

*Full Paper*

## **Poly (Eosin Y) Film based Sensor for the Determination of Epinephrine in the Presence of Uric Acid: A Voltammetric Study**

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*Received: 15 July 2017 / Received in revised form: 22 August 2017 /*

*Accepted: 22 August 2018 / Published online: 30 September 2018*

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**Abstract-** A sensitive and selective electrochemical method for the determination of Epinephrine using Eosin Y polymer film modified on the surface of carbon paste electrode was developed by using cyclic voltammetric technique. The Eosin Y polymer film modified electrode shows excellent electrocatalytic activity toward the oxidation of Epinephrine in 0.2 M phosphate buffer solution (PBS) of pH 7.0 at the sweep rate of 100 mV/s. The electrochemical parameter like the effect sweep rate and pH were investigated. The limit of detection was found to be 0.03  $\mu$ M. Simultaneous investigations resulted in excellent potential difference between Epinephrine and Uric acid by using cyclic voltammetric technique and the interference study was carried out using the differential pulse voltammetric technique. This work provides a simple and easy approach to selectively determine EP in the presence of UA. The analytical performance of this biosensor has been evaluated for detection of epinephrine injection in serum as real sample

**Keywords-** Epinephrine, Uric acid, Eosin, Cyclic Voltammetry, Electropolymerisation, Carbon Paste Electrode

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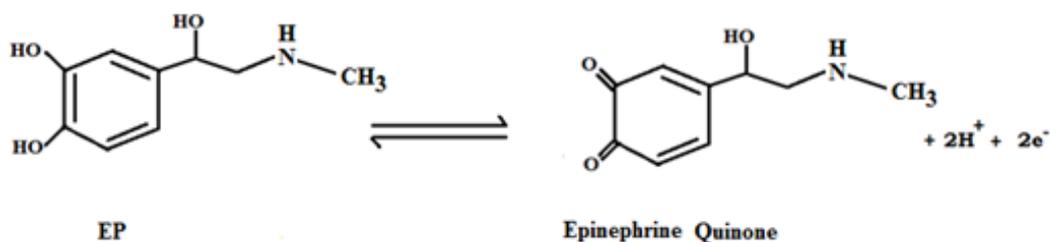
## 1. INTRODUCTION

Epinephrine (EP) (Scheme-1) or adrenaline a hormone secreted by the medulla of adrenal glands, is an important catecholamine neurotransmitter in them mammalian hormonal and central nervous system. EP belongs to the family of inhibitory neurotransmitters which are used for the message transfer in biology. The presence of EP in the body affects their regulation of blood pressure and the heart rate, lipolysis, immune system, and glycogen metabolism. It also serves as a chemical mediator for conveying the nerve pulse to different organs. Low levels of epinephrine have been found in patients with Parkinson's disease. When epinephrine is secreted into the bloodstream, it rapidly prepares the body for action in an emergency. It is a drug which has been used as a common emergency healthcare medicine for emergency treatment in severe allergic reaction, cardiac arrest, and sepsis. Therefore, the quantitative determination of epinephrine concentration in different human fluids, such as plasma and urine, is important for developing nerve physiology, pharmacological research and life science [1-2] Till date, the ability to detect EP with high selectivity and sensitivity is still a major target of electroanalytical research [3-5]. The main problem of measuring this monoamine in vivo is the very low EP concentration and the large excesses of interfering substances, such as Uric acid (UA), ascorbic acid (AA) dopamine (DA) and Folic acid (FA). One of the interferents in EP determination is uric acid (UA). It is a product of purine metabolism and abnormal changes in its physiological concentration are symptoms of some diseases like gout, hyperuricemia, leukaemia, pneumonia is also associated with enhanced urate levels [6–10]. Due to the importance of analysis of both EP and UA in body fluids, it is desirable to develop simple and direct methods for their simultaneous monitoring. Various chemically modified electrodes have been constructed in order to separate the oxidation potentials of EP and UA and to enhance the voltammetric response of these biologically important species. Some recently modified electrodes for simultaneous determination of EP and UA were constructed using organic redox polymers [11-12], Pd–Au nanoparticles [13-14], sol-gel carbon electrode [15], ruthenium oxide/hexacyanoferrate [16], self-assembled monolayer's (SAMs) [17], ionic liquids [18], and carbon nanotube paste electrode [19-20].

In recent years, the electroanalytical techniques have attracted the attention of researchers to develop the electrochemical sensors for the determination of electroactive compounds [21–26]. Over the past few decades, the voltammetric strategies are widely followed because of their simplicity, low cost, high sensitivity and fast response [27–32]. The carbon paste electrode (CPE) is a maximum usable working electrode over the opposite solid electrodes for the electroanalysis of electroactive molecules due to its realistic benefits which include, huge potential window, simple preparation, easy modification and low cost etc., [33,34] and also this modified electrodes is one of the exciting developments in the field of electroanalytical chemistry. Many different strategies have been employed for the modification of the electrode surface [35]. The motivations behind the modifications of the

electrode surface are (i) improved Electrocatalysis, (ii) freedom from surface fouling and (iii) prevention of undesirable reactions competing kinetically with the desired electrode process.

In this study, a poly (Eosin) modified carbon electrode was fabricated for used as electrochemical sensor and its electrochemical properties were investigated. It has ability to selectively determine EP in presence of UA by cyclic voltammetry method. The developed modified electrode shows high sensitivity, selectivity, and stability.



**Scheme 1.** Oxidation mechanism of EP



**Scheme 2.** structure of Eosin

## 2. EXPERIMENTAL PART

### 2.1. Materials and Methods

Cyclic voltammetric experiments were performed on a model CH660c (CH instrument). All the electrochemical experiments were carried out in a three electrode cell system, which contained a bare carbon paste electrode (BCPE)/ Poly (Eosin Y) film coated MCPE as the working electrode, a platinum wire and saturated calomel electrode as counter and reference electrode.

### 2.2. Reagents and Chemicals

Epinephrine (EP Molecular weight=183.204, purity 99%), Uric acid (UA Molecular weight=168.110, purity 99%), and Eosin Y (Molecular weight=647.890 purity 99%), were obtained from Himedia. Graphite powder of 50 mm size was purchased from Loba and silicon oil was purchased from Himedia. All the chemicals are of analytical grade quality and were used as supplied without further purification.  $25 \times 10^{-4}$  M UA was prepared in 0.1 M

sodium hydroxide,  $25 \times 10^{-4}$  M EP was prepared in 0.1 M Perchloric acid ( $\text{HClO}_4$ ), and  $25 \times 10^{-4}$  M Eosin was prepared in double distilled water. Phosphate buffer solution (PBS) of same ionic strength were prepared (0.2 M) in distilled water by mixing appropriate ratio of  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  and  $\text{Na}_2\text{HPO}_4$ .

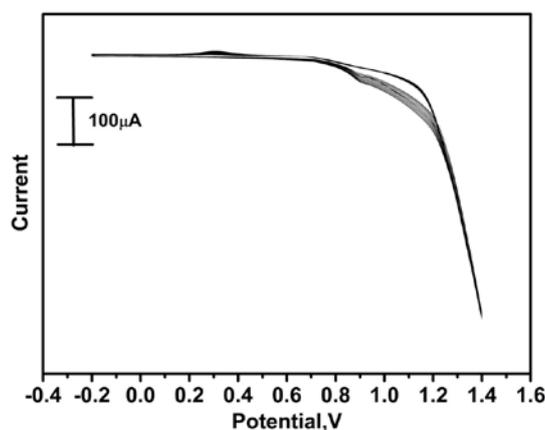
### 2.3. Preparation of bare carbon paste electrode

Bare carbon paste electrodes (BCPE) were made with silicon oil (30%), and graphite powder (70%). The two components were thoroughly mixed in an agate mortar for about 30 min. The BCPE was packed into a homemade Teflon cavity having a current collector and was polished on a weighing paper.

## 3. RESULT AND DISCUSSION

### 3.1. Electrochemical polymerization of Eosin Y on CPE

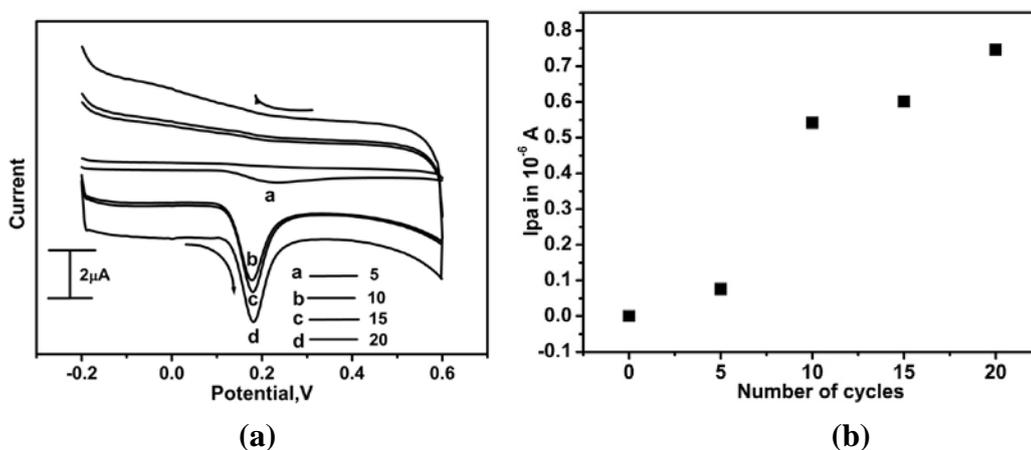
The paste packing procedure was same as that at bare carbon paste electrode (BCPE). The poly (Eosin Y) modified carbon paste electrode (MCPE) was prepared by placing 1 mM Eosin Y with 0.1 M NaOH in an electrochemical cell. The potential window changed into maintained from -0.2 to +1.4 V with sweep rate of 100 mV/s for ten multiple cycles. Fig. 1 suggests that during first cycle a small anodic peak was observed corresponding to the oxidation of Eosin Y monomer. In the process of multiple cycles, the voltammograms has slowly decreased with the increase of cyclic time. It shows that, the poly (Eosin Y) film was turned into produced and deposited at the surface of BCPE [36-37]. Once electropolymerization process complete; the MCPE was rinsed carefully with double distilled water.



**Fig. 1.** Cyclic voltammograms for the electropolymerization of 0.5 mM of Eosin Y at 0.1 M NaOH as a supporting electrolyte for 10 cycles with scan rate of 100 mV/s

### 3.2. Effect of multiple cycles

Fig. 2a shows the cyclic voltammograms for the different cycle of electropolymerized Eosin Y modified carbon paste electrode at a sweep rate of 100 mV/s, with an Epinephrine concentration of  $1 \times 10^{-5}$  M in 0.2 M phosphate buffer solution (pH 7). The graph of anodic peak current ( $I_{pa}$ ) versus the number of cycles were plotted. From the graph, it was found that current will shows linearly increases by increasing the number of cycles (from 5-20) as shown in Fig. 2b. But, a better catalytic performance was observed for the electrode which was modified by ten consecutive cycle sweeps [38]. Therefore, ten cycles were chosen for the electropolymerization of Eosin Y as optimum for the study of all other parameters



**Fig. 2.** a) Cyclic voltammograms of 0.1 mM EP at different Cycle of electropolymerised Eosin Y in a carbon paste electrode in a 0.2 M phosphate buffer (pH 7) solution at a scan rate of 100 mV/s; b) Graph of anodic peak current versus number of cycles

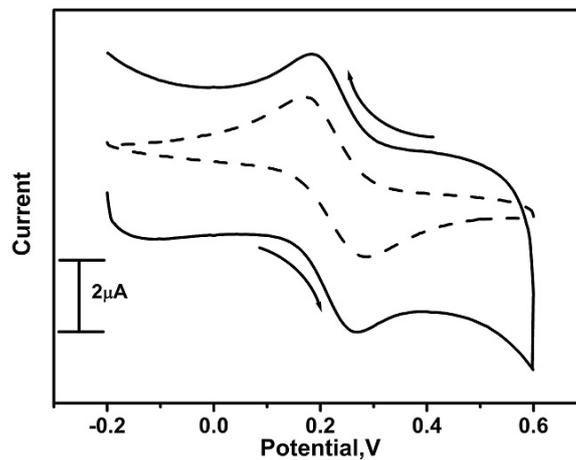
### 3.3. Electrochemical characterization of potassium ferrocyanide at poly (Eosin Y) MCPE

The freshly prepared stock solution of 1mM potassium ferrocyanide in 1 M KCl was taken in the electrochemical cell. Fig. 3 shows the electrochemical response for the oxidation of 1 mM potassium ferrocyanide at BCPE (dashed line) and poly (Eosin Y) MCPE (Solid line) in 1 M KCl solution as a supporting electrolyte with a sweep rate of 100 mV/s. In the BCPE, voltammogram of potassium ferrocyanide showed the poor electrochemical response shows low redox peak current due to the slow electron transport phenomenon. On the other hand, the poly (Eosin Y) MCPE shows the voltammetric response was apparently enhanced in the redox peak current, due to the fast rate of electron transfer kinetics. The result shows a dramatic change in the voltammetric response from polymerized electrode

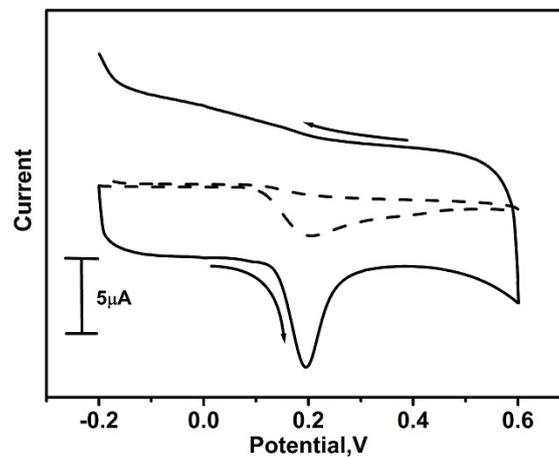
The obtainable surface area for reaction of species in solution can be calculated by the Randles-Sevcik equation (1) [39]

$$I_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} C_0 \nu^{1/2} \quad (1)$$

Where  $I_p$  is the peak current in A.  $C_0$  is the concentration of the electroactive species ( $\text{mol cm}^{-3}$ ),  $n$  is the number of electrons exchanged,  $D$  is the diffusion coefficient ( $\text{cm}^2\text{s}^{-1}$ ) and  $\nu$  is the sweep rate ( $\text{Vs}^{-1}$ ) and  $A$  is the electroactive surface area ( $\text{cm}^2$ ). The maximum surface area was obtained for Poly (Eosin Y) MCPE ( $0.0395 \text{ cm}^2$ ) as compared with BCPE ( $0.0298 \text{ cm}^2$ ).



**Fig. 3.** Cyclic voltammograms of 1 mM potassium ferrocyanide at BCPE (dashed line) and poly (Eosin Y) MCPE (solid line) at the sweep rate of 100 mV/s



**Fig. 4.** Cyclic voltammograms in 0.2 M phosphate buffer solution pH 7.0 at BCPE (dashed line) and poly (Eosin Y) MCPE (Solid line) of 0.1 mM EP with sweep rate of 100 mV/s

### 3.4. Electrochemical response of EP at poly (Eosin Y) MCPE

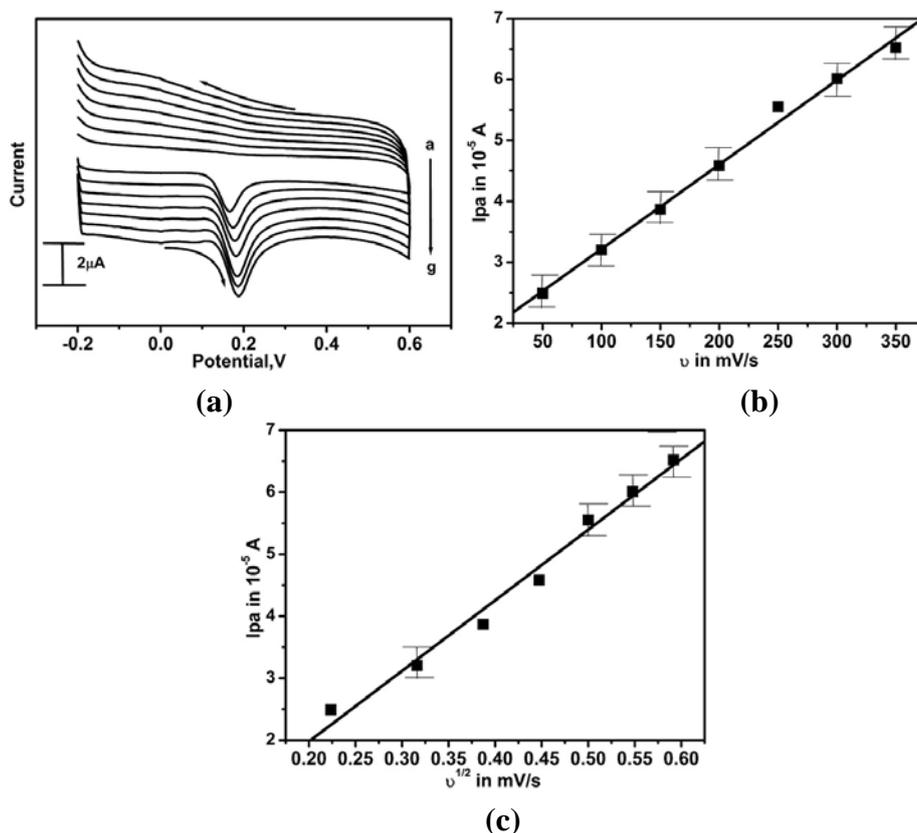
The cyclic voltammograms obtained for the electrochemical response of 0.1 mM EP at BCPE and poly (Eosin Y) MCPE in 0.2 M PBS (pH 7.0) at the sweep rate 100 mV/s was recorded (Fig. 3), which indicates the formation of only oxidation peak at both BCPE (dashed line) and poly (Eosin Y) MCPE (solid line) in the potential range of -0.2 to 0.6 V versus SCE.

However, there is an absence of reduction peak was observed in the backward scan, suggesting that the electrode reaction of epinephrine was totally irreversible process as reported in the literature [40,18].

The oxidation peak current of EP at the poly (Eosin Y) MCPE increased 2.8 times than that of BCPE. This enhancement for poly (Eosin Y) MCPE has significant electrocatalytic ability towards the oxidation of EP

### 3.5. Effect of sweep rate

The effect of sweep rate for the electrochemical behaviour of EP at poly (Eosin Y) MCPE in PBS (pH 7.0) was studied by cyclic voltammetric technique. Fig. 5a shows, oxidation peak current of EP was increased with the increase of sweep rates from 50 to 400 mV/s. In order to calculate the electrode process, the graph of anodic peak current versus sweep rate ( $\nu$ ) and the square root of the sweep rate ( $\nu^{1/2}$ ) were plotted as shown in Fig. 5b and Fig. 5c.



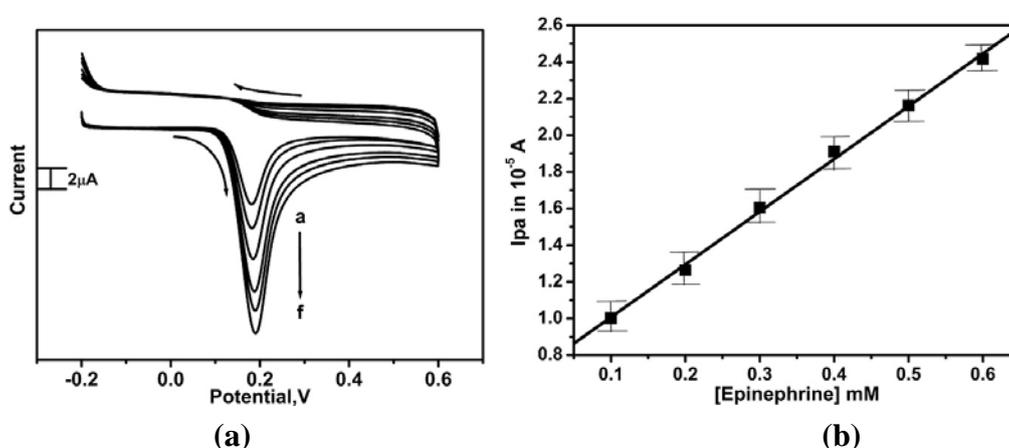
**Fig. 5.** a) Cyclic voltammograms of 0.1 M EP at different Sweep rates at poly (Eosin Y) MCPE in 0.2M PBS of pH 7.0; b) Graph of anodic peak current versus sweep rates; c) Graph of anodic peak current versus square root of the sweep rates

The obtained graph results showed that the peaks current increase linearly, with correlation coefficients 0.9996 and 0.9958 respectively. From the above scrutiny, it is clear

that overall electrode process was controlled by both adsorption and diffusion procedures occurring at poly (Eosin Y) MCPE [41-42].

### 3.6. Effect of EP concentration at Poly (Eosin Y) MCPE

The Fig. 6a depicts the cyclic voltammograms of different concentrations of EP in 0.2 M PBS (pH 7.4) and sweep rate of 100 mV/s at poly (Eosin Y) MCPE. It was clearly observed that, the anodic peak current increased linearly with increase in the concentration EP from  $1 \times 10^{-6}$  to  $6 \times 10^{-6}$ . The graph of anodic peak current versus concentration of EP was constructed and it shows almost straight line with good linearity as shown in Fig. 6b. Having correlation coefficients value 0.9986.



**Fig. 6. a)** Cyclic voltammograms of different concentration of EP at poly (Eosin Y) MCPE in 0.2 M PBS (pH 7.0) in the linear range of 0.1-0.6 mM at the sweep rate 100 mV/s; **b)** Graph of anodic peak current versus different concentration of EP

**Table 1.** Comparison of poly (Eosin Y) MCPE with other working electrodes

Sl.No	Electrode	Detection limit ( $\mu\text{M}$ )	Techniques	Ref.
1	TTABMCPE	0.12	DPV	[40]
2	p (taurine)ME	0.3	DPV	[45]
3	FCDMCNPE	35	DPV	[46]
4	FePc-ME	0.5	CV	[47]
5	Poly(caffeic acid)MGCE	0.6	CV	[48]
6	Poly (1-Methylpyrrole) M GCE	0.56	CV	[49]
7	Pen SAM-MAuE	0.1	CV	[50]
8	Poly( Eosin Y )MCPE	8.56	CV	Present work

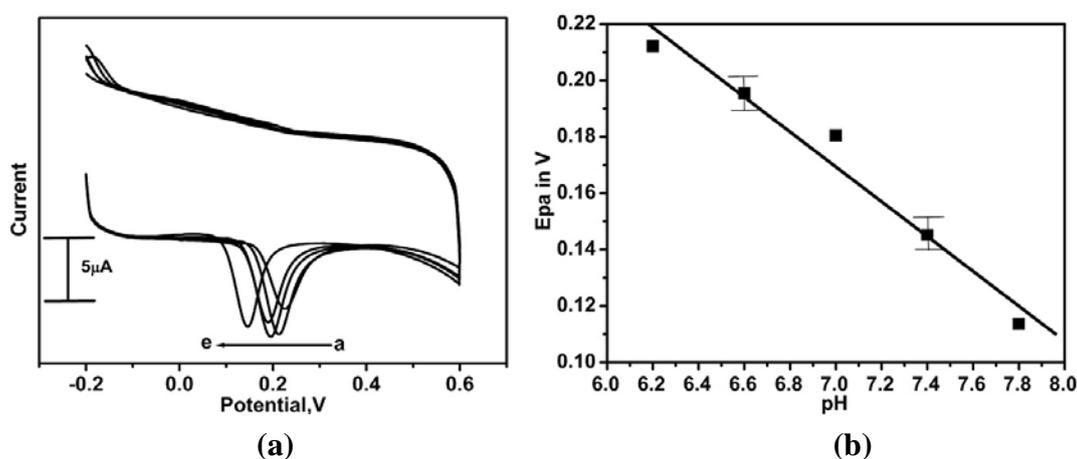
The limit of detection (LOD) was calculated by using the formula (2) [43]

$$\text{LOD} = 3S/M \quad (2)$$

Where  $S$  is the standard deviation and  $M$  is the slope obtained from the calibration plots. The detection limit of EP was found to be  $8.6 \mu\text{M}$ . The performance of modified electrode was compared with other reported modified electrodes and given it in table 1.

### 3.7. Effect of pH

The effect of the solution of pH has a significant contribution on the electrocatalytic oxidation of EP at the poly (Eosin Y) MCPE. Fig.7a shows cyclic voltammograms of  $0.1 \text{ mM}$  EP at poly (Eosin Y) MCPE. The oxidation peak potentials were strongly dependent on pH, suggesting that  $\text{H}^+$  ion participation in the oxidation processes. The graph of anodic peak potential ( $E_{\text{pa}}$ ) versus pH of EP was constructed as shown in Fig. 7b. Good linearity was obtained between the anodic peak potential and pH of the solution in the range of 6.2 to 7.8. The slope value of  $61 \text{ mV/pH}$  was obtained which is nearly equal to the theoretical value of  $59 \text{ mV}$  at  $25^\circ\text{C}$  suggesting the participation of an equal number of protons and electrons in the oxidation of EP at the poly (Eosin Y) MCPE [44,18]. The oxidation mechanism of EP was shown in Scheme 1.

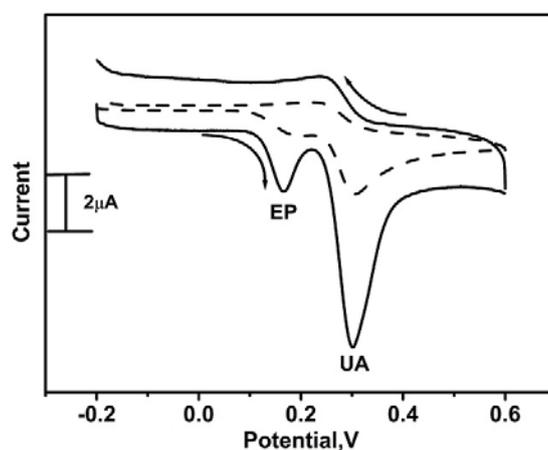


**Fig. 7. a)** (A) Cyclic voltammograms obtained for oxidation of  $0.1 \text{ mM}$  EP at poly (Eosin Y) MCPE in  $0.2 \text{ M}$  PBS of different pH values (a–e: 6.2 to 7.8) at the sweep rate  $100 \text{ mV/s}$ ; **b)** Graph of anodic peak potential versus different pH of EP

### 3.8. EP and UA determination by Simultaneous method

The simultaneous determination of EP and UA was demonstrated by cyclic voltammetric technique. The Fig. 8 shows cyclic voltammograms of the solution containing  $0.1 \text{ mM}$  EP,  $0.1 \text{ UA}$  at pH  $7.0$  PBS at the sweep rate of  $100 \text{ mV/s}$ . In BCPE, (dashed line) shows two well-distinguished anodic peaks potentials at around  $199$  and  $304 \text{ mV}$ , corresponding to the oxidation of EP and UA; respectively with a potential difference, EP-UA was  $105 \text{ mV}$ . However, at the poly (Eosin Y) MCPE shows the increase in the anodic peak currents for

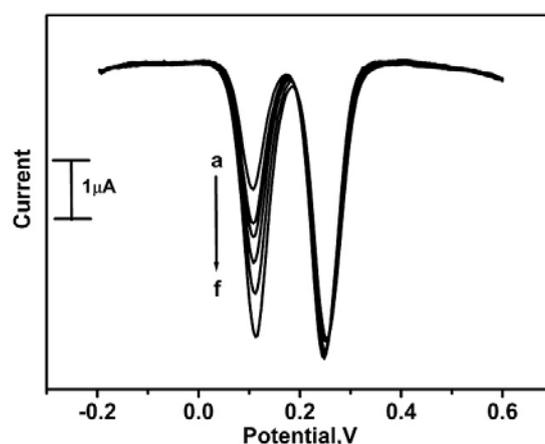
both EP and UA (solid line). The anodic peak potential of EP and UA was observed at 164 mV and 300 mV respectively. Thus, the peaks for EP and UA were clearly separated from each other. The potential separation was found to be 136 mV. This potential difference was enough to identify EP in the presence of UA at poly (Eosin Y) MCPE.



**Fig. 8.** Cyclic voltammograms obtained for oxidation of 0.1 mM EP and 0.1 mM UA in 0.2 M PBS (pH 7.0) at BCPE (dashed line) poly (Eosin Y) MCPE (solid line) at the sweep rate of 100 mV/s

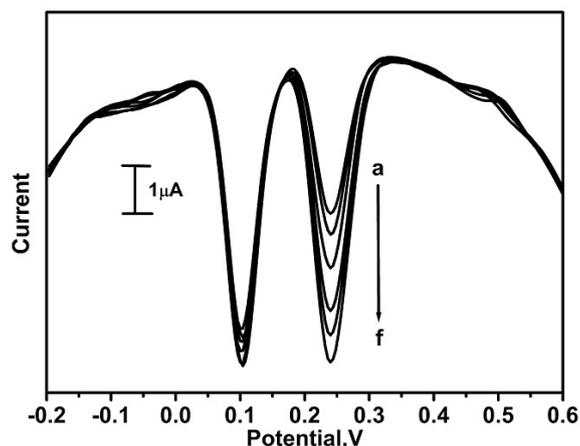
### 3.9. Interference

The interference study was carried out in a mixture of samples containing EP and UA with different concentration by using DPV technique. The concentration of one analyte changed while the other one was kept constant vice versa.



**Fig. 9.** Differential Pulse voltammograms of different concentration of EP (a-f; 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 mM) in the presence of constant UA (0.1 mM)

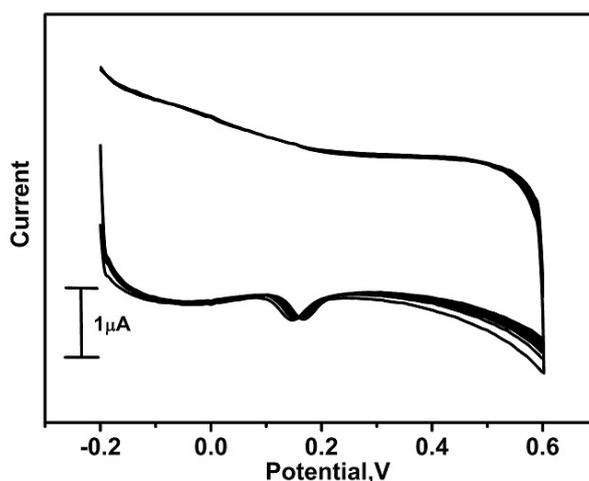
Fig. 9 shows that an increase the anodic peak current linearly on increase EP concentration from 0.1 to 0.6 mM. The concentration of anodic peak current of 0.1 mM UA remained unchanged in the experiment. Similarly, UA was increased from 0.1 to 0.6 mM when 0.1 mM EP was kept constant (Fig. 10). This reveals that the oxidation of EP and UA can occur independently at the poly (Eosin Y) MCPE. These results indicate that the EP and UA have existed independently in their mixtures of samples at the poly (Eosin Y) MCPE [18].



**Fig. 10.** Differential Pulse voltammograms of different concentration of UA (a-f; 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 mM) in the presence of constant EP (0.1 mM)

### 3.10. Stability of the poly (Eosin Y) MCPE

The procedure of electrode preparation is easy and rapid, it is important for the electrode to be stable for a long time.



**Fig. 11.** Cyclic voltammograms for 10 multiple cycles of 0.1 mM EP in 0.2 M phosphate buffer solution pH 7.0 at sweep rate 100 mV/s

The stability of poly (Eosin Y) MCPE was studied for the 0.1 mM EP at the sweep rate of 100 mV/s by CV method. The reproducibility of the MCPE was shown in the Fig. 11 with the 10 successive voltammograms were taken to check the stability of poly (Eosin Y) MCPE. Even after 10 cycles, there is no change in the peak current and peak potential. The overall study reveals the excellent catalytic activity and reproducibility of poly (Eosin Y) MCPE towards the electroactive species.

### 3.11. Analytical application

The modified electrode was applied to the determination of Epinephrine injection. The EP injection sample purchased from Harson Laboratories with a specified content of EP of 0.0018 g/mL. The sample was used after suitable dilution 0.2 M phosphate buffer was used for diluting the injection samples [51]. The results were shown in Table 2. The trials were carried out for five times (n=5) for every analysis at Poly (Eosin Y) MCPE. The percentage recoveries obtained from the experiments were sustainable, showing good efficiency of the modified electrode for the determination of EP in the injection sample.

**Table 2.** Determination of Epinephrine using injection sample (n=5)

DA added (mM)	Found (mM)	Recovery (%)
0.1	0.105	105.0
0.3	0.302	100.6
0.4	0.396	99

## 4. CONCLUSION

The poly (Eosin Y) MCPE was used to determine the electrochemical response of EP. The poly (Eosin Y) MCPE enhanced anodic peak current strongly. The poly (Eosin Y) MCPE showed excellent selectivity and electro catalytic activity towards the oxidation of EP in the presence of UA. The poly (Eosin Y) MCPE has the limit of detection was observed at 0.03  $\mu$ M of EP by CV method. Hence, poly (Eosin Y) MCPE is acting as a good sensor for the determination of EP in presence of UA.

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