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Electrochemical Oxidation of Dopamine at Polyethylene glycol Modified Carbon Paste Electrode: A Cyclic Voltammetric Study

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Polyethylene glycol (PEG) modified carbon paste electrode (CPE) was fabricated for the detection of dopamine and potassium ferricyanide. It showed an excellent sensitivity towards the oxidation of dopamine (DA) in 0.1M phosphate buffer (PBS) at 6.6 pH and potassium ferricyanide in 1 M KCl solution. Effect of scan rate, concentration and pH were studied by the cyclic voltammetric technique. The concentration effect of modifier in the carbon paste electrode also reveals that the change in the electrode interface which would leads to the surface modification of the electrode, enhanced the interaction between the electrode and the cationic charged dopamine. The detection limit of dopamine is 1×10^{-5} M and the potassium ferricyanide is 1×10^{-4} M was observed for the PEG/CPE.

Keywords: Dopamine, Potassium ferricyanide, PEG/CPE, Cyclic voltammetry and PBS

1. INTRODUCTION

Potassium ferricyanide is the bright red coordination compound. It is soluble in water and its shows green fluorescence. Potassium ferricyanide is used as an oxidizing agent to remove silver from negatives and positives, a process called dot etching. Potassium ferricyanide is often used in physiological experiments as a means of increasing a solutions redox potential [1, 2]. Hu et al. [3, 4] studied potassium ferricyanide as a standard for modified cetyl trimethyl ammonium bromide carbon paste electrode. It is universal known compound to check the behaviour of electron transfer kinetics of the electrode.

Dopamine (DA) is one of the most important neurotransmitters and is present in the mammalian central nervous system. It is a catecholamine in the form of large organic cations and belongs to the family of excitatory chemical neurotransmitters [5]. It plays a crucial role in the functioning of the central nervous, cardiovascular, renal, and hormonal systems as well as in Parkinson’s disease [6-8]. Changes in DA concentration in biological samples are an important indication of possible body abnormalities or diseases. Therefore, determination of DA has become important and been given tremendous attention by neuroscientists and chemists in biomedical and bioanalytical research since its discovery during the 1950s. DA possesses high electrochemical activity and has been widely studied by electroanalytical techniques to significantly benefit biosciences [9, 10-12]. Detection of DA in the physiological environment with sensitivity has been an important role of electroanalytical research. It is well known that detection of DA directly with plain electrodes, such as carbon and metallic electrodes is ineffective. So it is important to establish a fast, sensitive method for the detection of DA by the modification of bare electrodes and makes their detection possible by electrochemical methods based on anodic oxidation [13].

During the last decades, new electrodes using organic molecules as sensing elements have been developed. Due to their ease of construction and low cost, the modified electrodes are most widely used. Also the modification of these electrodes is simple because it only requires mixing the modifier with the carbon paste. In this way, it is possible to add a wide variety of products (inorganic or organic substances [14, 15], biomolecules, animal or plant tissues [16] etc

Several approaches to chemically modify electrochemical sensors have been adopted including chemisorptions, covalent modification or polymer modification [17].

Polyethylene glycol is a commercially available polyether which is used in the clinical research. PEG is nontoxic, non immunogenic, and approved by the U.S. Food and Drug Administration for various clinical uses [18]. PEG is being used in the repair of motor neurons damaged in crush or laceration incidence in vivo and in vitro. When coupled with melatonin, 75% of damaged sciatic nerves were rendered viable [19]. In many cases, PEG has been applied as a ‘‘stealth material’’ because it is inert to most biological molecules such as proteins [20]. Many forms of PEG surface modification have been used to render a surface protein resistant and to enhance surface biocompatibility [21]. In the presence of cells, PEG is passive to constituents of the cell environment because they prevent adsorption of proteins. Mizutani et al. [22] have shown that a carbon paste electrode incorporating polyethylene glycol (PEG) - modified glucose oxidase exhibits a higher glucose response than an electrode incorporating native glucose oxidase. C.Saby et al. fabricated the poly (ethylene glycol) incorporated modified glucose oxidase and various mediators carbon paste electrode for the glucose determination [23]. Yinghong Xiao et al. [24] have shown that the highly sensitive and selective method to detect dopamine in the presence of ascorbic acid by polymeric composite MUA- PEG modified electrode.

As a part of our research work on the development modified electrodes, we extended our work on the detection of dopamine [25-30]. In this work polyethylene glycol modified carbon paste electrode was fabricated and characterized by cyclic voltammetry. The polyethylene glycol modified electrode showed good electrocatalytic oxidation of dopamine. On the basis of the electrochemical response of dopamine the polyethylene modified carbon paste electrode can be used for the development of sensor.

2. EXPERIMENTAL PART

2.1. Reagents and chemicals

Potassium ferricyanide [$K_3Fe(CN)_6$,] dopamine, KCl, perchloric acid, sodium dihydrogen orthophosphate dihydrate, di-sodium hydrogen phosphate anhydrous and polyethylene glycol used were of analytical grade quality from sd. Fine chemicals. All the above reagents solutions were prepared by dissolving in double distilled water. Graphite powder was acquired from Lobo chemie.

2.2.Apparatus

Cyclic voltammetry was conducted with Model EA-201 Electroanalyser (EA-201, Chemilink System) with a traditional three-electrode system. The PEG/CPE was used as the working electrode, with a saturated calomel electrode (SCE) as the reference electrode and all the potentials reported here are referred to this electrode; and a platinum electrode as the auxiliary electrode. The pH of the buffer solution was measured with the digital pH meter MK VI.

2.3. Fabrication of the carbon paste electrode.

The traditional CPE was prepared by hand-mixing of graphite powder with silicon oil at a ratio 70:30 in an agitate mortar. The homogeneous carbon paste electrode was packed into a cavity of a homemade carbon paste electrode (3.0 mm in diameter). The PEG/CPE surface was smoothed on a piece of weighing paper. The electrical contact was provided by copper wire connected to the paste in the end of tube.

3. RESULTS AND DISCUSSION

3.1. Electrochemical response of $K_3Fe(CN)_6$ at PEG modified carbon paste electrode.

Electrochemical response of $K_3Fe(CN)_6$ at PEG modified carbon paste electrode is as shown in the figure. 1a. The cyclic voltammogram of the bare carbon paste electrode (dashed line) was low current signal in response to the unmodified and roughness of the electrode surface, and was $\Delta Ep=51mV$. However, the voltammetric response was apparently improved at PEG modified carbon paste electrode, which revealed by the enhancement of the peak currents (ip) due to the negative charge of the modifier on the PEG/CPE could enhances by anionic- anionic repulsion and the potential difference between the reduction and the oxidation peak curves (solid line) shifted slight towards away to the bare one and was $\Delta Ep = 61$ mV.

Fig. 1b shows the voltammograms of $K_3Fe(CN)_6$ (solid line) and the blank solution (dashed line) at PEG modified carbon paste electrode. No peaks were observed at the blank supporting electrolyte which revealed that there was no peak interferences of the modifier PEG at the oxidation and reduction peak current of the potassium ferricyanide.

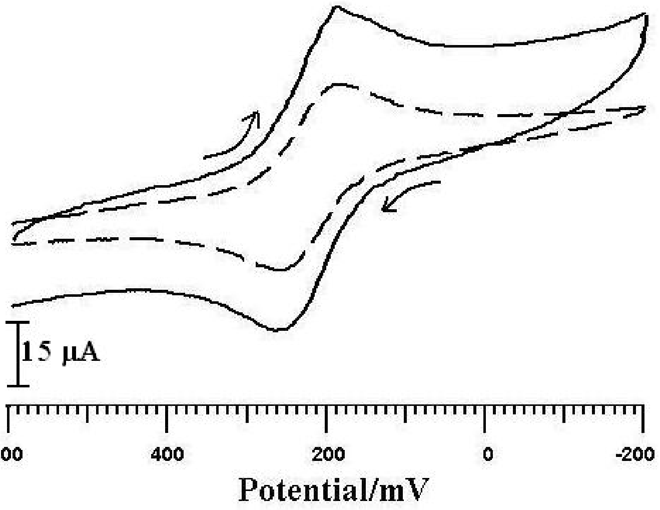

Figure 1a. Cyclic voltammograms of 1 mM $K_3Fe(CN)_6$ at bare carbon paste electrode(dashed line) and at PEG modified carbon paste electrode (solid line). Supporting electrolyte 1 M KCl at scan rate 100 mVs^{-1}

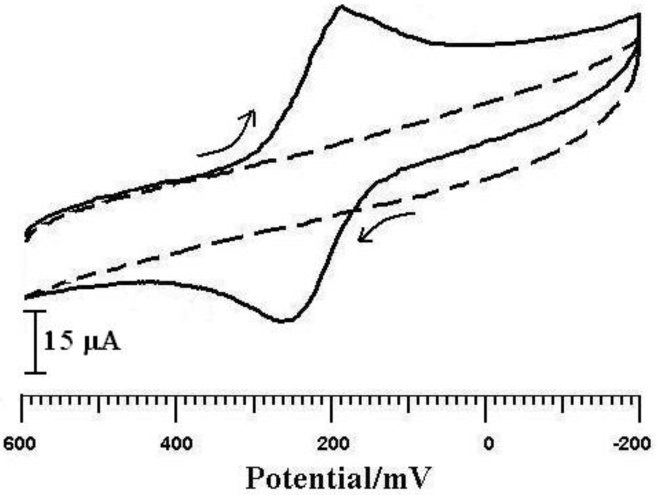

Figure 1b. Cyclic voltammograms of blank supporting electrolyte 1 M KCl (dashed line) and 1 mM $K_3Fe(CN)_6$ in 1 M KCl (solid line) at PEG modified carbon paste electrode at scan rate 100 mVs^{-1}

3.2. Effect of concentration.

Fig. 2a showed the successive enhancement of cyclic voltammograms peak current on increasing $K_3Fe(CN)_6$ concentration from 0.5×10^{-4} M - 4.0 $\times10^{-4}$ M. The plot of peak current (obtained by measuring the cathodic peak current height) versus the respective concentration of $K_3Fe(CN)_6$ was found to be linear in the range 0.5×10^{-3} M – 4.0×10^{-3} M and the correlation coefficients was 0.9959 as shown in Fig. 2b. Fig.2c shows the cyclic voltammogram of detection limit of the PEG modified carbon paste electrode. The sensitivity of the modified electrode was 1×10^{-4} M which shown in the cyclic voltammogram(c) the well redox peaks can be found at CV (a & c: 1×10^{-3} M and 5×10^{-4} M).

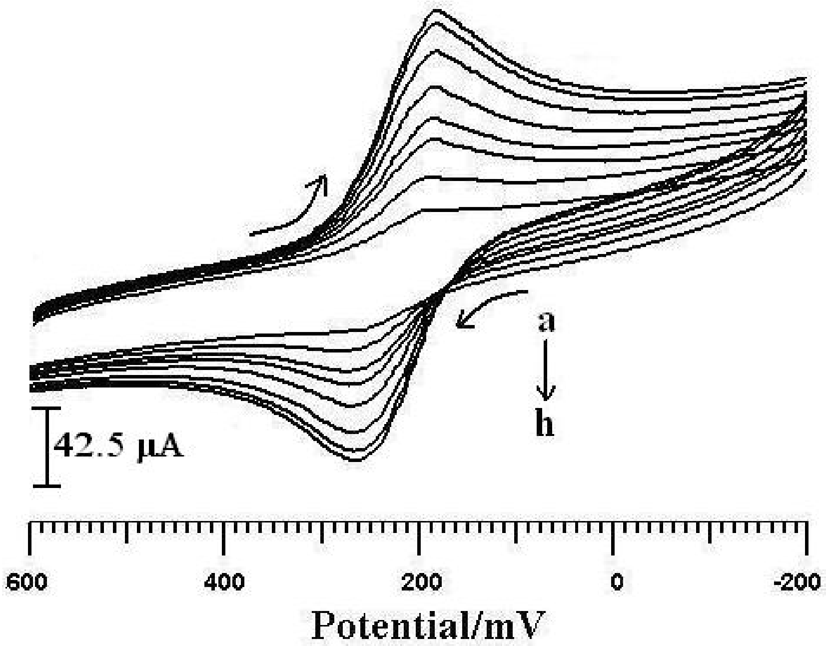

Figure 2a. Cyclic voltammogram of different concentration of $K_3Fe(CN)_6$ at PEG modified carbon paste electrode (a = 0.5, b = 1.0, c=1.5, d=2.0, e=2.5, f=3.0, g=3.5, h=4.0 mM). Supporting electrolyte 1 M KCl at scan rate 100 mV s^{-1}

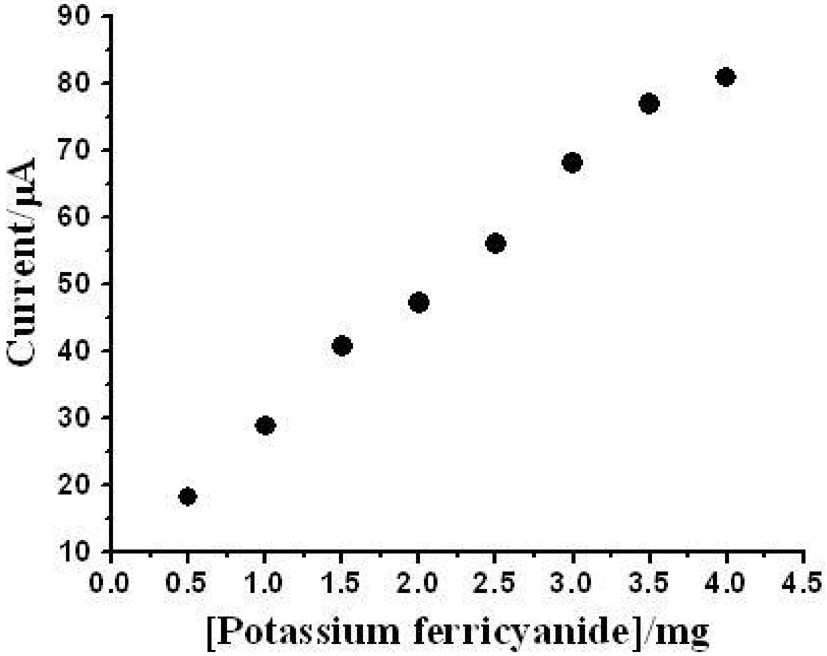

Figure 2b. Effect of concentration variation of $K_3Fe(CN)_6$ at PEG modified carbon paste electrode. Supporting electrolyte 1 M KCl at scan rate 100 mV s^{-1}

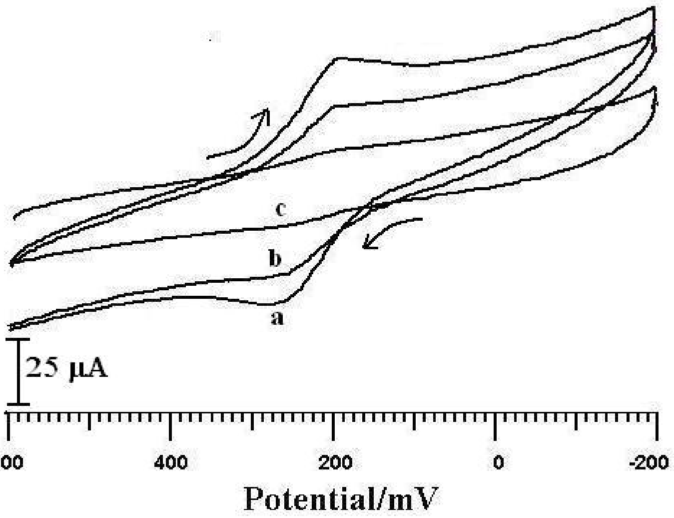

Figure 2c. Cyclic voltammogram of detection limit of $K_3Fe(CN)_6$ (a=1×10^{-3} M, b=5×10^{-4} M, c=1×10^{-4} M) at PEG modified carbon paste electrode in 1 M KCl at 100 mV/s.

3.3. Effect of scan rate.

Fig. 3a and 3b shows the adsorption-controlled behaviour of $K_3Fe(CN)_6$ at the PEG/CPE which was revealed by the linear dependence of reduction peak current on the scan rate and its correlation coefficient was 0.9966. PEG could form a special ion complex with $K_3Fe(CN)_6$ through electrostatic interaction [31] and might be adsorbed at the interface between the hydrophobic surface and the aqueous solution [3, 27]. The proposed behaviour of $K_3Fe(CN)_6$ at a carbon paste electrode in the presence of PEG might arise from the interaction between PEG and $K_3Fe(CN)_6$, i.e., the electrochemical response of $K_3Fe(CN)_6$ in the presence of PEG could be utilized to investigate the adsorptive behaviour at a PEG/carbon paste electrode.

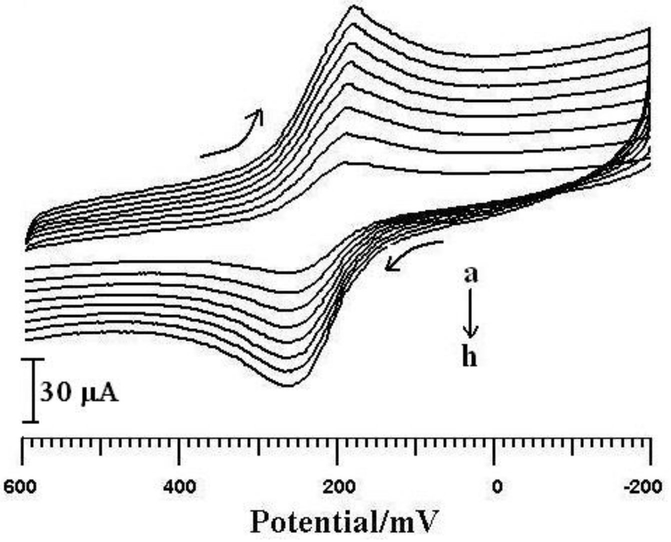

Figure 3a. Cyclic voltammogram of scan rate variation of 1 mM $K_3Fe(CN)_6$ at PEG modified carbon paste electrode a = 50mV/s, b = 100mV/s, c = 150 mV/s, d = 200 mV/s, e = 250 mV/s ,f = 300 mV/s, g=350 mV/s, h = 400 mV/s. Supporting electrolyte 1 M KCl.

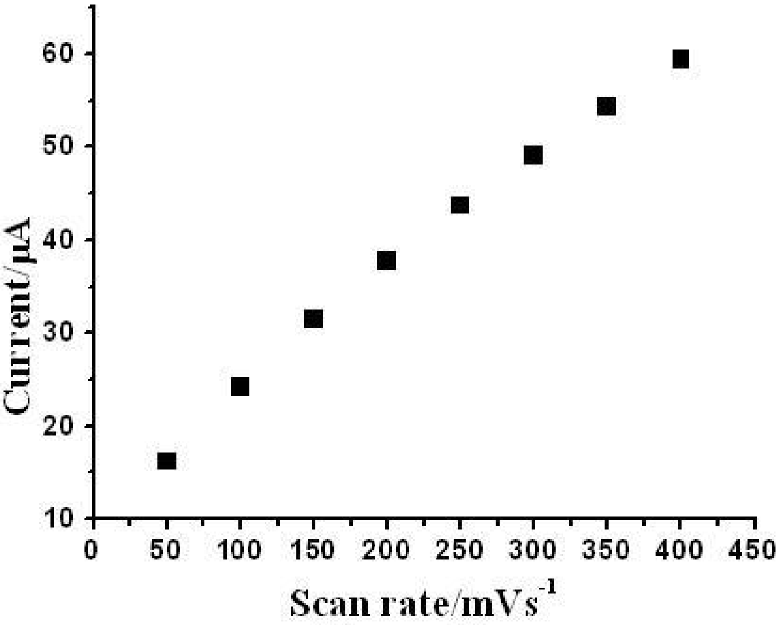

Figure 3b. Effect of scan rate variation of $K_3Fe(CN)_6$ at PEG modified carbon paste electrode. Supporting electrolyte 1 M KCl.

3.4. Effect of PEG on peak current and peak potential.

Figure.4 shows the effect of PEG concentration on the peak current of 1×10^{-3} M $K_3Fe(CN)_6$. When the concentration of polyethylene glycol is higher both i_{pc} and i_{pa} gets increases from 1- 4 mg PEG/CPE and above that the peak currents could not identify due to their high background current. Hence the 2mg PEG/CPE was selected for its good consistent sensitivity for the $K_3Fe(CN)_6$ to the bare carbon paste electrode.

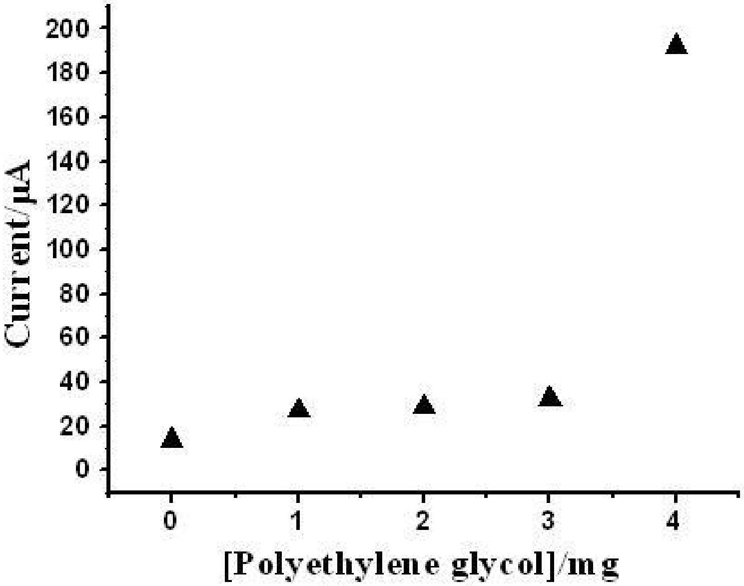

Figure 4. Effect of modifier concentration on peak current for 1 mM $K_3Fe(CN)_6$ at PEG modified carbon paste electrode. Supporting electrolyte 1 M KCl at scan rate 100 mV s^{-1}.

3.5. Electrochemical response of dopamine at PEG modified carbon paste electrode

The electrochemical response of dopamine at PEG modified carbon paste electrode is shown in the Fig.5. The cyclic voltammogram of dopamine at bare carbon paste electrode was low current signal (dashed line). However, the voltammetric response was apparently improved at PEG modified carbon paste electrode, reflected by the enlargement of the peak currents (ip) and the potential difference (ΔEp) slightly shifted towards the positive side between the reduction and the oxidation peak curves (solid line).

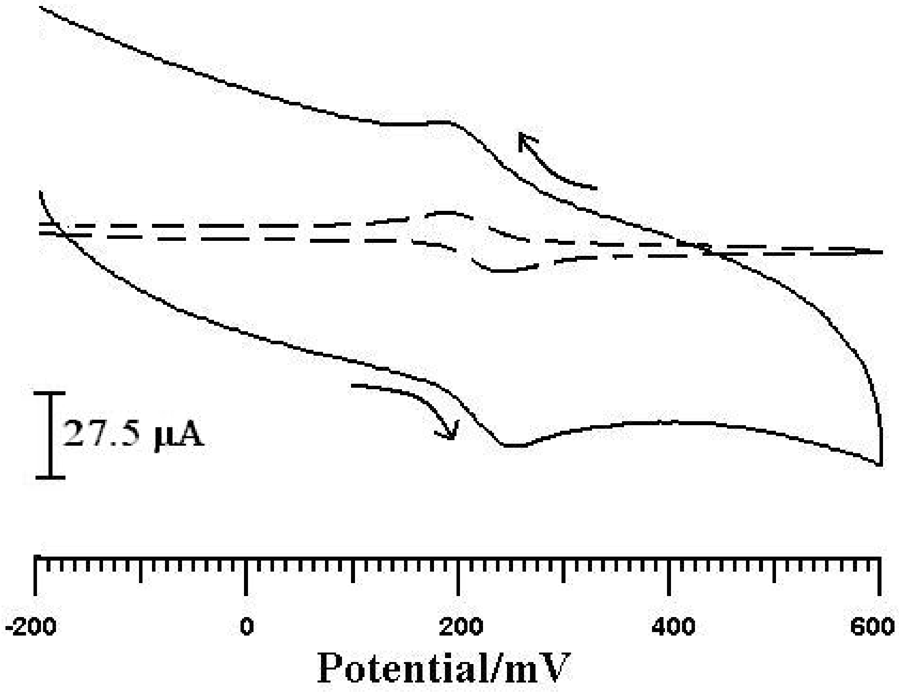

Figure 5. Cyclic voltammograms of 1 mM dopamine at bare carbon paste electrode (dashed line) and PEG modified carbon paste electrode (solid line) in 0.1 M phosphate buffer at scan rate 100 mVs^{-1}

3.6. Electrochemical behavior of PEG modified carbon paste electrode.

Figure.6a shows the electrochemical activity of the PEG modified carbon paste electrode. The cyclic voltammogram (dashed line) represents the no redox activity of the polyethylene glycol is exhibiting in the supporting electrolyte phosphate buffer at pH-6.6 and (solid line) shows well demarkable reversible redox peak for the 1×10^{-4} M dopamine at 0.1 M phosphate buffer (pH-6.6). Figure. 6b shows the calibration plot of polyethylene glycol sensitivity tendency towards the dopamine. Lower the concentration of the modifier lower is the current response, by increasing the concentration of which increases gradually upto 4 mg and it enhances much at 5 mg in which the redox peak couldn't clearly distinguishable due to its higher background current. Hence 3 mg concentration of polyethylene glycol was taken to study the dopamine.

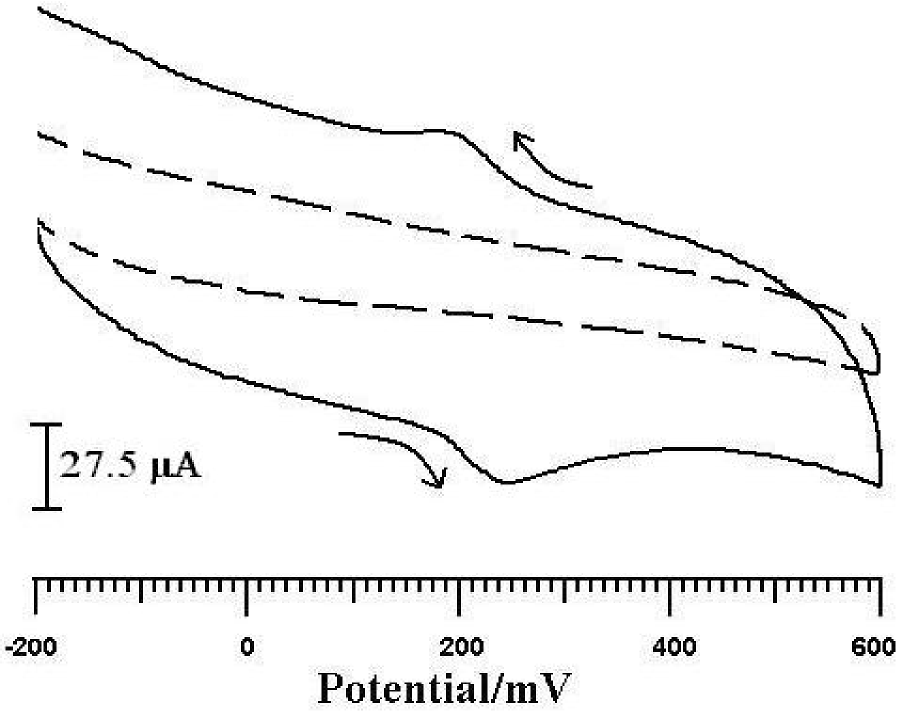

Figure 6a. Cyclic voltammograms of polyethylene glycol modified carbon paste electrode (dashed line) and 1×10^{-4} M dopamine at PEG/CPE (solid line) in 0.1 M phosphate buffer at pH-6.6

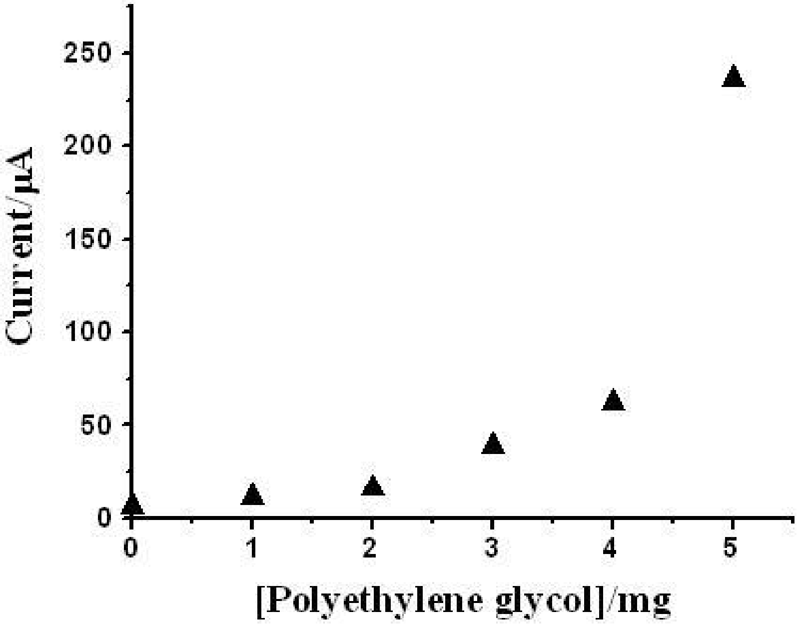

Figure 6b. Effect of modifier concentration on peak current for 1× 10^{-4} M dopamine at PEG modified carbon paste electrode. Supporting electrolyte 0.1 M phosphate buffer at scan rate 100 mVs^{-1}.

3.7 Effect of scan rate.

The cyclic voltammogram of 1 mM dopamine at polyethylene glycol modified carbon paste electrode Fig.7a shows the increase in the peak currents by increasing the scan rate from 50 mV/s to 400 mV/s and the peak currrents i_{pa} & i_{pc} were shifted slight towards apart. The interdependence graph of anodic current v/s scan rate is linear which reveals the electron transfer mechanism was adsorption controlled and the correlation coefficient is 0.9998 shown in the Figure. 7b

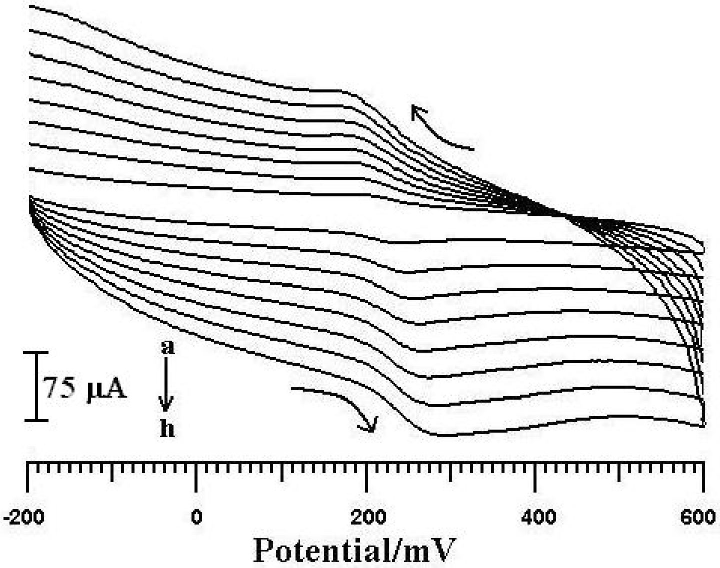

Figure 7a. Cyclic voltammogram of 1×10^{-4} M dopamine at different scan rate (a – h; a=50, b= 100, c=150, d=200, e=250, f=300, g=350, h=400 mV/s) at PEG/CPE in 0.1 M phosphate buffer at pH-6.6.

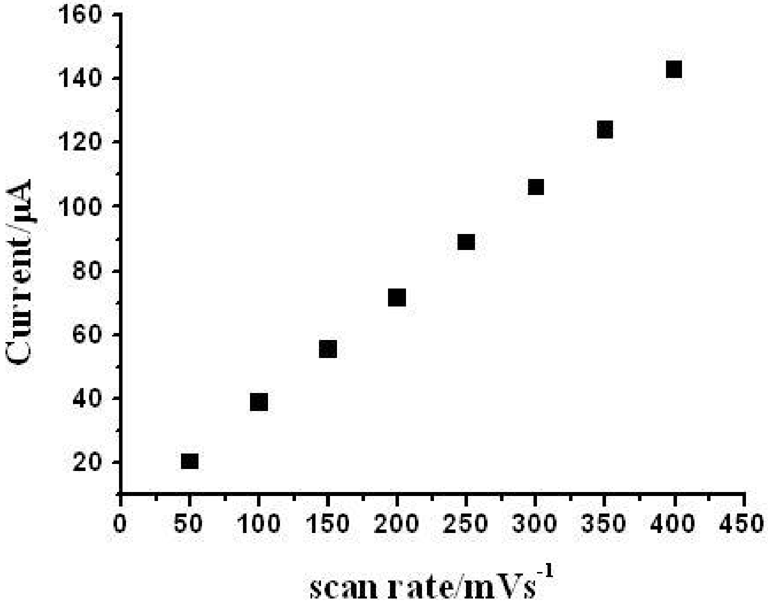

Figure 7b. Effect of scan rate variation of dopamine at PEG modified carbon paste electrode. Supporting electrolyte 0.1 M phosphate buffer at pH-6.6.

3.8. Effect of concentratation.

The cyclic voltammogram of different concentration of dopamine is seen in the Figure.8a which shows the increase in both the anodic peak current (i_{pa}) and cathodic peak current (i_{pc}) due to vary the concentration of dopamine from 0.5×10^{-4} to 3.5×10^{-4}M. Figure. 8b shows the linear relationship between the anodic peak current and the concentration. The correlation coefficient value was found at 0.9998.

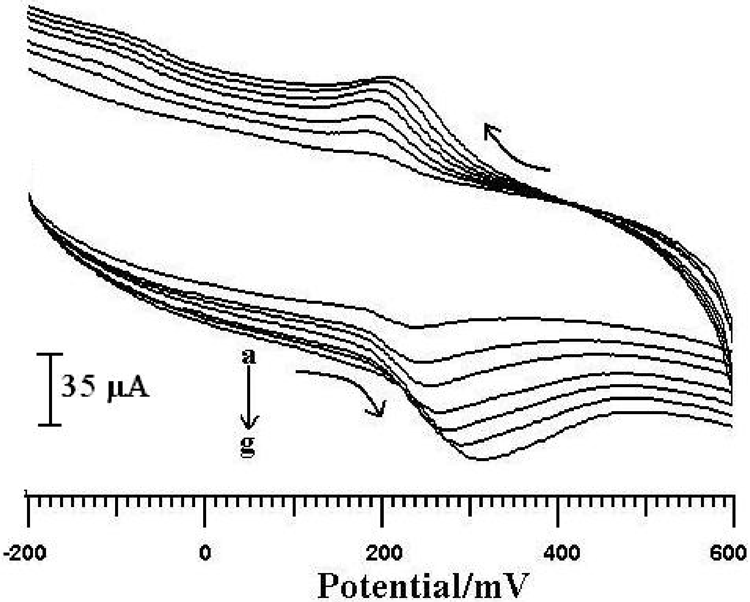

Figure 8a. Cyclic voltammograms of different concentration of dopamine (10^{-4} M) (a-g; a=0.5, b=1, c=1.5, d=2.0, e=2.5, f=3, g=3.5) at PEG/CPE at 100 mV/s in phosphate buffer at pH-6.6.

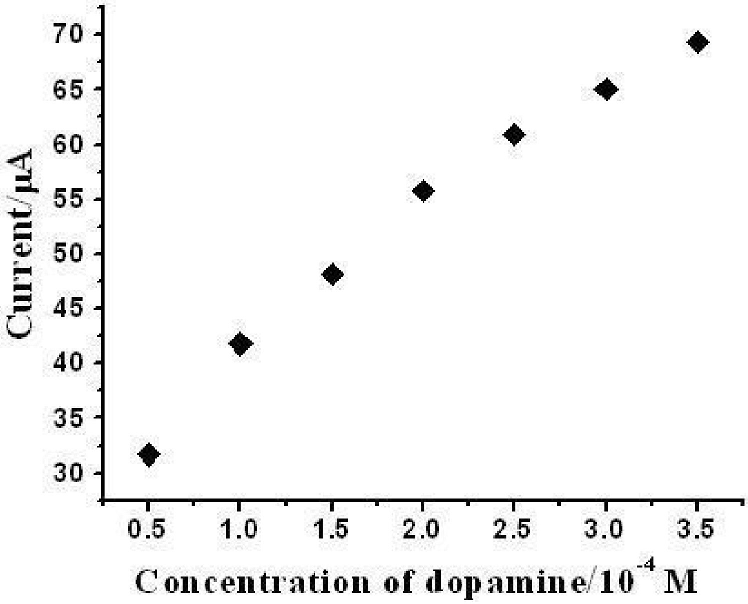

Figure 8b. Effect of concentration variation of dopamine at PEG modified carbon paste electrode. Supporting electrolyte 0.1 M phosphate buffer at scan rate 100 mV s^{-1}.

3.9. Sensitivity dependence of dopamine on PEG/CPE:

Figure. 9 shows the cyclic voltammogram of detection ability of the polyethylene glycol modified carbon paste electrode of the dopamine. The voltammogram (b & c; 5 × 10^{-5} M, 1×10^{-4} M) exhibit the well remarkable redox peak but it is not shown at the (a= 1×10^{-5}M) and hence the detection limit of dopamine on PEG/CPE is 1×10^{-5} M.

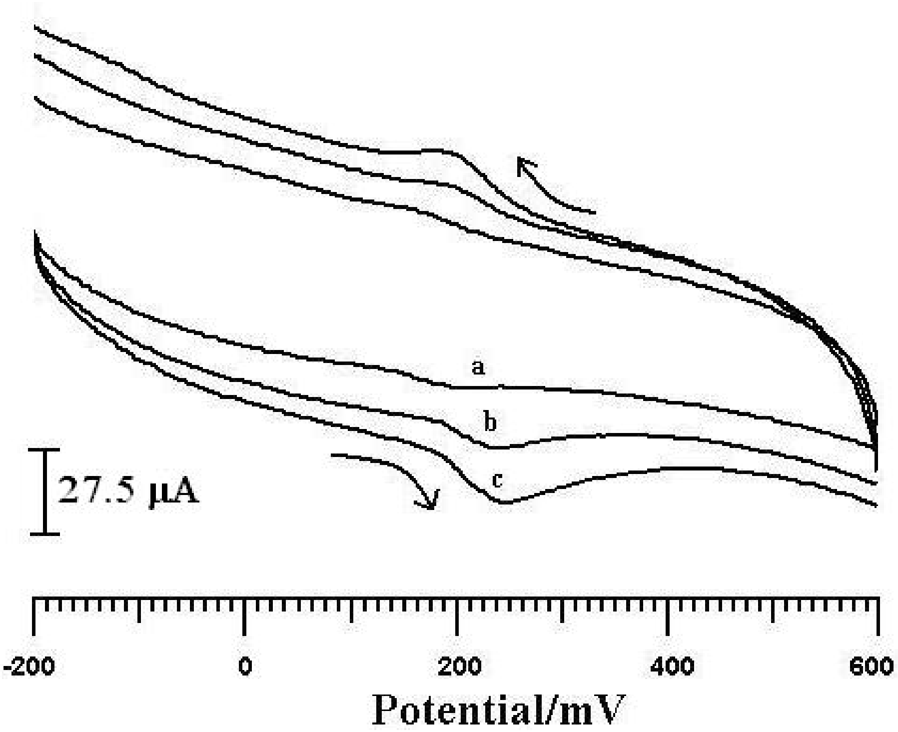

Figure 9. Cyclic voltammograms of the detection limit of dopamine (a=1×10^{-5}M, b=5×10^{-5}M & c= 1×10^{-4}M) on PEG/CPE in 0.1 M phosphate buffer at scan rate 100 mVs^{-1}.

3.10. Effect of pH variation.

As the pH increases from the lower to the higher, the anodic peak current shifted towards the negative side and the well redox peak is arrived at the near neutral pH-6.6 (Figure-10a) with the peak potential difference is comparatively better than the other either acidic or basic pH.

Figure 10b shows the anodic peak potential dependent on pH reveals the easy oxidation of the dopamine at the negative peak potential and hence the oxidation of the dopamine is studied at the pH 6.6.

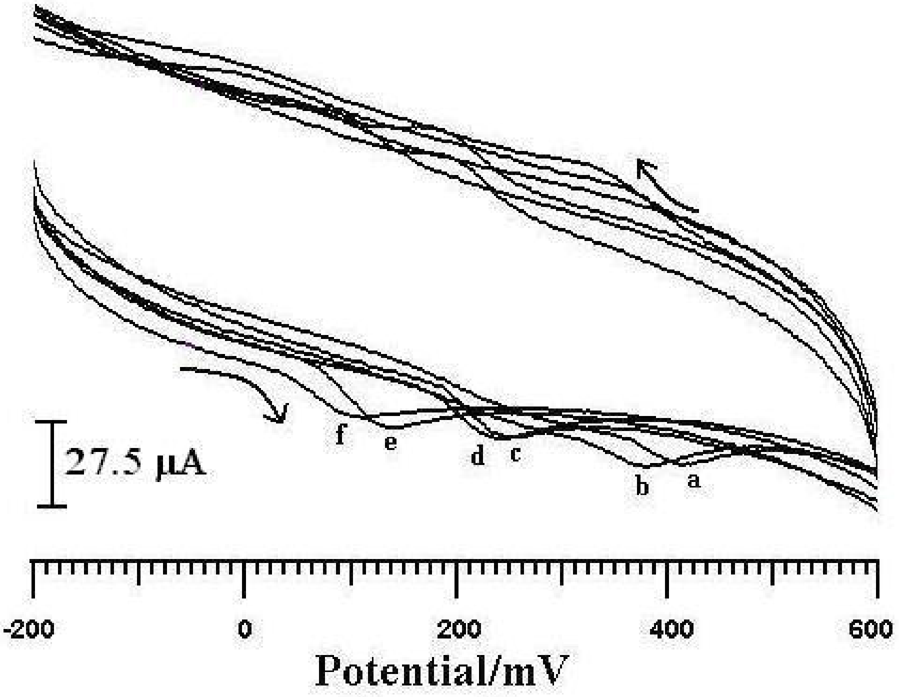

Figure 10a. Cyclic voltammogram of 1×10^{-4} M dopamine at different pH (4.5, 5.5, 6.5, 7.5, 8.5, 9.5) in 0.1M phosphate buffer at 100 mV/s.

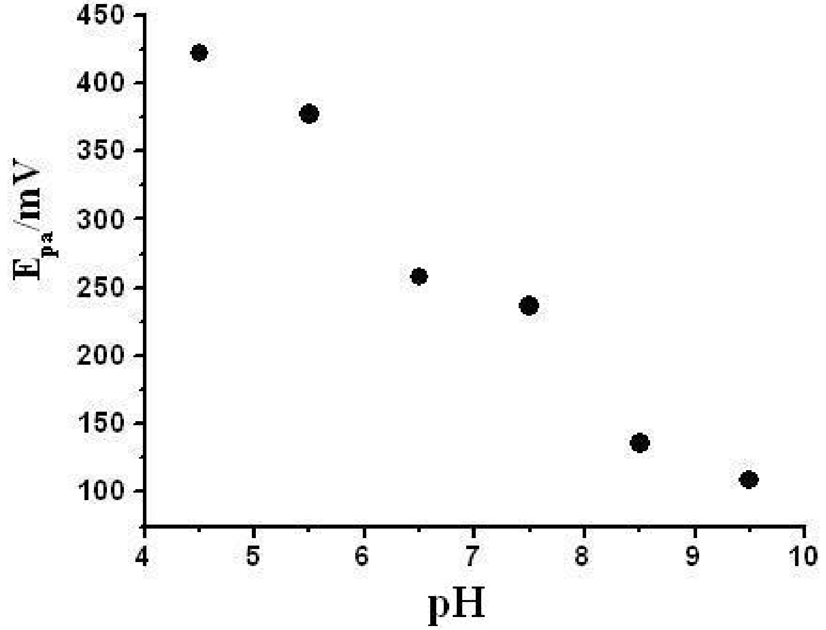

Figure 10b. Effect of variation of pH on the anodic peak potential of 1×10^{-4} M dopamine in phosphate buffer solution at pH-6.6 on PEG/CPE.

4. CONCLUSIONS

In the present study, PEG modified carbon paste electrode has been successfully developed with high sensitivity and rapid response for potassium ferricyanide and dopamine at pH- 6.6. The concentration of the modifier was selected for potassium ferricyanide is 2 mg and for the dopamine is 3 mg. The PEG/CPE exhibits the wide detection range of 1×10^{-5}M dopamine and 1×10^{-4}M $K_3Fe(CN)_6$. The reproducibility of the CV response makes the prepared modified system very useful in the construction of simple devices for potassium ferricyanide and dopamine. These results create a new approach to determine the catecholamine neurotransmitter and it exhibits as sensor.

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