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Simultaneous voltammetric measurement of ascorbic acid and dopamine at poly (vanillin) modified carbon paste electrode: A cyclic voltammetric study

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ABSTRACT

Polymerized film of vanillin was prepared on to the surface of carbon paste electrode in alkaline solution by cyclic voltammetric (CV) technique after pretreatment by H_2SO_4 media. The poly vanillin (VA) film coated carbon paste electrode (CPE) exhibited excellent electrocatalytic activity toward the oxidation of dopamine (DA) and ascorbic acid (AA) in 0.2M acetate buffer solution at pH 7. This modified electrode exhibited a potent and persistent electron-mediating behavior followed by well-separated oxidation peaks towards DA and AA. The modified electrode shows good sensitivity, selectivity and stability and has been applied to the determination of DA and AA.

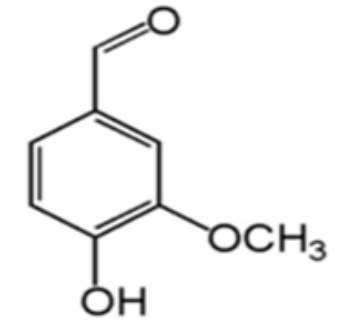
Keywords: Carbon paste modified electrode, poly (vanillin), Electropolymerisation, Dopamine, Ascorbic acid, Cyclic voltammetry.

INTRODUCTION

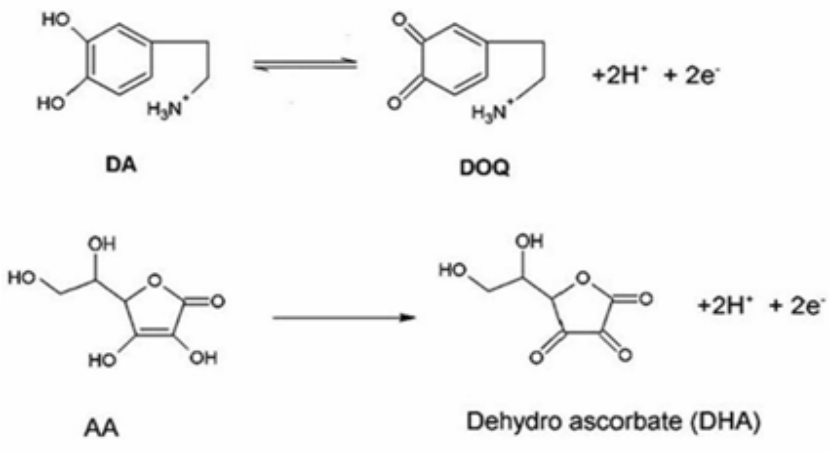
Polymer modified electrodes (PMEs) have received great attention in recent years, as the polymer film have good stability, reproducibility, more active sites, homogeneity in electrochemical deposition and strong adherence to the electrode surface [1,2]. Electropolymerisation is a good approach to immobilize polymers to prepare PMEs.

Dopamine (DA) is an important neurotransmitter molecule of catecholamines, and its deficiency leads to brain disorders such as Parkinson's disease and schizophrenia [1–3]. Similarly ascorbic acid (AA) has been used for the prevention and treatment of common cold, mental illness, infertility and cancer [4]. DA and AA are the compounds of great biomedical and neurochemical interest, and they are always present together in biological tissues. Thus simultaneous determination of DA and AA is a problem of critical importance in field of neurochemistry and biomedical chemistry. Both DA and AA are compounds that can be determined by electrochemical methods based on anodic oxidation. However, a major problem is that the oxidation potentials for AA and DA occur almost in the same potential at unmodified electrodes, which result in overlapped voltammetric responses, making their discrimination highly difficult [3]. Most of the studies on these compounds demonstrated the possibility for the separate determination of either AA [5–7] or DA [8–10] by eliminating the other using different membranes or selecting particular potentials. It was reported that stearic acid [11], Nafion [12], polypyrrole [13], and micellar [14]

could selectively detect DA in the presence of AA based on the cationic permeability of the polymer. However, it is most important to develop a sensor,Which can determine both AA and DA simultaneously Some efforts have been taken to fabricate modified electrodes for the simultaneous determination of DA and AA, such as poly(neutral red)-modified electrode [15], poly(phenosafranine)electrode [16], poly (N,N-dimethylaniline)-modified electrode[17], sol–gel composite electrode [18], chlione- and acetylcholine-modified glassy carbon electrode [19], carbon polyvinyl chloride composite electrode [20], tetrabromo-pbenzoquinone-modified carbon paste electrode [21], ferrocenederivative mediators at glassy carbon electrode [22], the positively charged surfactant cetylpyridinium chlorideadsorbed onto the electrode surface [23], the coated and intercalated carbon nanotube-modified electrodes [24], poly(benzophenone-4) electrode [25], epinephrine/Nafionmodifiedelectrode [26], multiwalled carbon nanotubes with incorporated β-cyclodextrin combined with polyaniline filmmodified electrode [27], poly(3,4-ethylenedioxy)thiophene electrode [28], poly (vinyl alcohol)-modified electrode [29],oracet blue modified electrode [30], didodecyldimethylammonium bromide-modified electrode [31], poly(manganese (III)-5-[o-(1-imidazolyl)butoxyl] phenyl-10, 15, 20-triphenylporphrine chloride)-modified electrode [32], poly(3,4-ethylenedioxythiophene)-modified electrode [33], and nano-cobalt phthalocyanine-modified electrode [34].Caffeic acid (3,4-dihydroxycinnamic acid) [35]. In the study of simultaneous voltammetric measurement of AA and DA often coexists with AA in real samples studying the simultaneous voltammetric measurement of AA and DA is very significant. To our knowledge there is no report about the voltammetric behaviors and determination of DA and AA at the poly (VA) modified CPE, Vanillin, 4-hydroxy-3-methoxybenzaldehyde, is an organic compound with the molecular formula $C_8H_8O_3$. Its functional groups include aldehyde, ether, and phenol is shown in scheme.1. It is the primary component of the extract of the vanilla bean. It is also found in roasted coffee. Synthetic vanillin, instead of natural vanilla extract, is sometimes used as a flavoring agent in foods, beverages, and pharmaceuticals. Vanillin has been used as a chemical intermediate in the production of pharmaceuticals and other fine chemicals. The present study relates to the electrochemical deposition of poly (VA) acid on a carbon paste electrode to develop a sensor for selective and sensitive detection of DA and AA individually in the presence of the other species. This ability to determine AA and DA in a mixture has a significant attraction in biological and chemical researches. The scheme of oxidations of DA, and AA is shown in scheme 2. Recently related works have been done by our research group [36-44].



Scheme.1.Structure of vanillin



Scheme.2. The scheme of oxidations of DA, and AA.

MATERIALS AND METHODS

2.1. Apparatus and procedure

Cyclic voltammetry (CV) was performed in a model EA-201 Electroanalyser (Chemilink system). All the experiments were carried out in a conventional electrochemical cell. The electrode system contained a carbon paste working electrode (3.0mm in diameter) a platinum wire as counter electrode and a saturated calomel electrode(SCE) as a reference .

2.2. Preparation of carbon paste electrode

The carbon paste electrode was prepared by hand mixing of 70% graphite powder and 30% silicone oil were mixed to produce a homogeneous carbon paste which was then packed into the cavity of a home made carbon paste electrode and smoothed on a weighing paper.

2.3. Preparation of pre treated and poly VA modified CPE

The 1mM VA was placed in the electrochemical cell containing 0.05M H_2SO_4. The CPE was pretreated by scanning in the solution from –400 to 1200mV at 100mVs^{-1} for 10 times. After this, the same CPE has enforced under sweeping from –400 to 1200mV at 100mVs^{-1} for multiple cycles (10 cycles) in the solution containing 1mM VA with 0.01M NaOH. The poly (VA) fabricated modified CPE after polymerization was washed with water and used for the determination of DA and AA.

RESULTS AND DISCUSSION

3.1. Fabrication of poly (VA) film

Fig.1 Shows the CV of (VA) Electropolymerisation over range of -400 to 1200mV at 100mV/s for 10 cycles. During the polymerized process an anodic peak corresponding to the oxidation of VA descended gradually with cyclic time increasing. A anodic peak formed with incessant scans and peak current also decreased continuously trends will be stabilized after 10 cycles, these facts suggests that the initial formed poly(VA) film had a leaching process with scan cycles increasing up to 10 times, which may be implied a self adjustment of the polymer film thickness at CPE. The electro deposited behavior of VA at modified CPE.

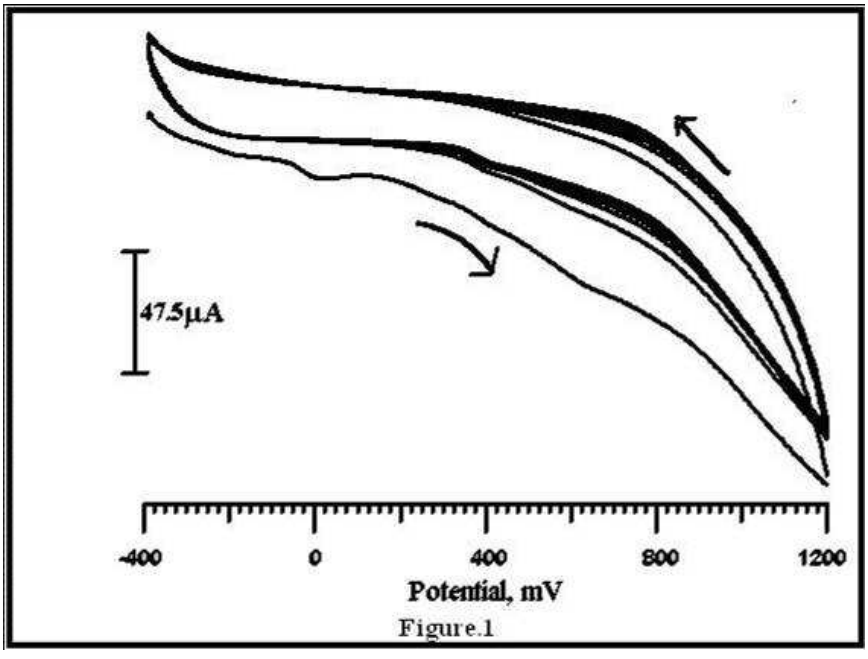


Figure 1. Cyclic voltammogram of poly (VA) film modified CPE. Contains 1mM VA in 0.01M NaOH at 10 cycles with sweep rate of 100 mvs^{-1}.

3.2 Electrocatalytic oxidation of DA at poly (VA) modified CPE

Cyclic voltammogram of $1X10^{-3}$M DA at pH 7 acetate buffer at a bare CPE and poly (VA) film modified CPE was recorded as shown in Fig. 2. At bare CPE (solid line) a pair of redox peak showed poor electrocatalyticactivity with anodic peak potential at 201mV and cathodic peak potential at 150mV. Under the same condition poly (VA) modified CPE (dashed line) gave birth to significantly enhanced peak current and more qusireversible electron transfer process to DA with slight shift in redox peak potentials. A well defined redox wave of DA was observed with anodic and cathodic peak potential at 292mV and 195mV respectively. Intensive increase in peak current was also observed owing to the improvement in qusireversibility of electron transfer process and the larger real surface of poly (VA) film. This suggests an efficient oxidation reaction toward DA at the poly (VA) modified CPE.

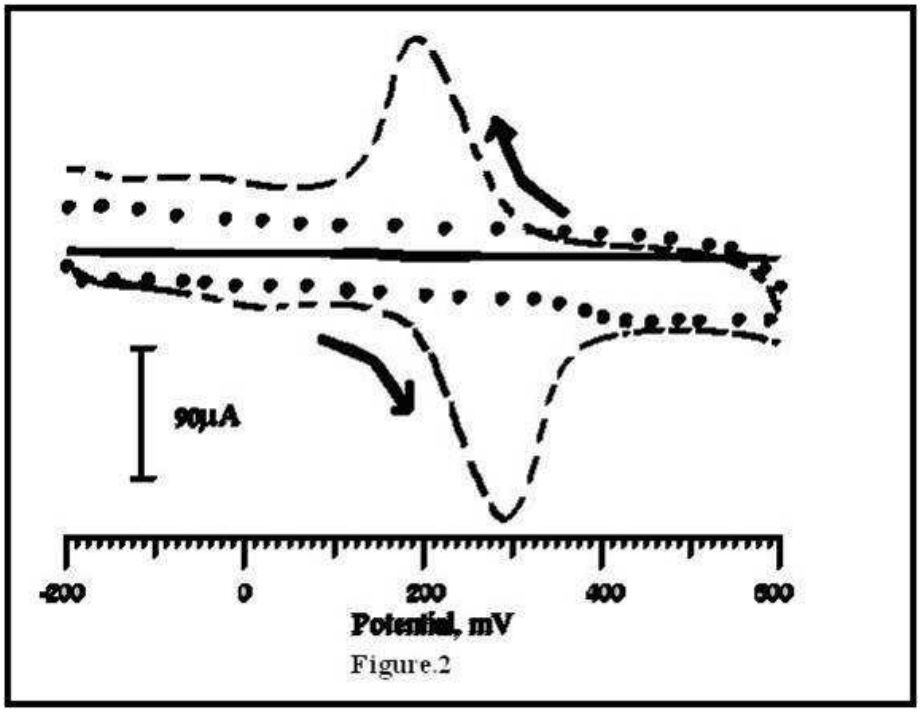


Figure 2. Cyclic voltammogram of $1X10^{-3}$ M DA in 0.2 M acetate buffer solution of pH 7 at bare CPE (dotted line) ,blank (solid line) and poly(VA) film coated CPE (dashed line).

3.3. The effect of scan rate on the anodic peak current of DA at poly (VA)

The effect of scan rate on the anodic peak current of DA was studied by cyclic voltammetry. As the scan rate increased, the anodic peak current (Ipa) increased (Fig.3a). A plot of current vs. square root of scan rate was within the range of 100 to 400 mV/s, with correlation coefficient 0.99696 (Fig.3b) suggesting a diffusion controlled process on the modified electrode surface.

3.4. Effect of DA concentration at Poly (VA)

Fig.4a. shows the DA different concentrations in pH 7.0 at the poly (VA) with 0.2 M acetate buffer at a scan rate 100 mV/s. As show in figure.4 the anodic and cathodic peak current of DA increases with increase in concentration The graph of peak current vs. concentration of DA was plotted showed the concentration is proportional to electrochemical peak current. The correlation coefficient was found to be 0.9802(fig.4b). Therefore the poly (VA) MCPE showed its good selectivity and sensitivity in the electrochemical detection of DA.

3.5 pH influences on biosensor response

The pH influence was investigated by cyclic voltammetric measurement at different pH values between 5.0 and 10 as shown in Figure 5. The maximum response current was observed at pH 7.0 in agreement. In order to obtain the maximum bioactivity and optimal sensitivity, acetate buffer solution of pH 7.0 was selected for our experiments.

3.6. Electrocatalytic oxidation of AA at poly (VA) modified CPE

Figure 6 shows cyclic voltammogram of $1x10^{-3}$M AA in pH 7 acetate buffer at a bare CPE (solid line) and poly(VA) film modified (dashed line) CPE at 100mV/s. At the bare CPE a wide oxidation peak at a potential of about 195mV was observed. However at poly (VA) modified CPE, peak was recorded with a potential at about 50mV, which was an evidence for the electrocatalytic oxidation of AA. The effect of pH on the response of poly (VA) modified CPE toward AA was examined by CV in solution. It could be observed that anodic peak current reaches maximum at pH 7.

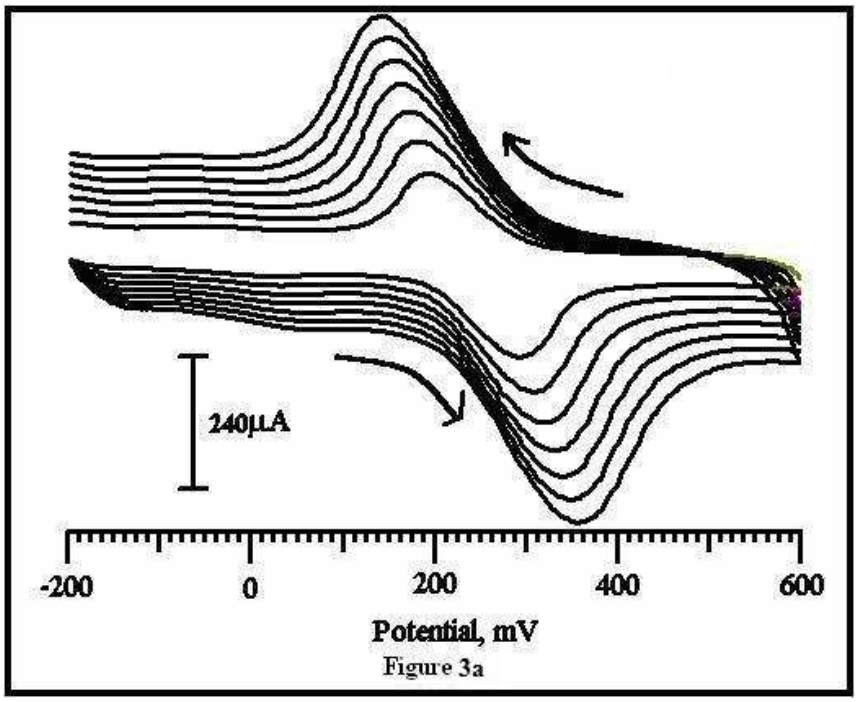


Figure 3a

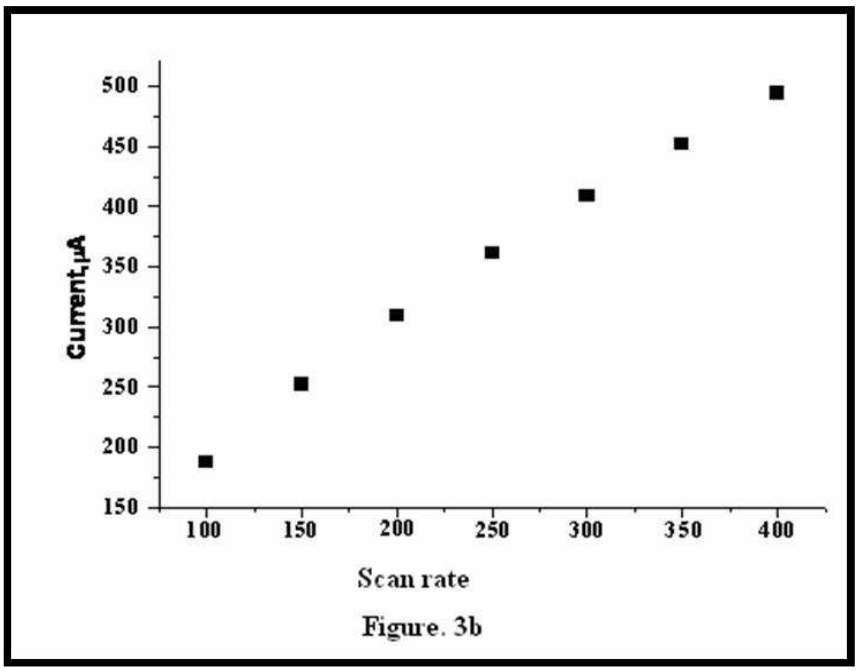


Figure. 3b

Figure 3a. Variation of scan rate for DA at poly (VA) film modified CPE (a- h); $100mVs^{-1}$ to $400mVs^{-1}$. (b) Graph of current vs square root of scan rate

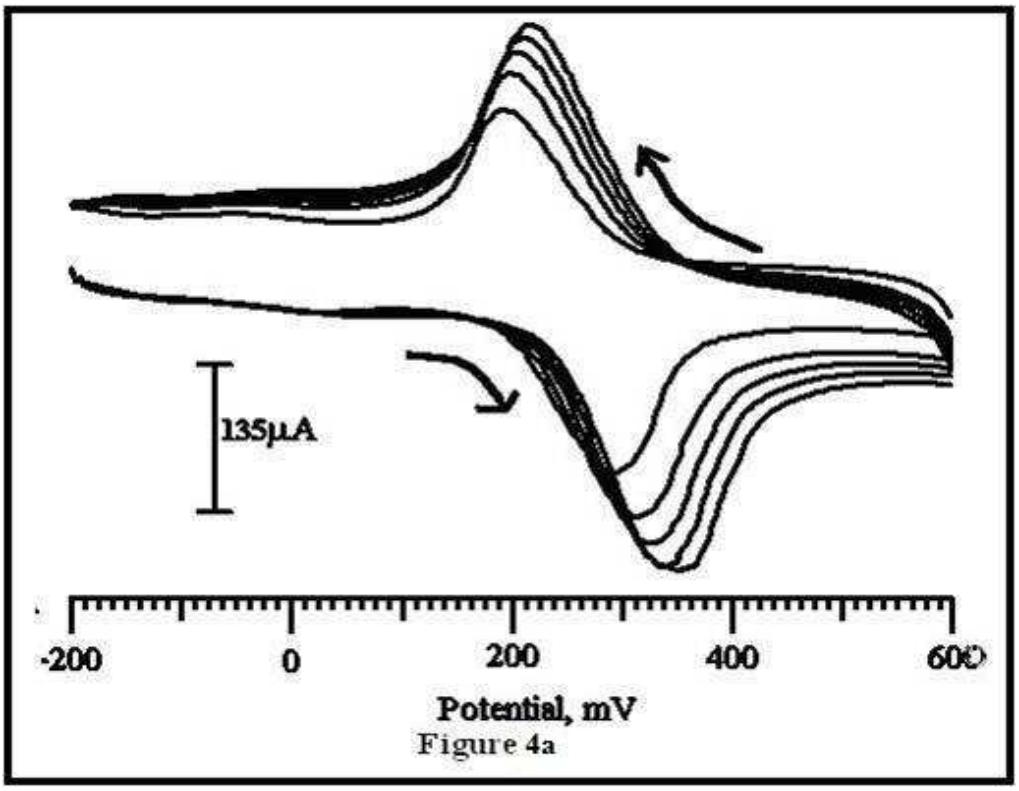


Figure 4a. Cyclic voltammogram of DA at different concentration (a – e; 1X10^{-3}M, 1.5X10^{-3}M, 2X10^{-3}M, 2.5X10^{-3}M), 3X10^{-3}

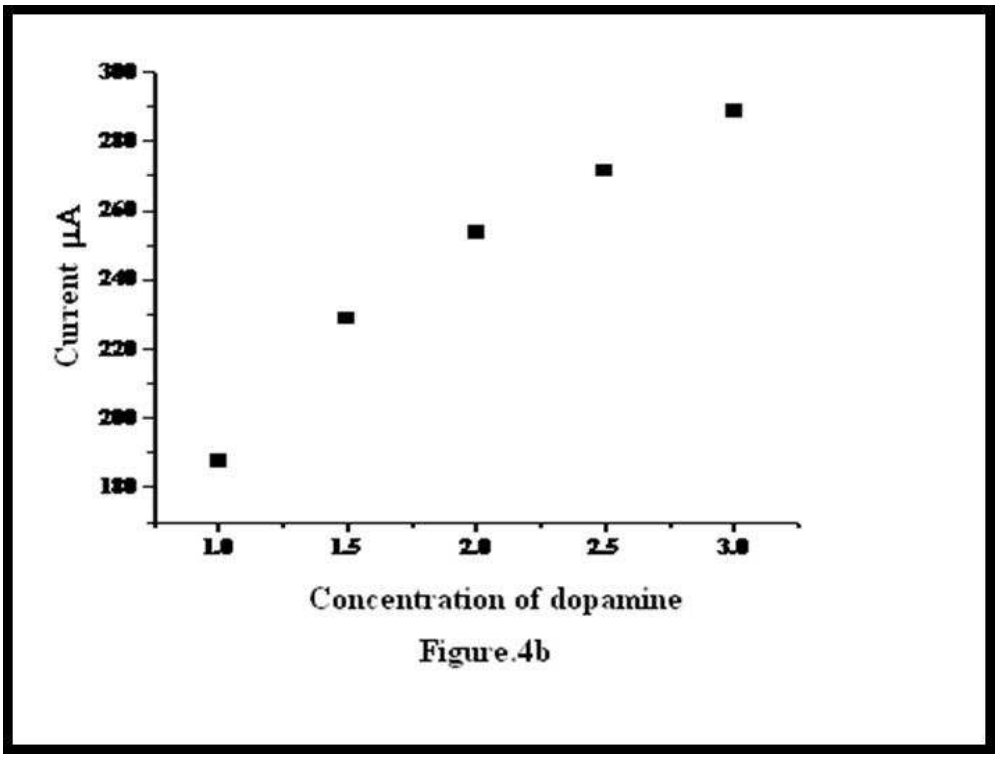


Figure 4.(b) Graph of current vs concentration of DA.

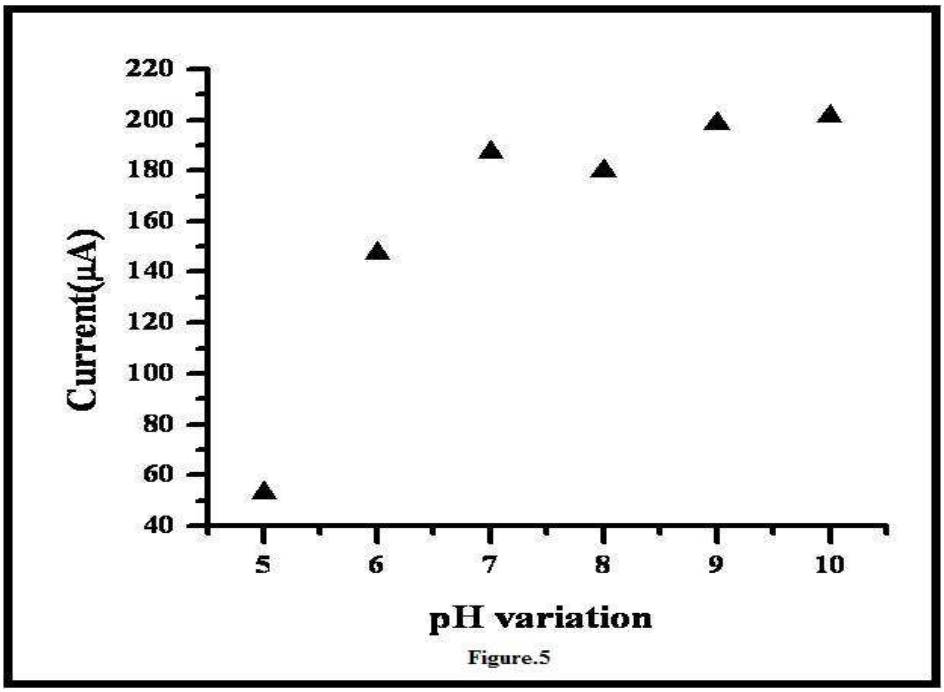


Figure 5. Effect of pH

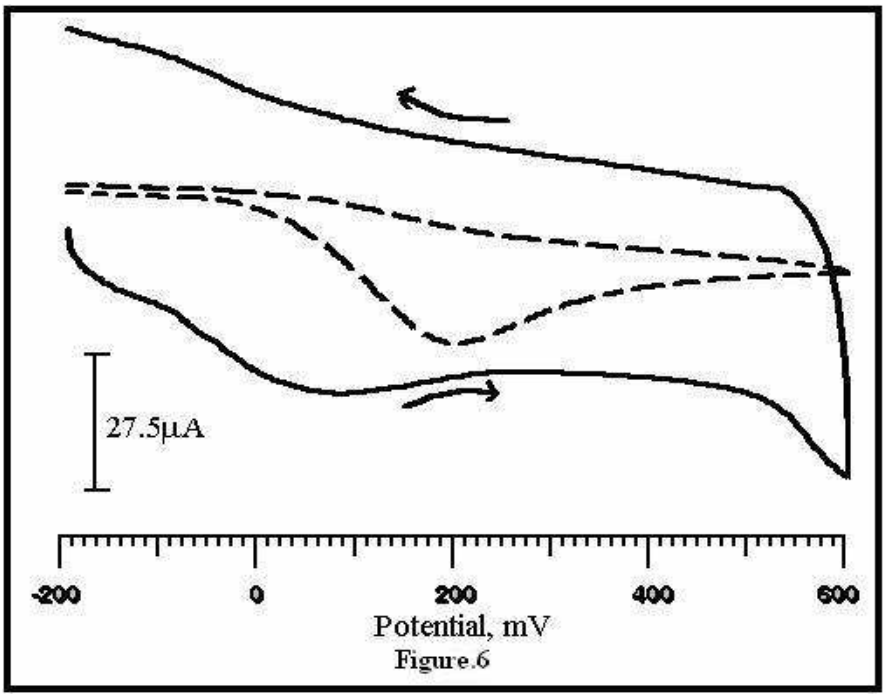


Figure.6. Cyclic voltammogram of 1X10^{-3} M AA in 0.2 M acetate buffer solution of pH 7 at bare CPE (solid line) and poly(VA) coated CPE (dashed line).

3.7. Simultaneous detection of DA in the presence of AA at poly (VA) MCPE

In order to examine the sensitivity and selectivity of poly (VA) MCPE the electrochemical behavior of a mixture of 0.5mM DA and 1mM AA was investigated using cyclic voltammetry. Fig.7 shows the cyclic voltammogram

obtained for DA and AA coexisting at bare CPE and poly (VA) MCPE. As shown in figure bare CPE (line curve) unable separate the voltammetric signal of DA and AA. Only one broad voltammetric signal for DA and AA was observed at approximately 195 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 (VA) MCPE resolved the voltammetric signal into two well defined voltammetric peaks at 40mV and 199mV corresponding to AA and DA respectively (solid line curve) This is because AA exists as anions in the pH 7.0,acetate buffer 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 (VA) MCPE. The separation between the oxidative peaks of DA and AA was approximately 159mV hence the simultaneous determination of DA in the presence of ascorbic acid is feasible at the poly (VA) MCPE.

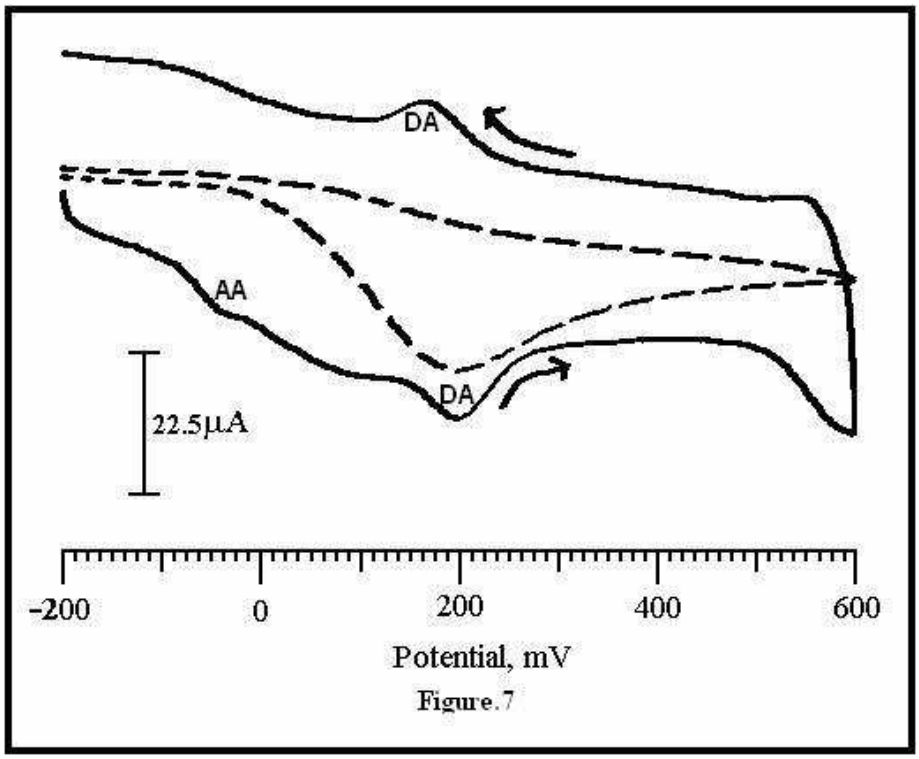


Figure 7. Cyclic Voltammetric determination of 0.5mM DA and 1X10^{-3}M AA at bare CPE (solid line) and at poly (VA) film coated CPE (dashed line).

CONCLUSION

In conclusion, were applied for the poly (VA) modification of CPE. This modified electrode exhibited high electrocatalytic activities towards the oxidation of DA and AA by significantly increasing their oxidation over potentials and enhancing the peak currents. Peak separation between DA and AA could be obtained using cyclic voltammetry, indicating that the poly(VA) CPE facilitated their simultaneous determination. This electrochemical sensor showed excellent selectivity and high sensitivity.

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