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Electrocatalytic Response of Dopamine at Mannitol and Triton X-100 Modified Carbon Paste Electrode: A Cyclic Voltammetric Study

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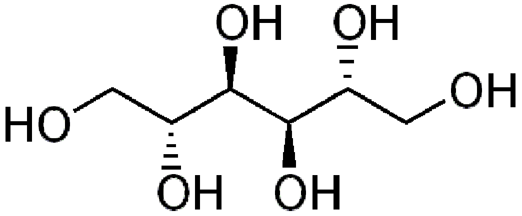
Present work describes the procedure that has been optimized for the determination of dopamine at Mannitol and TX-100 modified carbon paste electrode by cyclic voltammetric technique is 0.2 M acetate buffer solution at pH 6.0. The carbon paste electrode (CPE) modified with Mannitol and TX-100 showed very good sensitivity for dopamine. The effect of scan rate, concentration, pH variation was studied. Increase of dopamine concentration shows linear increase in redox peak currents. The preparation of the modified electrode was easy and renewed by simple polishing gives very good reproducibility, high stability in its voltammetric response and low detection limit for DA.

Keywords: Dopamine, Mannitol, TX-100, Carbon paste electrode, Cyclic Voltammetry

1. INTRODUCTION

Dopamine (DA), 3, 4-dihydroxyphenylethylamine, is an important neurotransmitter of the catecholamine group that exists in the mammalian central nervous system and is characterized by presenting very strong electrochemical activity [1]. In recent years, there has been considerable interest in developing new methods to measure this neurotransmitter in biological samples such as brain tissues [2, 3]. It is therefore very important to take into account both selectivity and sensitivity in the development of new voltammetric sensors for the determination of DA. Several works in the literature describes the development of new methodologies that employ chemically modified electrodes for the determination of DA in the presence of AA [4–10]. The intensive use of chemically modified electrodes has gained much attention now a days because of their interesting features for analytical use, such as good sensitivity, high selectivity, reproducibility, better stability and anti-fouling behavior [11]

TX-100 surfactant is a linear molecule with a hydrophilic (attracted to water) head and a hydrophobic (repelled by water) end. Due to its unique molecular structure, surfactant has been extensively used in the fields of electrochemistry [12, 13] and electroanalytical chemistry [14,15] for various purposes. Surfactants, containing hydrophobic and hydrophilic groups, can change the properties of the electrode /solution interface and subsequently influence the electrochemical processes of other substances. Adsorption of surfactant aggregates on the electron transfer, gently enhance the peak current, change the redox potential or charge transfer coefficients or diffusion coefficients, as well as alter the stability of electrogenerated intermediates or electrochemical products.



Scheme 1. Structure of Mannitol

Mannitol is an organic compound with the formula $C_6H_8(OH)_6$. This polyol is used as an osmotic diuretic agent and a weak renal vasodilator. It was originally isolated from the secretions of the flowering ash, called manner after their resemblance to the Biblica food and is also been referred to as mannite and manna sugar [16]. It is found in abundance in nature, particularly in exudates from trees, marine algae and fresh mushrooms. It is commercially available in variety powder and granules forms. The use of mannitol in food is broadly permitted by FDA food additive regulations. The Joint Food and Agriculture Organization/World Health Organization Expert Committee on Food Additives (JECFA) has reviewed the safety data and concluded that mannitol is safe. Mannitol has monographs in the United States Pharmacopoeia/National Formulary, as well as the various Pharmacopoeias around the world. Mannitol is included in the Food Chemical Codex (FCC).

In this work, the electrochemical oxidation of dopamine has been studied at mannitol and TX-100 modified carbon paste electrode in acetate buffer using cyclic voltammetric techniques. This study reveals that anodic process is dominated by adsorption and diffusion of dopamine simultaneously. Effect of anodic peak potential (Epa) anodic peak current (i_{pa}) has been discussed and reversible voltammogram was observed.

2. EXPERIMENTAL PART

2.1. Reagents and Chemicals

DA was purchased from Himedia Company and used without further purification, 10^{-5}M TX-100 was prepared in double distilled water. The DA sample was prepared in 0.1 M perchloric acid. Freshly prepared solutions were used in each experiment. All chemicals were of analytical grade quality and were used without further purification. The water used was a double distilled, and in all the measurements the acetate buffer solution was prepared by mixing standard stock solutions of 0.2 M CH_3COOH and CH_3COONa and adjusting the pH with 0.2 M CH_3COOH or 0.2 M NaOH

2.2. Apparatus and procedure

Cyclic voltammetry (CV) was performed in a model EA-201 Electroanalyser (Chemilink system). All 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 saturated calomel as a reference electrode.

2.3. Preparation of carbon paste electrode.

The carbon paste electrode was prepared as fallows 70% graphite powder and 30% silicone oil were mixed by hand to produce a homogeneous carbon paste .The paste was then packed into the cavity of a homemade carbon paste electrode and smoothed on a weighing paper. Similarly the modified carbon paste electrode was prepared by grinding different concentration of Mannitol along with graphite powder

3. RESULTS AND DISCUSSION

3.1. Electrocatalytic Oxidation of Dopamine at Mannitol Modified Carbon Paste Electrode.

Fig.1. shows the cyclic voltammograms obtained for the electrochemical response of DA at Mannitol modified carbon paste electrode (MMCPE) solid line and Bare carbon paste electrode (BCPE) dotted line in 0.2 M acetate buffer solution pH at 6.0 containing 1 mM DA at scan rate 50 mV/s. At BCPE, the oxidation and reduction peak potentials of DA occurs at 274 and 166 mV respectively. Under the identical conditions, MMCPE produces significantly increased peak current and more reversible electron process of DA with the oxidation and reduction peak potentials at 246 and 185 mV respectively. The remarkable enhancement of peak currents provides clear evidence of electrocatalytic effect of MMCPE.

3.2 Influence of Mannitol

One of the most effective parameters in modified electrodes performances is the compositions. The effect of the modifier on the development of sensors for DA has been studied [17-22] In our study mannitol was varied from 0.25 mg to 6 mg for investigation of 1 mM DA in 0.2 M acetate buffer solution pH 6.0 .This is shown more distinctively in fig.2, the plot of anodic peak current verses concentration of mannitol. As the figure illustrates DA oxidation peak is enhanced at 0.5 mg of the modifier and then decreases when the amount of modifier was increased further. This may be due to a decrease in oxidation sites in the paste and consequent reduction of the actual electrode area. Therefore the role of modifier is to enhance the peak current and also decreases the over potential for the oxidation and reduction of DA.

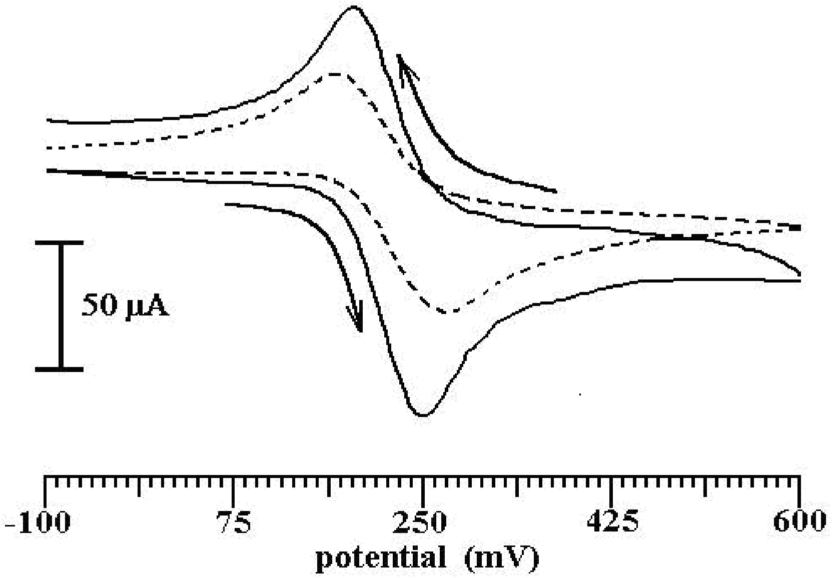


Figure 1. Cyclic voltammograms obtained for the electrochemical response of DA at mannitol MCPE (solid line) and bare carbon paste electrode (dashed line) in 0.2 M acetate buffer solution pH 6.0 containing 1 mM DA scan rate 50 mV/s.

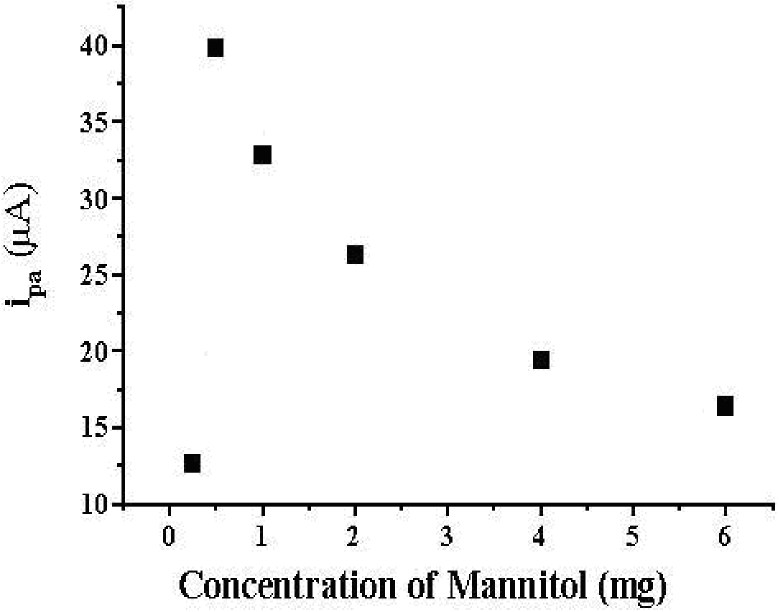


Figure 2. Plot of anodic peak current of DA verses concentration of mannitol in 1 mM DA pH 6.0. Acetate buffer solution.

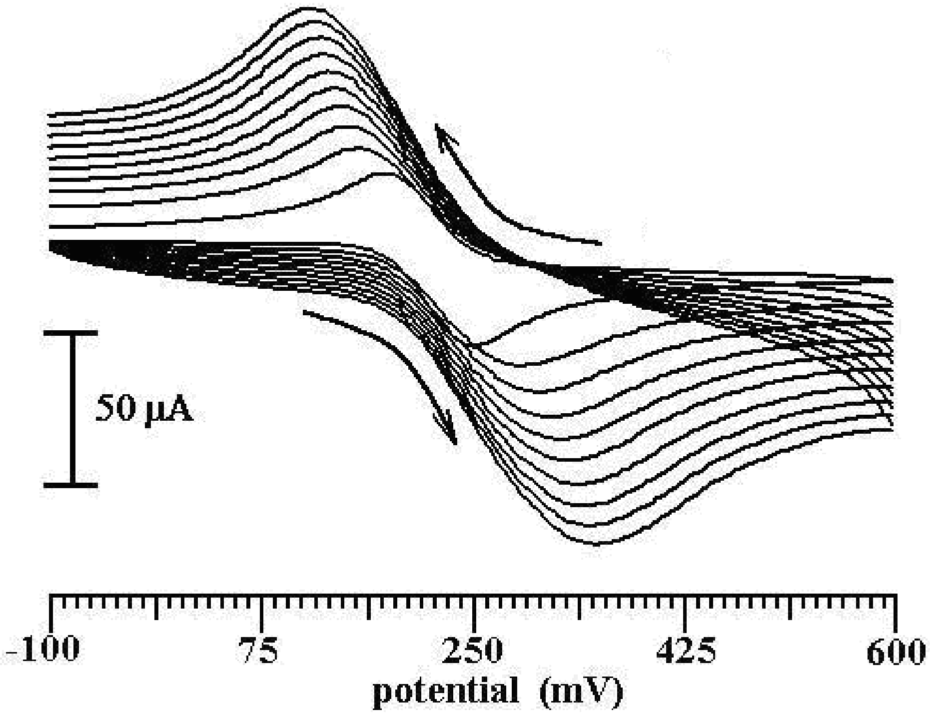


Figure 3a. Shows the CVs obtained from 1mM DA in 0.2 M acetate buffer solution pH 6.0 at mannitol modified carbon paste electrode scan rate,50,100, 150,200,250,300, 350,400, 450,500.

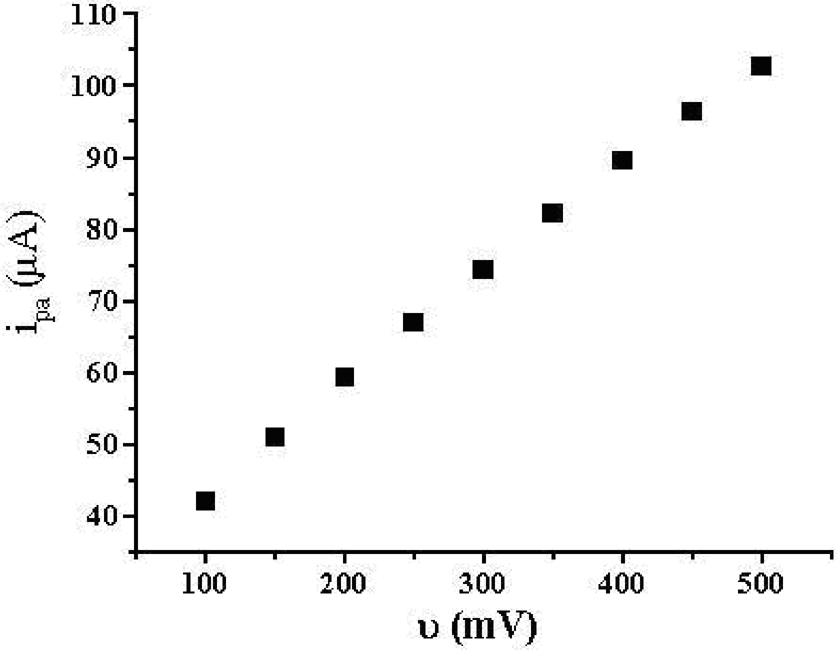


Figure 3b. Plot of anodic peak current verses scan rate.

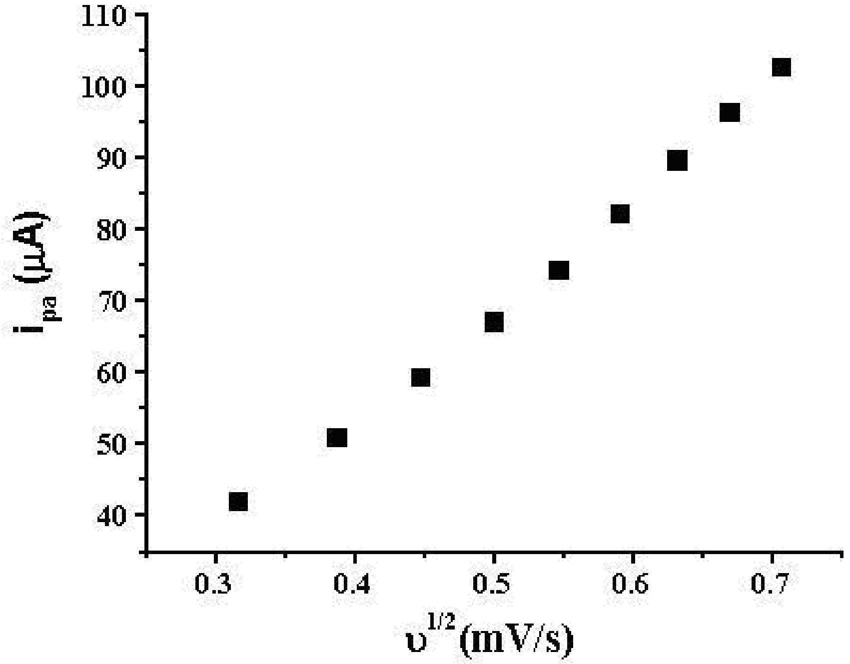


Figure 3c. Plot of anodic peak current verses square root of scan rate.

3.3. Effect of scan rate at Mannitol Modified Carbon Paste Electrode.

The effect of scan rate on the anodic peak current of DA was investigated experimentally. Fig.3a. shows the CVs obtained from 1mM DA in 0.2 M acetate buffer solution pH 6.0 at MMCPE. The anodic peak current was proportional to the scan rate in the range from 50 to 500 mV as shown in fig.3b. The linearity of the plot was good and the correlation coefficient was 0. 99898. It was therefore assumed that the electrode reaction of DA at the MMCPE was typical of an adsorption controlled process. Further the study showed that a good linear relationship was obtained between the anodic peak current and square root of scan rate (fig.3c) in the range 100 to 500 mV with correlation coefficient 0.99777 which indicates a diffusion controlled process occurring at the mannitol MCPE. These results reveal that the anodic process is dominated by diffusion and adsorption of DA simultaneously [20-23].

3.4. Effect of Concentration of Dopamine at the Mannitol Modified Carbon Paste Electrode.

Fig.4a shows the CVs at mannitol MCPE at different concentration of DA in 0.2 M acetate buffer solution (pH 6.0) at scan rate 50 mV/s. As shown in figure 4b the anodic peak current of DA increases with increase in concentration of DA. The linear relationship between current and concentration is obtained with correlation coefficient 0.99890 [24].

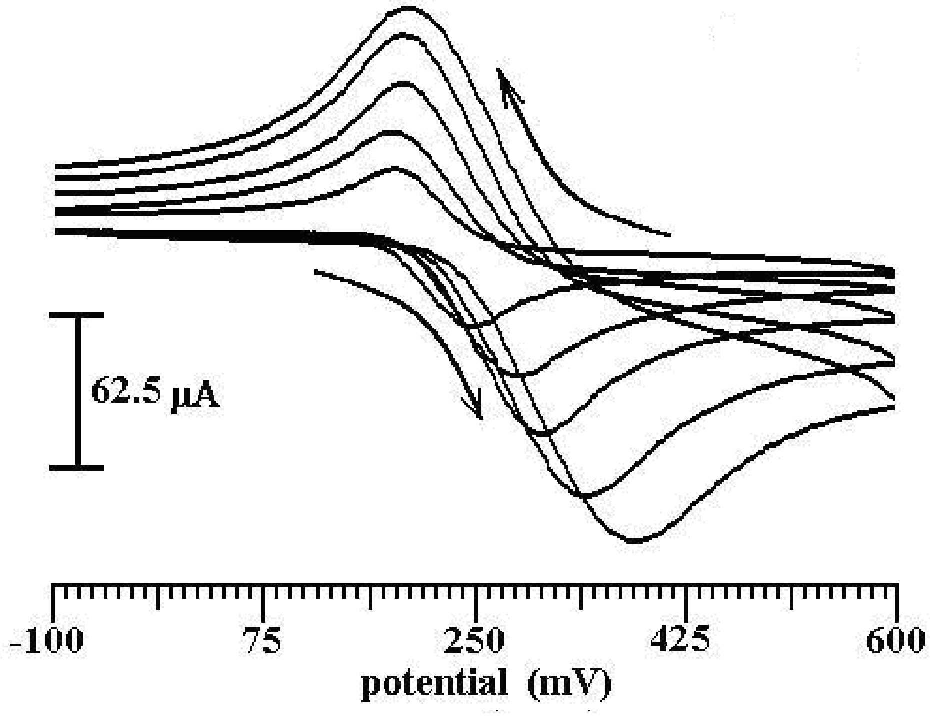


Figure 4a. Shows the CVs at mannitol modified carbon paste electrode at different concentration of DA (1, 2,3,4,5 mM) in 0.2 M acetate buffer solution (pH 6.0) at scan rate 50 mV/s.

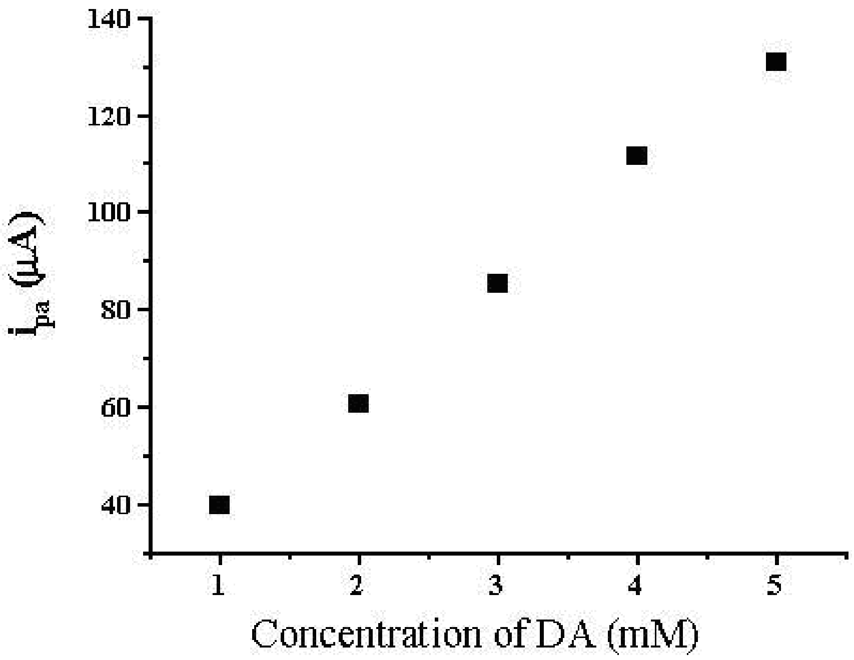


Figure 4b. Plot of anodic peak current verses the concentration of DA.

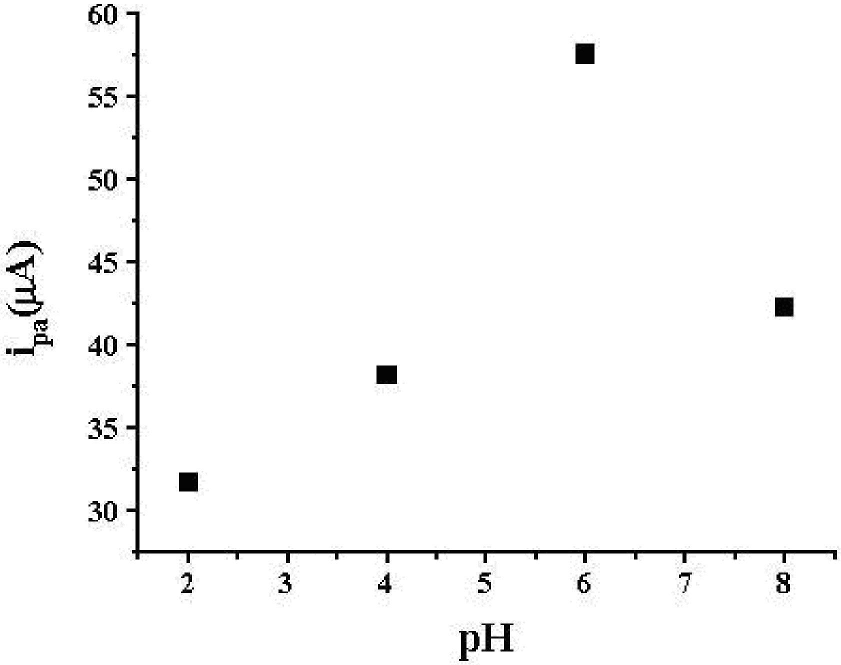


Figure 5a. Plot of anodic peak current verses pH.

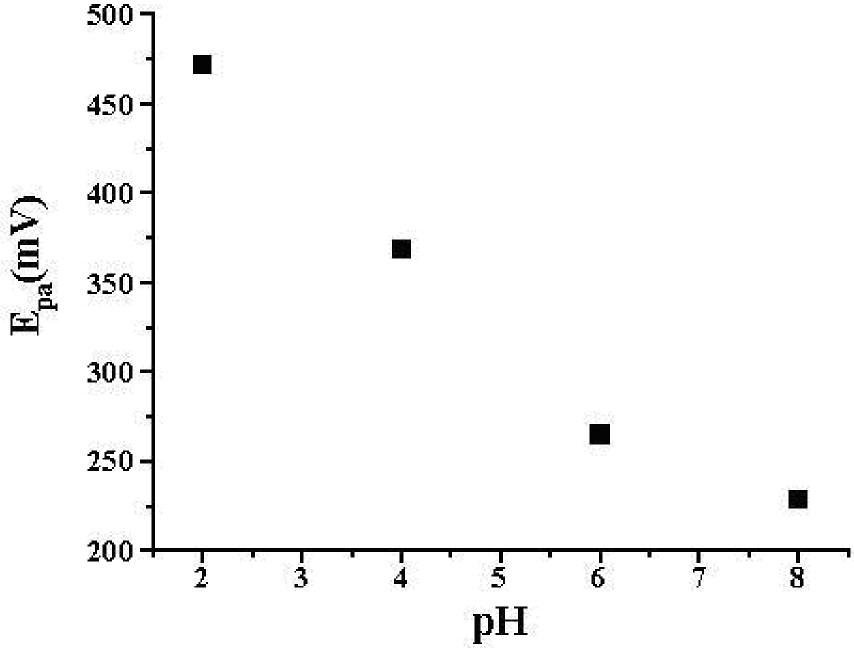


Figure 5b. Plot of anodic peak potential verses pH.

3.5. Effect of pH on DA at Mannitol Modified carbon paste Electrode.

To optimize the electrochemical response of modified carbon paste electrode for the oxidation and reduction of DA, the effect of pH on the electrode response was studied. The effect of solution pH over the range 2 to 8 was investigated. As shown in fig.5a the anodic peak current increased with increase in pH till it reached 6.0. When the pH was greater than 6.0 the anodic peak current decreased. The results indicate that at pH 6.0 the oxidation and reduction of DA was better as compared to other pH. Therefore this pH was chosen as the experimental pH value in the electrochemical detection of DA. The influence of pH on the anodic peak potential of DA was also investigated (fig.5b) in the pH range from 2 to 8, the anodic peak potential decreases with increase of pH which indicates that uptake of electrons is accompanied by equal number of protons [25-30]. Since DA involves a two electrons change process the number of electrons and protons will be equal to two.

3.6. Electrochemical response of dopamine at Mannitol modified carbon paste electrode on to the surface with TX-100

The experiment was carried out with TX-100 and the electrochemical responses dopamine at MMCPE in 0.2 M acetate buffer as a supporting electrolyte at pH 6.0 at a scan rate of 50 mVs^{-1} was shown in Fig.6 shows cyclic voltammogram of dopamine at BCPE (solid line) MMCPE (dashed line) and at TX-100MMCPE (dotted line).The voltammetric response is apparently improved in the presence of 40µLTX-100 reflected by the enlargement of cathodic and anodic peak current (dotted line).

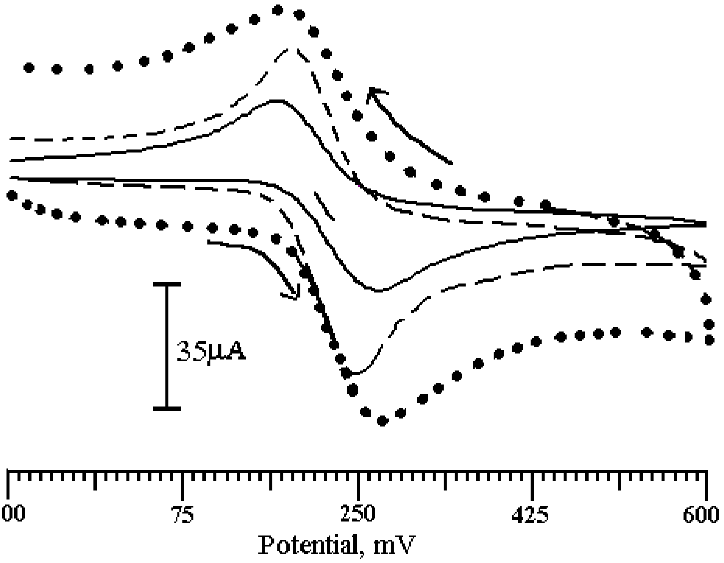


Figure 6. Cyclic voltammogram of DA at BCPE (solid line), MMCPE (dashed line) and 40µLTX-100 modified CPE (dotted line).Scan rate 50 mV/s.

3.7.Effect of TX-100concentration

The concentration of TX-100. Fig.7a clearly tells that TX-100 exhibits remarkable enhancement effect on the oxidation and reduction peak current of dopamine. However, the oxidation and reduction peak current of dopamine is closely related to the concentration of TX-100. The oxidation and reduction peak current increases greatly as TX-100 concentration was increased from 5μL to 40μL, the background current gradually increases while increasing the TX-100 concentration. The graph of concentration vs current shows very good linearity with correlation coefficient of 0.99539(fig.7b)

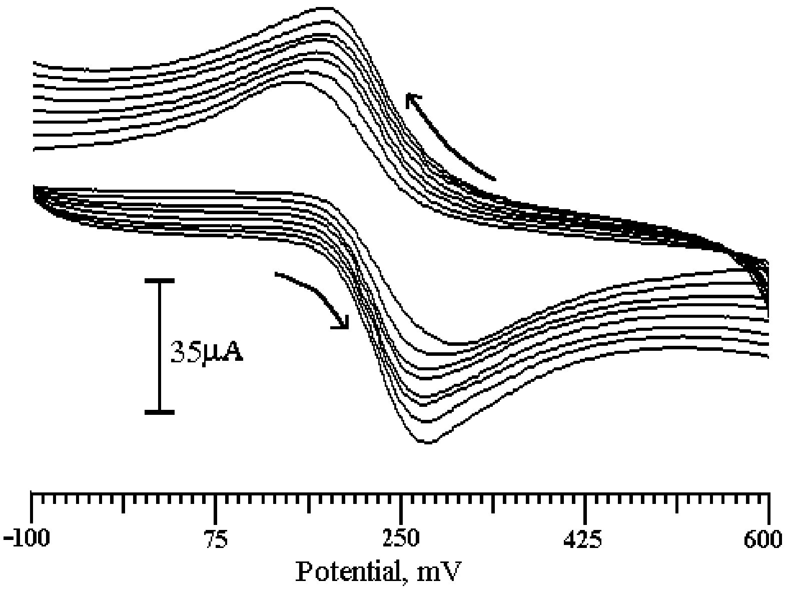


Figure 7a. Cyclic voltammogram of TX-100 different concentration (5μL-40μL).

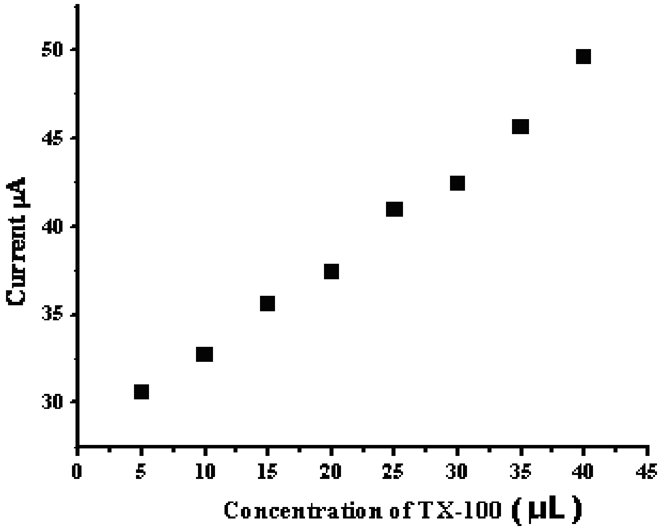


Figure 7b. Plot of anodic peak current verses concentration of TX-100.

3.8. Effect of Scan Rate on DA at TX-100 Mannitol Modified Carbon Paste Electrode.

The redox peak currents increase with increase in scan rate in the range from 50 to 500mVs^{-1} (Fig.8a). The graph of *Ipa* vs square root of scan rate shows very good linearity with correlation coefficient of 0.99643. The Fig.8b confirming that the electrode process at the electrode surface has some diffusion-controlled and the carbon paste electrode which might be able to explain the enhancement effects of surfactants in some electroanalytical systems [31-32].

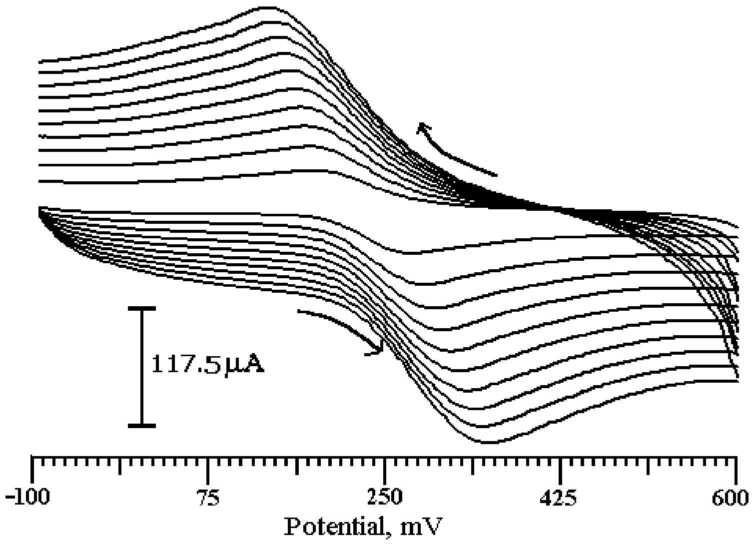


Figure 8a. The effect of scan rate on dopamine at TX-100 40µL surfactant immobilized MMCPE.

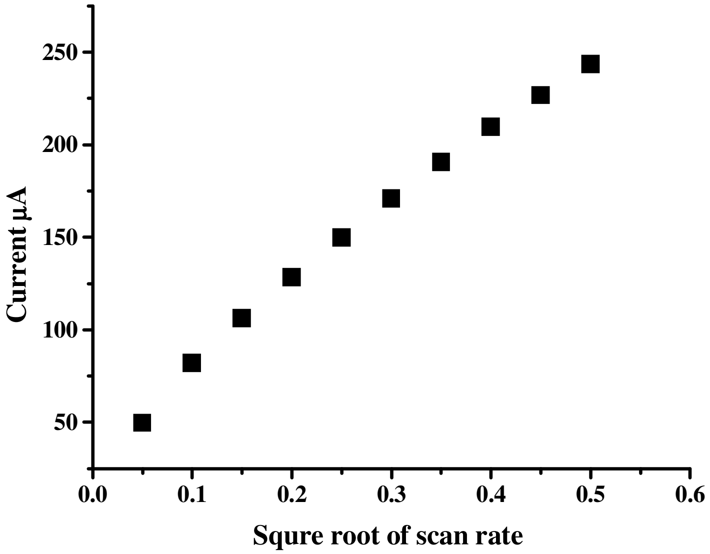


Figure 8b. Plot of anodic peak current verses square root of scan rate.

4. CONCLUSIONS

The MMCPE and TX-100 modified carbon paste electrode shows a good electrocatalytic activity towards the determination of dopamine. Cyclic voltammograms of the resulting chemically modified electrode shows the presence of reversible redox couple of dopamine. It is expected that with its low cost, easy preparation and high electrocatalytic behavior. Mannitol modified carbon paste electrode has application in the fields of electroanalytical chemistry and biosensors.

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