

*Full Paper*

## **Electrochemical Studies of Dopamine, Ascorbic Acid and Their Simultaneous Determination at a Poly (Rosaniline) Modified Carbon Paste Electrode: A Cyclic Voltammetric Study**

**Jamballi G. Manjunatha<sup>1,2</sup> Bahaddurghatta E. Kumara Swamy<sup>1,\*</sup> and Mohamad Deraman<sup>2</sup>**

<sup>1</sup>*Department of P.G. Studies and Research in Industrial Chemistry, Kuvempu University, Jnana Sahyadri, Shankaraghatta, Karnataka, India*

<sup>2</sup>*School of Applied Physics, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia*

\*Corresponding Author, Tel.: +91-8282-256225; Fax: +91-8282-256255

E-Mail: [kumaraswamy21@yahoo.com](mailto:kumaraswamy21@yahoo.com)

*Received: 22 April 2013 / Accepted: 21 July 2013 / Published online: 30 August 2013*

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**Abstract-** A sensitive and selective electrochemical method for the determination of dopamine was developed using a rosaniline polymer film modified carbon paste electrode. The rosaniline polymer film modified electrode showed excellent electrocatalytic activity towards the oxidation of dopamine (DA) in phosphate buffer solution (pH 7.0). The interference studies show that the modified electrode exhibits excellent selectivity in the presence of ascorbic acid (AA). A significant improvement in cyclic voltammetric responses to DA and AA (well-defined voltammetric peaks at potentials around 205, -43 mV for DA and AA respectively) and a prominent enhancement of voltammetric sensitivity was observed at the rosaniline polymer film modified CPE. Hence, this work provides a simple and easy approach to selective detection of dopamine in the presence of ascorbic acid.

**Keywords-** Electrochemistry, Rosaniline, Electropolymerisation, Dopamine, Ascorbic Acid

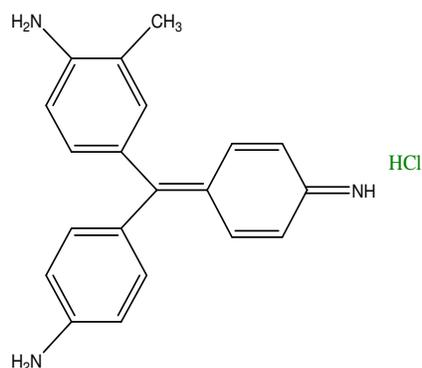
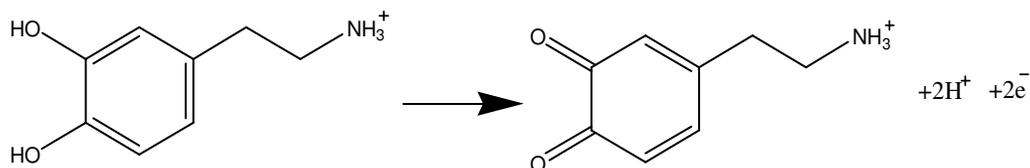
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## 1. INTRODUCTION

Dopamine is an important neurotransmitter in mammalian central nervous systems and low levels of dopamine have been found in patients with Parkinson's disease [1]. Dopamine has therefore attracted tremendous attention in biomedically oriented research. Because dopamine is an electro active compound, it can be studied electrochemically. However, the direct redox reactions of dopamine at a bare carbon paste electrode are reversible and require high over potentials and also dopamine and ascorbic acid are always occurs together in biological environments. The oxidation potential of ascorbic acid is close to that of dopamine, resulting in an overlapped voltammetric response. In order to resolve these problems, numerous modified electrodes have been used to investigate the electrochemical behavior of dopamine [2–7] and eliminate the interference of ascorbic acid or separate the electrochemical response of dopamine and ascorbic acid [8–11]. Thus, it is important to develop sensitive, fast and selective methods for the detection of DA, UA and AA. In the past decades, various chemically modified electrodes have been used to analyze these biological molecules [12–14].

Among these methods, polymer modified electrodes (PMEs) have many advantages in the detection of biomolecules because of their selectivity, sensitivity and homogeneity in electrochemical deposition, strong adherence to the electrode surface and chemical stability of the film [15,16]. Various PMEs were studied towards the electro catalytic oxidation of DA, UA and AA [17-21]. For example, a glassy carbon electrode (GCE) modified with poly (*N,N*-dimethylaniline) could simultaneously detect AA and DA which coexisted in a homogeneous solution [18]. There have been reports concerned the use of glutamic acid [19], amino benzoic acid [20], and *p*-nitrobenzenazo resorcinol [21] as an electro polymerized layer to modify GCE for the detection of DA. Furthermore, conducting polymer incorporating metallic or semiconducting nanoparticles provide an exciting system, and these materials hold potential for applications in electronics, sensors, and catalysis [22-24]. They have synergistic chemical and physical properties based on the constituent polymer and introduced metal. By tuning a polymer backbone with nanoscale material, realization of nano-electronic sensor devices with superior performance is possible [25-27].

The present investigation report the electro polymerization of poly(rosaniline) has not been reported previously, and no electrochemical studies of the poly(rosaniline) have been found in literature. In this paper, we report for the first time a polymer film of rosaniline (chemical structure is illustrated in Scheme 1) to modify CPE and describe the electrochemical behavior of DA and AA. The DA oxidation is a two-electron and two-proton process at the poly(rosaniline) modified CPE. Based on the different electro catalytic activities of the modified electrode toward these species, a sensitive and selective method for simultaneous determination of DA in the presence of and AA was established. Recently related works have been done by our research group [28-37].

**Scheme 1.** Structure of Rosaniline**Scheme 2.** Mechanism of DA oxidation

## 2. EXPERIMENTAL

### 2.1. Material and methods

Cyclic voltammetry experiments were carried out with a model EA-201 Electro Analyser (Chemilink Systems) connected to a personal computer for control and data storage. All electrochemical experiments were performed in a standard three-electrode cell. The bare or poly(rosaniline) modified CPE was used as a working electrode, platinum wire as counter electrode and saturated calomel electrode (SCE) as reference electrode. All potentials reported were versus the SCE.

Dopamine hydrochloride (DA), rosaniline, ascorbic acid (AA) were obtained from Himedia chemicals and were used as received. All other chemicals were of analytical grades. Phosphate buffer solutions (PBS 0.2 M) was prepared by mixing standard stock solutions of 0.2 M  $\text{Na}_2\text{HPO}_4$  and 0.2 M  $\text{NaH}_2\text{PO}_4$ . Freshly prepared solutions of DA and AA were used in all experiments.

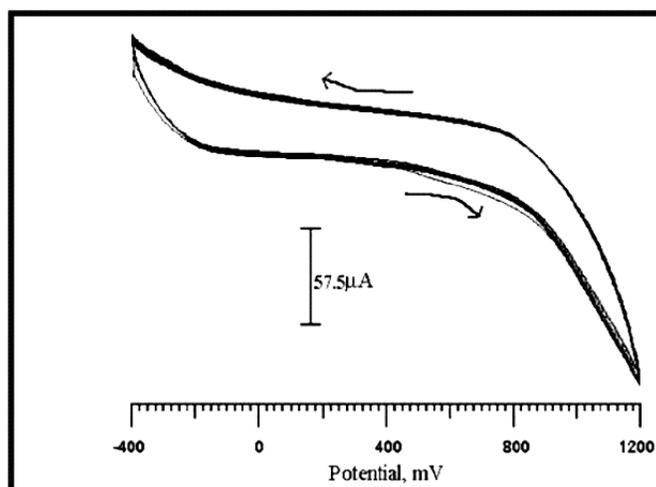
### 2.2. Preparation of bare carbon paste electrode

The bare carbon paste electrode was prepared by hand mixing of graphite powder and silicon oil in the ratio of 70:30 (w/w) in an agate mortar until a homogenous paste was

obtained. The prepared carbon paste was tightly packed into a PVC tube (3 mm internal diameter) and the electrical contact was provided by a copper wire connected to the paste in the end of the tube.

### 2.3. Preparation of pre treated and poly rosaniline modified CPE

The CPE was pretreated by scanning in 0.05 M  $\text{H}_2\text{SO}_4$  containing 1 mM rosaniline in the potential from  $-400$  to  $1200$  mV at  $100$  mV/s for 10 times. After this, the same CPE was enforced under sweeping from  $-400$  to  $1200$  mV at  $100$  mV/s for 10 cycles in  $0.01$  M NaOH containing 1 mM rosaniline as shown in Fig. 1, after polymerization the poly (rosaniline) film modified CPE was rinsed with distilled water and used for the determination of DA and AA.



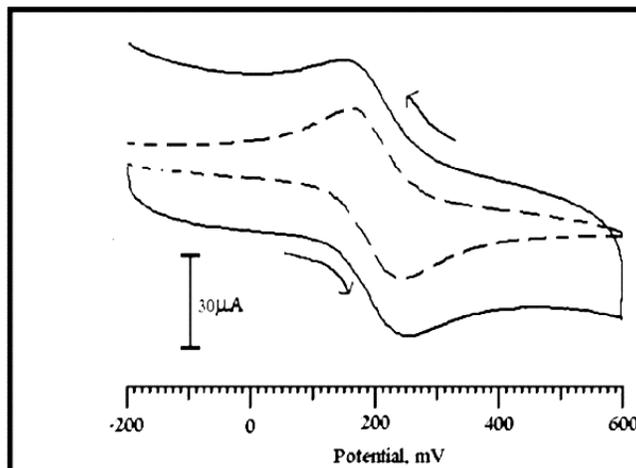
**Fig. 1.** Cyclic voltammogram of preparation of poly (rosaniline) film coated CPE in  $0.01$  M NaOH,  $1$  mM rosaniline for 10 cycles at sweep rate of  $100$  mV/s

## 3. RESULTS AND DISCUSSIONS

### 3.1. Electrochemical investigations of potassium ferrocyanide at Poly(rosaniline) modified CPE

Fig. 2 shows the electrochemical response of  $1$  mM potassium ferrocyanide in  $1$  M KCl at bare carbon paste electrode (BCPE) (dashed line) and poly (rosaniline) modified carbon paste electrode (solid line). The dashed line shows the electrochemical response of BCPE having the cathodic peak current ( $I_{pc}$ )  $22.5$   $\mu\text{A}$  and anodic peak current ( $I_{pa}$ )  $34$   $\mu\text{A}$ . The electrochemical cathodic peak potential ( $E_{pc}$ )  $163$  mV and anodic peak potential ( $E_{pa}$ )  $240$  mV. After modification with poly(rosaniline) MCPE shows enhancement of both

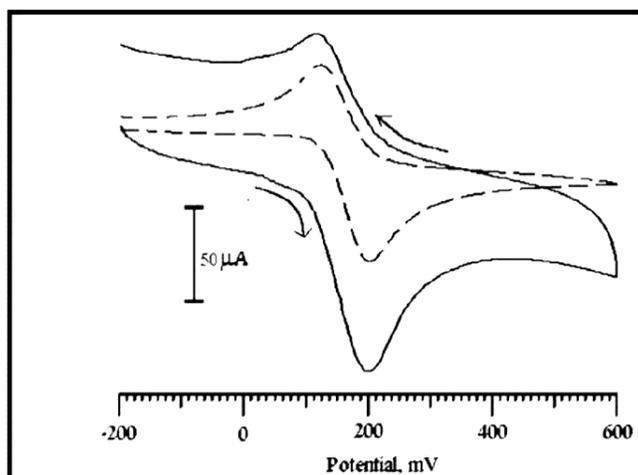
electrochemical anodic peak current ( $I_{pa}$ )  $-53 \mu\text{A}$  and cathodic peak current ( $I_{pc}$ )  $37.8 \mu\text{A}$ . The anodic peak potential is  $243 \text{ mV}$  and cathodic peak potential is  $168 \text{ mV}$ .



**Fig. 2.** Cyclic voltammograms for the electrochemical responses of  $\text{K}_4[\text{Fe}(\text{CN})_6]$  at bare (dashed line) and poly (rosaniline) modified CPE (solid line) in  $1 \text{ M KCl}$  containing  $1 \text{ mM K}_4[\text{Fe}(\text{CN})_6]$  at scan rate  $100 \text{ mV/s}$

### 3.2. Electrochemical investigation of dopamine at poly (rosaniline) modified CPE

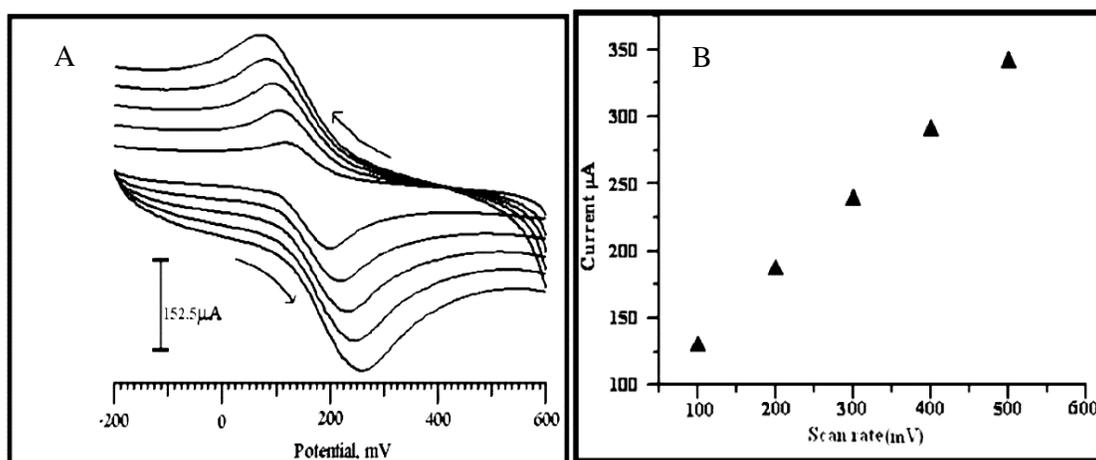
The electrochemical behavior of DA at the poly (rosaniline) MCPE was investigated using cyclic voltammetry and the cyclic voltammograms are shown in Fig. 3. At the bare CPE the cyclic voltammogram of DA (dashed line) showed a pair of redox peak with the anodic peak potential at  $203 \text{ mV}$  and the cathodic peak potential at  $125 \text{ mV}$  in PBS (pH 7.0). The peak-to-peak separation was  $78 \text{ mV}$ . However for the poly (rosaniline) MCPE the anodic peak was located at  $193 \text{ mV}$  and the corresponding cathodic peak potential was located at  $118 \text{ mV}$ . The peak-to-peak separation was calculated as  $75 \text{ mV}$ . The results of the enhancement of the peak current showed the excellent catalytic ability of poly (rosaniline) MCPE.



**Fig. 3.** Cyclic voltammogram of 1 mM DA in 0.2 M phosphate buffer solution of pH 7 at bare CPE (dashed line) and poly (rosaniline) film coated CPE (solid line)

### 3.3. Effect of scan rate on the peak currents of dopamine

The effect of scan rate on the anodic peak current of DA was studied. As the scan rate increased, the oxidation peak current ( $I_{pa}$ ) increased. The  $I_{pa}$  was directly proportional to the scan rate ( $v$ ) over the range of 100-500 mV/s (Fig. 4A) which suggested a surface-controlled process at the modified electrode surface [38]. The correlation coefficient of  $r^2=0.99976$  (Fig. 4B).

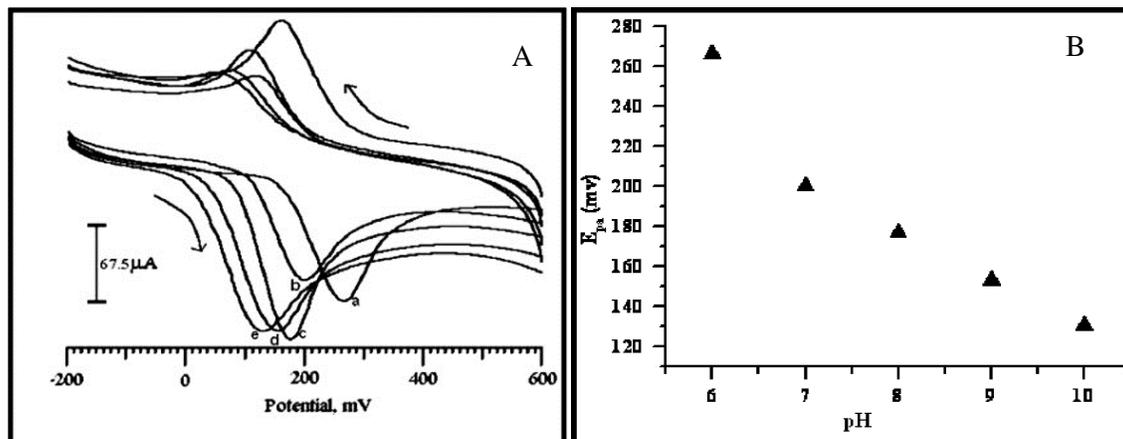


**Fig. 4.** (A) Cyclic voltammograms of 1 mM DA on the poly (rosaniline) modified CPE at different scan rates (100, 200, 300,400, 500 mV/s) in 0.2 M phosphate buffer solution pH 7.0 and (B) The plot of the redox peak current vs. the scan rate

### 3.4. Effects of pH of DA Solution

The effect of pH on the formal potential and anodic peak current was investigated by cyclic voltammetry in the solution containing 1 mM DA. The values of  $E^{\circ}$ , which was dependent on the pH value of the buffer solution, show that the redox couple of the DA includes some proton transfer in the redox processes. According to the Nernst equation, the slope of  $-32 \text{ mV pH}^{-1}$  reveals that the proportion of the electron and proton involved in the reaction is 1:1. As DA oxidation is a two electron process, the number of protons involved is also predicted to be two. Therefore, a mechanism for the DA oxidation can be proposed in Scheme 2.

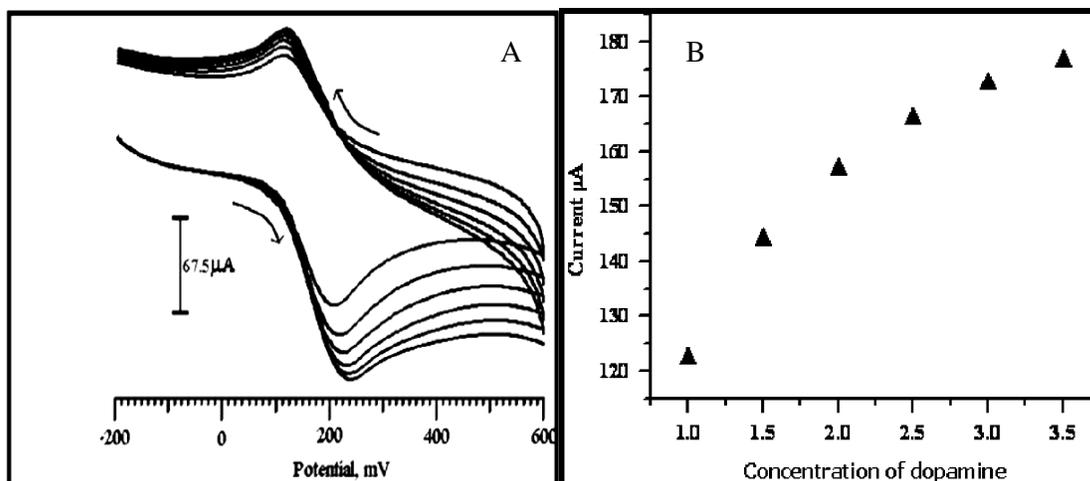
The effect of pH on the electrode signal and oxidation potential was investigated by cyclic voltammetry in the solution containing 1 mM DA (shown in Fig. 5A). The  $E_{\text{pa}}$  vs. pH graph clearly indicates that the catalytic peak shifts to a more negative potential with increasing pH (Fig. 5B).



**Fig. 5.** (A) Cyclic voltammograms obtained at the poly (rosaniline) modified CPE in 0.2 M phosphate buffer solutions in pH values, (a) 6 (b) 7 (c) 8 (d) 9 (e) 10 containing 1 mM DA at scan rate of 100 mV/s and (B) the plot of standard redox peak potential ( $E_{\text{pa}}$ ) of DA on cyclic voltammograms vs. pH values

### 3.5. Calibration Curve

The determination of DA concentration at the poly (rosaniline) modified carbon paste electrode was performed with cyclic voltammetry (Fig. 6A). The oxidation peak current of DA was selected as the analytical signal. The results showed that anodic peak current was proportional to the concentration over the range of 1-3.5 mM. The correlation coefficient of  $r^2=0.96026$  as shown in Fig. 6B.



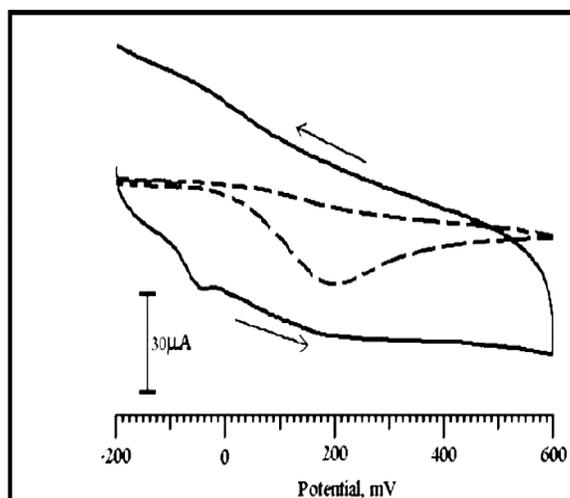
**Fig. 6.** (A) Cyclic voltammogram of DA at different concentration (1-3.5 mM). (B) Graph of current vs. concentration of DA

### 3.6. Electrochemical response of ascorbic acid at the poly (rosaniline) modified CPE

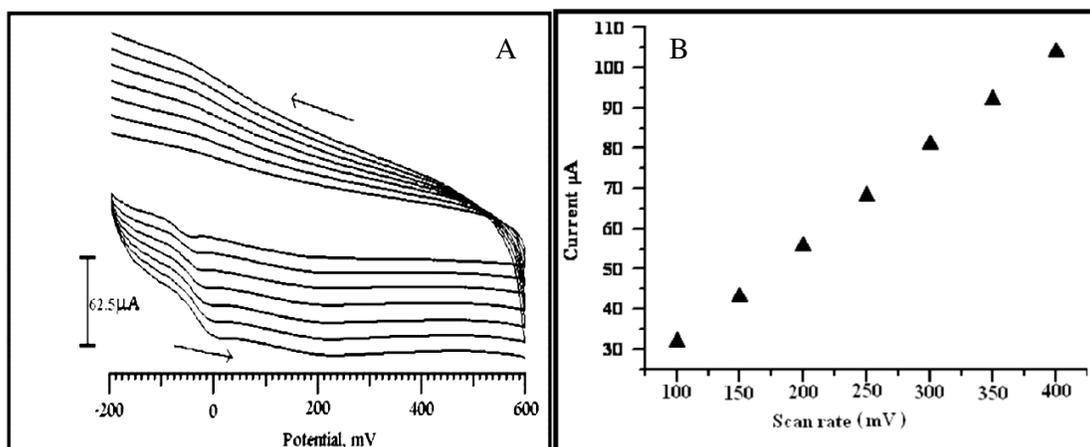
Fig. 7, shows the cyclic voltammograms of AA at the bare CPE (dashed line) and poly (rosaniline) MCPE (solid line). At the bare CPE the oxidation peak occur at around 200 mV. Oxidation of AA at bare electrode is generally believed to be totally irreversible and requires high overpotential due to fouling of the electrode by the adsorption of oxidized product of AA. However at the poly (rosaniline) MCPE, the oxidation peak potential of AA was obtained at around -42 mV which is shifted to less positive potential as compared to that of bare CPE, indicating that the poly (rosaniline) film on the electrode surface favors the oxidation process of AA. This film prevents the fouling of the electrode surface, hence faster electron transfer kinetics of AA at the poly (rosaniline) MCPE. Since the oxidation peak of AA is shifted to less positive potential it would not interfere with the measurement of DA.

### 3.7. Effect of scan rate on the peak currents of Ascorbic acid

Fig. 8A shows the cyclic voltammograms of AA at the Poly (rosaniline) modified CPE at different scan rates. The oxidation peak potential was observed it is shifting positively with the increase of the scan rate and in addition exhibited a linear relation to the scan rate with correlation coefficient  $r^2=0.99984$  (Fig. 8B). This result indicates that irreversible oxidation process of AA at the poly (rosaniline) modified CPE is adsorption controlled process.



**Fig. 7.** Cyclic voltammograms obtained for the oxidation of 1 mM AA at poly (rosaniline) MCPE (solid line) and BCPE (dashed line) at scan rate 100 mV/s

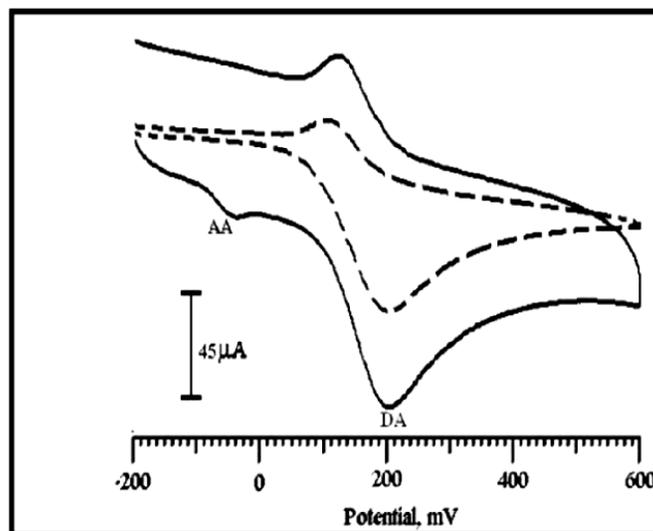


**Fig. 8.** (A) Cyclic voltammograms for the oxidation of 1 mM AA at different scan rate 100, 150, 200, 250, 300, 350, 400 mV/s in 0.2 M phosphate buffer solution (pH 7.0) (B) is the plot of anodic peak current vs. scan rate

### 3.8. Simultaneous detection of DA in the presence of AA at poly (rosaniline) MCPE

In order to examine the sensitivity and selectivity of poly (rosaniline) MCPE the electrochemical behavior of a mixture of 0.5 mM DA and 1 mM AA was investigated using cyclic voltammetry. Fig. 9 shows the cyclic voltammograms obtained for DA and AA coexisting at bare CPE and poly (rosaniline) MCPE. As shown in figure bare CPE cannot separate the voltammetric signal of DA and AA (dashed line). Only one broad voltammetric

signal for DA and AA was observed at approximately 203 mV. The fouling of the electrode surface by the oxidation products results in a single voltammetric peak for DA and AA. Therefore it is impossible to use bare electrode for the voltammetric determination of DA in the presence of AA. Moreover the poly (rosaniline) MCPE resolved the voltammetric signal into two well defined voltammetric peaks at 43 and 205 mV corresponding to AA and DA respectively (solid line) this is because AA exists as anions in the pH 7 PBS, hence the electrostatic repulsion between the AA anions and the negatively charged groups on the electrode surface retarded the electron transfer and shifted the oxidation potential of AA towards more negative value so that the oxidation peak of DA could be separated from that of AA. As the oxidation potential of AA is readily oxidized well before the oxidation potential of DA is reached. Thus the catalytic oxidation of AA is possible at the poly (rosaniline) MCPE. The separation between the oxidative peaks of DA and AA was approximately 162 mV, hence the simultaneous determination of DA in the presence of ascorbic acid is feasible at the poly (rosaniline) MCPE.

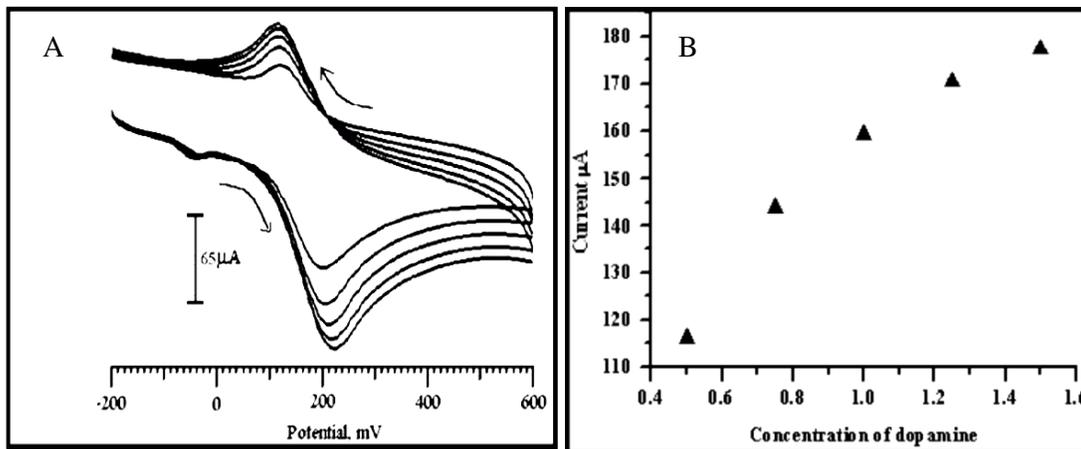


**Fig. 9.** Simultaneous determination of 0.5 mM DA, and 1 mM AA at bare CPE (dashed line) and at poly (rosaniline) film coated CPE (solid line)

### 3.9. Effect of DA concentration in the presence of AA at Poly (rosaniline) MCPE

Fig. 10A shows the CVs at the poly (rosaniline) MCPE for 1 mM AA and DA at different concentrations in pH 7.0 (0.2 M PBS) at a scan rate 100 mV/s. As show in Fig. 10B the anodic and cathodic peak current of DA increases with increase in concentration while the anodic peak current of AA remains constant due to its constant concentration in the

experiment. Therefore the poly (rosaniline) MCPE showed its good selectivity and sensitivity in the electrochemical detection of DA in the presence of AA.



**Fig. 10.** (A) Cyclic voltammograms obtained at the poly (rosaniline) MCPE in 0.2 M PBS pH 7.0 containing 1 mM AA and DA with different concentrations (a) 0.5 (b) 0.75 (c) 1.0 (d) 1.25 (e) 1.50 mM at a scan rate of 100 mV/s (B) plot of redox peak current of DA vs. concentration

#### 4. CONCLUSION

The electropolymerisation of rosaniline on the carbon paste electrode produces a stable polymeric film. Cyclic voltammograms of the resulting poly (rosaniline) film indicates the presence of a chemically reversible redox couple. The formal redox potential of DA shifts in the negative direction with increasing solution pH, with a slope of 0.32 V. The poly (rosaniline) modified carbon paste electrode exhibits remarkable electrocatalytic effects on the oxidation of AA and DA. At the bare carbon paste electrode the oxidation signals of AA and DA merge and cannot be determined simultaneously. However the poly(rosaniline) modified carbon paste electrode clearly resolved the mixed voltammetric signal into two well defined voltammetric peaks at 43 mV and 205 mV corresponding to AA and DA respectively. The modified electrode showed high electrocatalytic activities towards the oxidation of DA in the presence of AA with good selectivity and sensitivity. It is expected that with its high electrocatalytic behavior the poly (rosaniline) modified carbon paste electrode could hold great application in the fields of electro analytical chemistry and biosensors.

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