and 0.45 V, respectively. It can be seen that after the second scan the height of oxidation-reduction peak of polymer gradually increase and their position of potentials shift to positive values. The oxidation-reduction process for the polymer synthesized on Pt electrode may be shown as follows :



Or



Where subscripts s, f and m refer to solution, polymer and metal respectively, and A<sup>-</sup> and B<sup>+</sup> show the anion or cation intervening in the doping-undoping cycle.

### Influence of the electropolymerization conditions

The parameters affecting the electroactive properties of the PMPy films include: the type of dopant anion, method of electropolymerization and the operation temperature. Cyclic voltammograms (CVs) of the PMPy-ClO<sub>4</sub><sup>-</sup> films prepared by different electrochemical methods such as galvanostatically, potentiostatically and potentiodynamically in the chloroform solution, were recorded in aqueous LiClO<sub>4</sub> (0.1 M) and in the absence of the monomer (Fig.2).

It can be seen that, the PMPy film prepared by the galvanostatic method was oxidized at relatively lower potential values than others and gave redox peaks with a low charging current in comparison to other methods used. Therefore we used galvanostatic method for the preparation of polymeric film on the surface of the Pt electrode. The PMPy films prepared by all methods used were very stable and quasi-metallic dark-green.

The CVs of the PMPy-coated Pt electrodes prepared in solution of dopant anion such as per-chlorate, hexaflu-

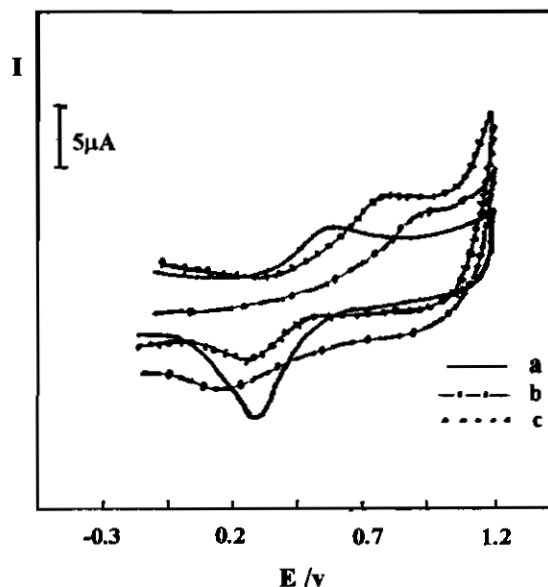


Fig. 2 : The CVs of PMPy-ClO<sub>4</sub><sup>-</sup> coated pt electrode in 0.1 M LiClO<sub>4</sub> aqueous solution. (1) galvanostatically, (2) potentiodynamically and (3) potentiostatically. The time of deposition was 150 s, V=50mVs<sup>-1</sup>.

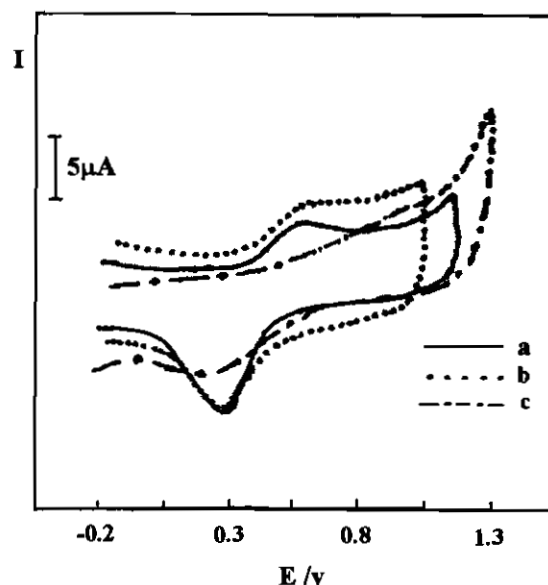


Fig. 3: The CVs of PMPy-coated pH electrode in 0.1 M LiClO<sub>4</sub> aqueous solution with pH 2.5, prepared in chloroform in the presence of various dopant anions at room temperature. (a) perchlorate, (b) hexafluorophosphate and (c) hydrogensulphate. The method of galvanostatic was employed (the current density 250 nA and the time of deposition 150 s), V=50 mVs<sup>-1</sup>.

orophosphate and hydrogensulphate in chloroform are showing in fig.3.

As can be seen, the PMPy film prepared by galvanostatic method in chloroform solution containing  $\text{ClO}_4^-$  was oxidized at a lower potential value and gave a smaller separation peak ( $\Delta E_p$ ) than the others. This may be attributed to (1) high oxidation level as high conductivity of polymer containing  $\text{ClO}_4^-$  [7], (2) relatively effective doping in the presence of 0.1 M  $\text{ClO}_4^-$  solution and (3) preventing release of the  $\text{ClO}_4^-$  ion in the PMPy- $\text{ClO}_4^-$  film placed in  $\text{ClO}_4^-$  solution [4]. For  $\text{IO}_4^-$  ion the stability of PMPy- $\text{IO}_4^-$  film was considerably low, probably owing to its high oxidizing power. The electropolymerization of N-methylpyrrole in  $\text{CHCl}_3$ -Iodide solution did not occur. On the other hand the chronopotentiogram recorded during the galvanostatic polymerization showed that the potential of working electrode did not remain at 1.1 V (electropolymerization potential of N-methylpyrrole) and immediately shifted to a very positive values. At the same time, the surface of the working electrode was contaminated by the formation of insoluble oligomers and conductivity of the electrode fell dramatically. This behaviour may be attributed to the nucleophilicity of  $\text{I}^-$  preventing the growth of the polymer chain[12].

The influence of temperature on the electroactive properties of the PMPy was examined using the PMPy- $\text{ClO}_4^-$ -coated Pt electrode prepared at various temperatures (0-35°C with temperature step of 5°C) in the chloroform solution of 0.25 M TBAP. The CVs of the PMPy-coated Pt electrodes prepared at different temperatures in water revealed that the electroactive behaviour of the polymer in temperature range examined are similar and do not vary.

#### Oxidation of ascorbic acid on the surface of PMPy-modified electrode

The CVs of ascorbic acid on bare and the PMPy-coated Pt electrodes in 0.1 M  $\text{LiClO}_4$  aqueous solution at pH 2.5 and 7 are show in fig.4. The oxidation peak of ascorbic acid is about 420 mV (pH=7) and 450 mV (pH=2.5) on the bare electrode which decreased to 265 mV and 325 mV at pH 7 and 2.5 on the PMPy-coated electrode respectively.

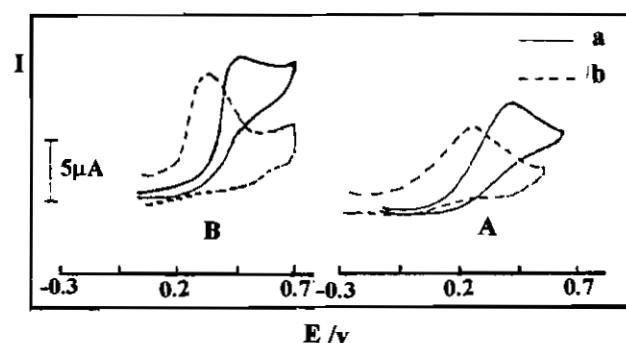


Fig. 4 : The CVs of  $10^{-3}\text{M}$  ascorbic acid (a) on bare pt electrode, (b) PMPy- $\text{ClO}_4^-$ -coated pt electrode in 0.1 M  $\text{LiClO}_4$  aqueous solution, A (pH 7), B (pH 2.5) with  $\nu=50\text{ mVs}^{-1}$ . The polymer was as same Fig.3.

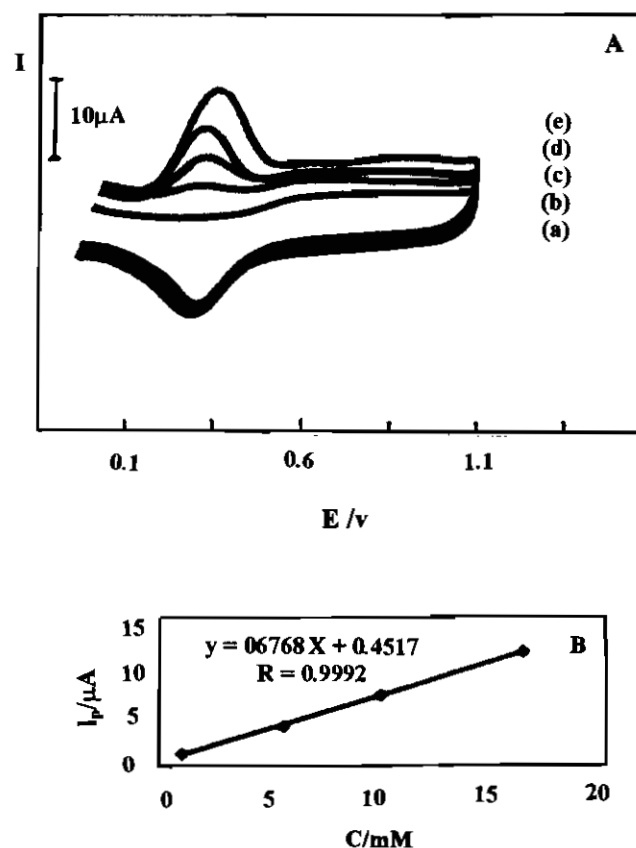


Fig. 5 : (A) The CVs of PMPy- $\text{ClO}_4^-$ -coated pt electrode in 0.1 M  $\text{LiClO}_4$  aqueous solution containing various concentration of ascorbic acid (a) 0, (b)  $9.9 \times 10^{-4}$ , (c)  $5.6 \times 10^{-3}$ , (d)  $9.9 \times 10^{-3}$  and (e)  $1.63 \times 10^{-2}\text{M}$ , pH 2.5. The polymer was as Fig.4,  $\nu=50\text{ mVs}^{-1}$ . (B) The plot of  $i_p$  against of the ascorbic acid concentration.

The decrease of the oxidation potential peak for ascorbic acid from 420 mV on the bare electrode to 265 mV on the PMPy-coated electrode in pH 7 illustrates the 155 mV electrocatalytic effect of the polymer on the oxidation of ascorbic acid in water. This electrocatalytic effect is less than the electrocatalytic effect of ppy polymer prepared in water [10] or alumina-coated/impregnated glassy carbon electrodes as these are equal to about 300 mV [11].

A plot of the oxidation peak current ( $i_p$ ) of ascorbic acid on the PMPy-coated electrode versus the  $V^{1/2}$  (square root of scan rate of potential) and  $V$  (scan rate of potential) according to fig.5A revealed a correlation coefficient of 0.9921 and 0.9691 respectively, indicating a probable linear diffusion (Fig.5B).

Fig. 6A indicates CVs of the PMPy-coated electrode in aqueous solution containing different concentration of ascorbic acid. As can be seen, the height of reduction peak (at reverse scan) for the polymer is constant in all cases and the peaks related to ascorbic acid show an increase with the increase in ascorbic acid concentration ( $r = 0.9993$ ). From the calibration curve (fig.6B) the limiting of detection on based of  $2\sigma$  is obtained  $2.8 \times 10^{-4}$  M for the PMPy-coated electrode.

#### Oxidation of hydroquinone (H<sub>2</sub>Q) on the PMPy-coated electrode

The CVs of H<sub>2</sub>Q on the bare and PMPy-coated electrodes in 0.1 M LiClO<sub>4</sub> aqueous solution at pH 2.5 are shown in fig.7. The separation of potential peaks ( $\Delta E_p$ ) is equal to 480 mV on the bare electrode which decreased to 125 mV on the PMPy-coated electrode at the scan rate of 100 mVs<sup>-1</sup>.

This decrease can be attributed to 355 mV electrocatalytic effect of the polymer on the oxidation of hydroquinone. The value of  $\Delta E_p$  for oxidation of hydroquinone on polypyrrole prepared in chloroform [4] is equal to 170 mV at the scan rate of 100 mVs<sup>-1</sup>. This value shows that the electrocatalytic effect of the PMPy is larger than the polypyrrole in oxidation of hydroquinone. On the other hand  $\Delta E_p$  value for the oxidation of hydroquinone on the PMPy prepared in acetonitrile (aprotic solvent with high dielectric constant in comparison to chloroform) is 60 mV at the scan rate of 10 mVs<sup>-1</sup> [2], showing that the elec-

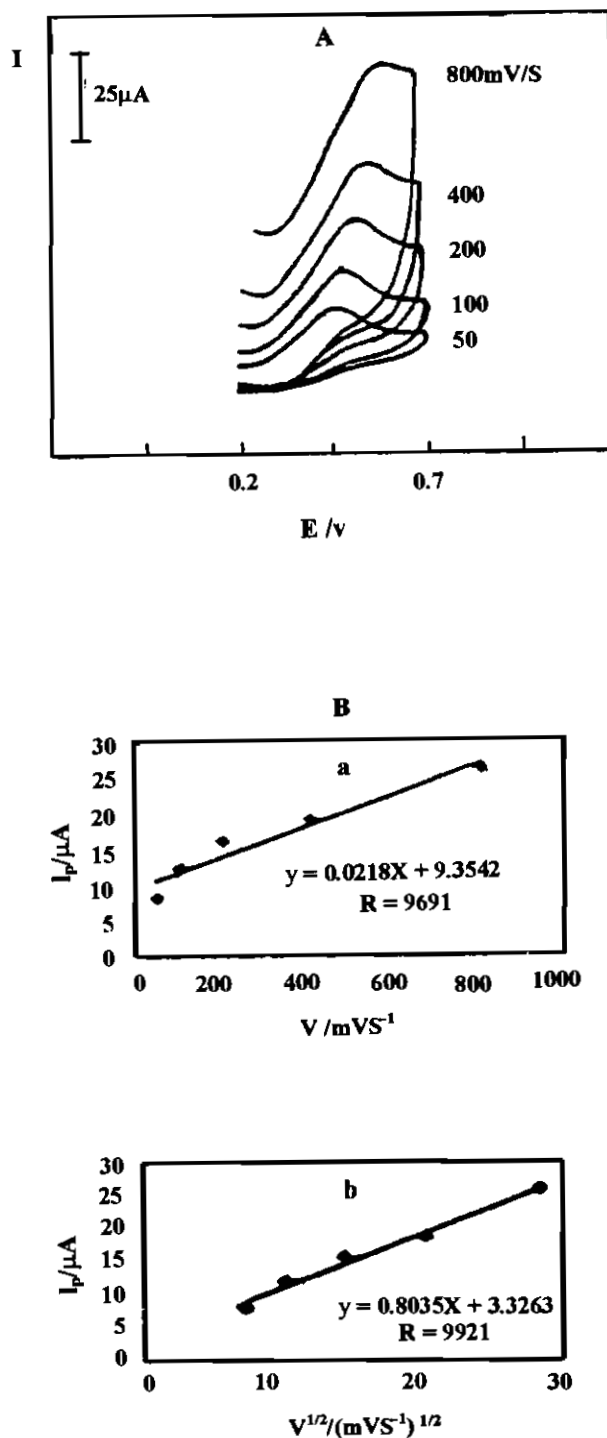


Fig. 6 : (A) The CVs of  $10^{-3}$  M ascorbic acid on PMPy-ClO<sub>4</sub><sup>-</sup>-coated pt electrode in 0.1 M LiClO<sub>4</sub> aqueous solution, pH 7 at various scan rates. The polymer was as Fig. 5. (B) The plot of  $i_p$  against the  $V$ (a) and  $V^{1/2}$  (b).

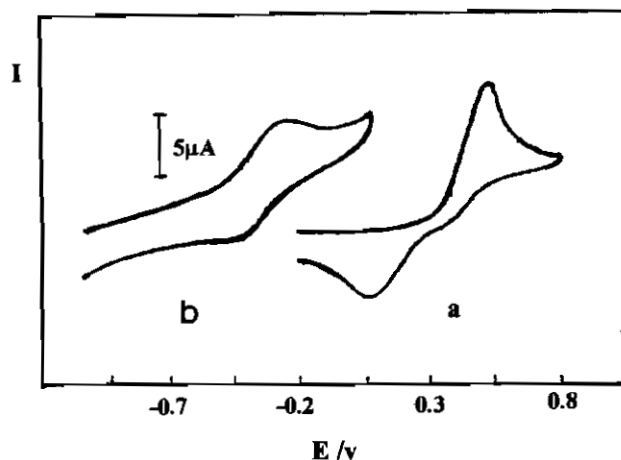


Fig. 7: The CVs of  $10^{-3}$  M hydroquinone (a) on bare Pt electrode and (b) on PMPy- $\text{C10}_4^-$ -coated Pt electrode in 0.1 M  $\text{LiClO}_4$  aqueous solution, pH 2.5,  $\nu=50$  mVs $^{-1}$ . The polymer was prepared by the galvanostatic method (the current density 250  $\mu\text{A}$ , the time of deposition 450 s).

trocatalytic effect of the PMPy prepared in acetonitrile than chloroform. However, the scan rate of potential used in this work is much smaller than the scan rate used of the present work (10 mVs $^{-1}$  in comparison to 100 mVs $^{-1}$ ). Fig.8A shows the CVs of H2Q on the PMPy-coated electrodes at the various scan rates. From this figure the curve of  $i_p$  vs.  $\nu^{1/2}$  and  $\nu$  were plotted (fig.8B) so that correlation coefficients were 0.9928 and 0.9741 for anodic current respectively. Also, the oxidation of hydroquinone on the PMPy-coated Pt electrode with various thicknesses reveals that current peaks does not depend on the thickness. These results provide evidence in favour of the occurrence of the electron transfer under diffusion controlled conditions at the polymer/solution interface.

Using the method proposed by Nicholson [8] that employs the relationship between the  $\Delta E_p$  and kinetic parameter,  $\psi$ , and the use of a working curve, the heterogeneous electron transfer rate constant ( $K^0$ ) value for oxidation of hydroquinone on the PMPy-coated Pt electrode was found to be about  $8 \times 10^{-4}$  cms $^{-1}$ , which is about 800-fold greater than the value on bare electrode ( $< 10^{-6}$  cms $^{-1}$ ) [9], and slightly greater than the value obtained at the PPy-coated Pt electrode for scan rate of 100 mVs $^{-1}$  [4].

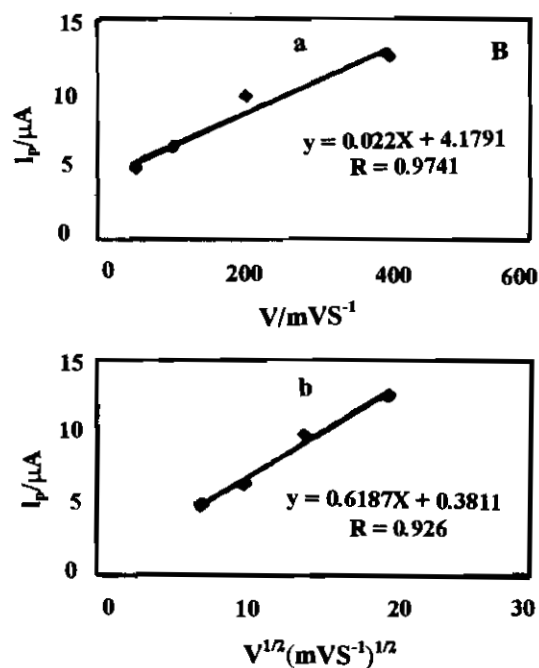
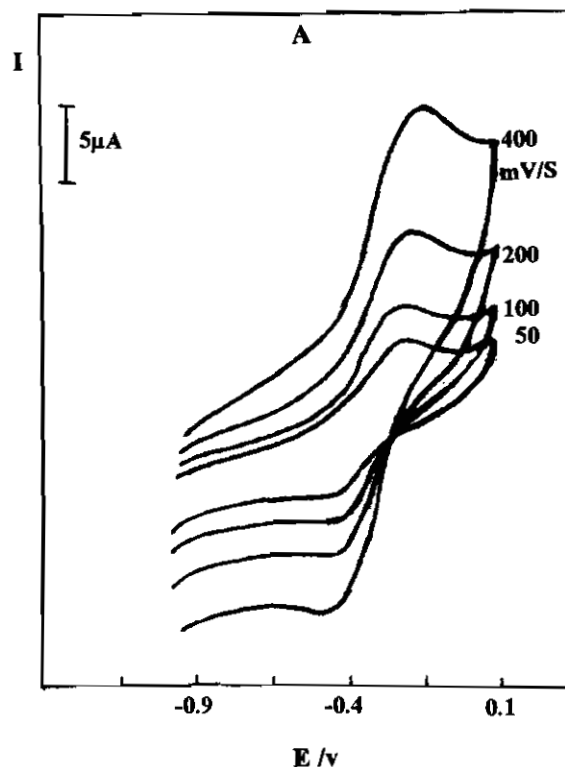


Fig. 8 : (A) The CVs of  $10^{-3}$  M hydroquinone on PMPy- $\text{C10}_4^-$ -coated Pt electrode in 0.1 M  $\text{LiClO}_4$  aqueous solution, pH 2.5 at various scan rates. The polymer was as Fig. 7. (B) The plot of  $i_p$  against of the  $\nu$ (a) and  $\nu^{1/2}$ (b).

## CONCLUSIONS

The results obtained from this study show that the electropolymerization of N-methylpyrrole can be performed in chloroform. The PMPy film formed on the Pt disk electrode was very stable, quasi-metallic and smooth. The electrochemical activity of the PMPy film is affected by the method of electropolymerization and dopant anion and the best activity is observed for galvanostatic method in the presence of perchlorate ion as a dopant anion. An obvious electrocatalytic effect of the PMPy-coated Pt electrode prepared in chloroform for oxidation of hydroquinone is observed in aqueous solution in comparison to PMPy-coated Pt electrode prepared in chloroform but the electrocatalytic effect of the PMPy prepared in acetonitrile is greater than the PMPy prepared in chloroform. Also the PMPy-coated Pt electrode shows the electrocatalytic effect on the oxidation of ascorbic acid but this effect is relatively small in comparison to the PPy-coated Pt electrode prepared in water. These findings suggest that for the aim of electrocatalysis of hydroquinone oxidation, the PMPy prepared in chloroform is better than PPy prepared in chloroform and acetonitrile is a better solvent than chloroform for preparation of PMPy. For ascorbic acid oxidation the PMPy prepared in chloroform does not act as good as polypyrrole prepared in water.

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