# Electro catalytic Oxidation of Epinephrine at SAOS Modified Carbon Paste Electrode

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**Abstract :** Electrochemical behavior of epinephrine (EN) on sodium alpha olefin sulfonate (SAOS) surfactant modified carbon paste electrode was explored in phosphate buffer solution using cyclic voltammetry. Epinephrine showed oxidation peak at 154 mV for SAOS modified CPE and electrochemical studies indicated that the oxidation of epinephrine at the electrode surface was diffusion controlled. A linear relationship with correlation coefficient of 0.99741 was obtained between the anodic peak current and concentration of epinephrine in the range of $5\times10^{-4}$ M to $1\times10^{-3}$ M. The low detection limit of $0.61\times10^{-5}$ M and low detection quantity of $2.108\times10^{-5}$ M has been observed for epinephrine. The SAOS modified electrode is easy to prepare and regenerate the electrode surface and exhibits high sensitivity, detection limit and high reproducibility.

**Keywords:** Epinephrine, Cyclic voltammetry, Carbon paste electrode, SAOS.

## Introduction

Epinephrine is a very essential catecholamine neurotransmitter in the central nervous system. Epinephrine (EN) is chemically known as 1-(3,4-dihydroxyphenyl)-2-methyloaminoethanol and its structure is shown in Fig.1. It exists in nervous tissue and biological body fluid as an organic cation. Adrenal glands synthesize the epinephrine and release into the bloodstream [1-4]. Recently, surfactant modified carbon paste electrode have exhibited excellent analytical performance for the detection of biomolecules [5–7]. Recently, for the electrochemical investigations, surface-active agents are used extensively in the research field. These molecules can be absorbed in the interfaces and surfaces due to the specific amphiphilic structure of surfactants [8]. Surfactant molecules adsorb on the electrode surface and make a layer of surfactant on the electrode surface, at low concentrations. Electrode surface gets charged by the adsorption of ionic surfactant on the electrode (anionic surfactants create negative charge and cationic surfactant create positive charge on the electrode surface) [10-12]. A large number of surfactant modified carbon paste electrodes have been developed in our laboratory [13-15]. In the present work, **s**odium alpha olefin sulfonate (SAOS) modified carbon paste electrode for the electrochemical determination of epinephrine by using cyclic voltammetric technique.

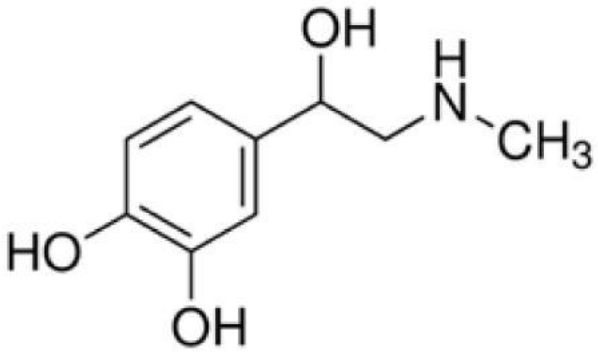



**Fig.1. Structure of epinephrine**

## Experimental

### Reagents

All the reagents used in this electrochemical study were all of analytical grade. Epinephrine used in study was purchased from Aldrich chemicals. En was dissolved in 0.1 N perchloric acid to prepare a stock solution of 1x10-3 M EN. By mixing equal volumes of 0.1 M sodium dihydrogen orthophosphate solution and 0.1 M disodium hydrogen orthophosphate solution, the phosphate buffer was prepared by adjusting the pH with 0.1N sodium hydroxide solution

or 0.1 N ortho-phosphoric acid solutions. All the experiments were carried out at the room temperature. $10X10^{-3}$ - M of SAOS stock solution was prepared by diluting with deionised water. Spectroscopic grade pure graphite powder was obtained from Loba Chemie. All the solutions were prepared with deionised water (Millipore water).

## Apparatus

An electrochemical analyzer (EA-201 chemlink systems) in a conventional three-electrode system was used for electrochemical measurements. Carbon paste electrode with a cavity of 3 mm diameter was used as the working electrode, saturated calomel electrode (SCE) was used as the standard reference electrode and platinum electrode was used as a counter electrode.

## Preparation of bare carbon paste electrode (Bare CPE)

A homogenous carbon paste was prepared by hand mixing of graphite powder 70% and silicon oil 30% in an agate mortar for about 30 min. Then the cavity of a Teflon tube electrode (3 mm diameter) was tightly packed by homogenous carbon paste to get a bare carbon paste electrode. The electrode was smoothened on a piece of transparent paper to get a uniform, smooth and fresh surface before electrochemical measurement.

## Preparation of SAOS modified carbon paste electrode

At room temperature SAOS solution (10 μL) was added by using micropipette on the surface of the BCPE and allowed it for about 5min. To remove unadsorbed SAOS, the electrode was later thoroughly rinsed with distilled water to get SAOS modified carbon paste electrode (SAOS modified CPE).

## Result and Discussion

### Electrochemical characterization of the modified electrode

The estimation of the electroactive surface of the modified electrode was done by using cyclic voltammetry. In $1x10^{-3}$ M $K_4[Fe(CN)_6]$ solution containing 1M KCl as supporting electrolyte the cyclic voltammograms of bare CPE (solid line) and SAOS modified CPE (dashed line) were recorded at a scan rate of 50 $mVs^{-1}$ and are represented in Fig. 2. The electrochemical response of bare CPE is having the anodic peak current ($I_{pa}$) of 5.8 μA and cathodic peak current ($I_{pc}$) of 3.8 μA . The electrochemical anodic peak potential ($E_{pa}$) of 261mV and cathodic peak potential ($E_{pc}$) of 158mV are represented by solid line curve. There is an enhancement of both electrochemical cathodic peak current ($I_{pc}$) to 8.9 μA and anodic peak current ($I_{pa}$) to 12.9 μA and cathodic peak potential ($E_{pc}$) to 224 mV and anodic peak potential ($E_{pa}$) to 285 mV for the SAOS modified CPE represented by dotted line curve. The SAOS modified electrode exhibited an effective area of 0.0346 $cm^2$.

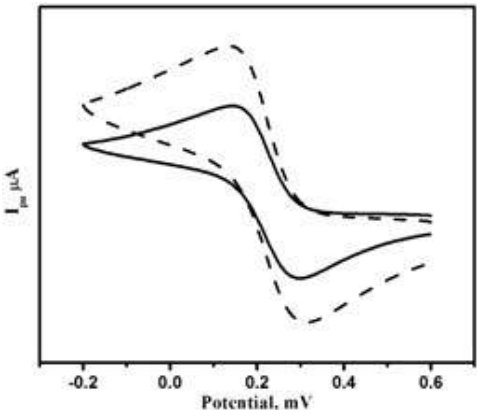



**Fig. 2. Cyclic voltammograms of $1x10^{-3}$M $K_4[Fe(CN)_6]$ in 1M KCl at bare CPE (solid line) and SAOS modified electrode (dashed line) at scan rate 50 $mVs^{-1}$.**

## Electrocatalytic oxidation of epinephrine at SAOS modified CPE

By cyclic voltammetry the electrochemical behavior of epinephrine at the SAOS modified CPE was investigated. The cyclic voltammograms of epinephrine at pH 7.0 in phosphate buffer at blank solution (solid line), at bare CPE (dotted line) and at SAOS modified CPE (dashed line) were recorded. The cyclic voltammograms are shown in Fig.3. Epinephrine shows an oxidation peak at 172 mV and an anodic peak current of 2.9 μA for bare CPE, whereas for SAOS modified CPE an oxidation peak is obtained at 154 mV and an anodic peak current of 33.4 μA is observed and the voltage was in the range of -0.2 to 0.6V (dashed line). The electrochemical reaction is a totally irreversible

process because no reduction peak was observed in the reverse scan. The shape of the peak turns sharper and the response was considerably improved at the SAOS modified electrode compared to the bare CPE due to slow electron transfer and the oxidation peak is broad. The peak potentials shifted to negative direction and the peak current increased significantly. The results in the enhancement of the peak current showed the excellent catalytic ability of SAOS modified CPE.

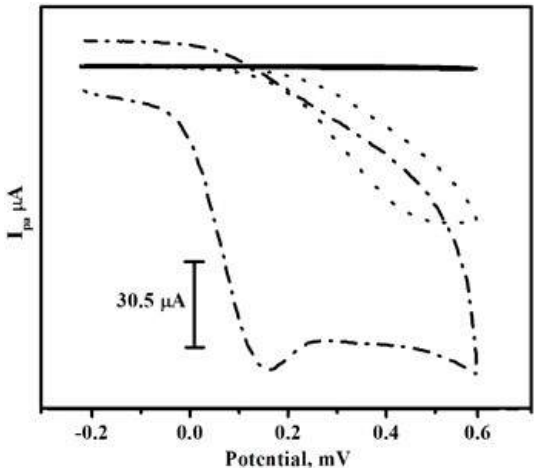



**Fig.3. Voltammograms of 1mM EN blank solution in phosphate buffer (solid line), at bare CPE (dotted line) and SAOS modified CPE (dashed line) at 50 $mVs^{-1}$.**

## Effect of pH

The effect of pH was investigated at different pH values between 3.0 and 9.0 by cyclic voltammetric measurement. With increase in pH from 3.0 to 6.5, the oxidation peak current also increases and becomes maximum. The peak potential shifted negatively. As shown in Fig. 4a, a great decrease in the oxidation peak current is observed beyond pH 7.0, then it decreases gradually with the further increase in the pH of solution. The current was maximum at pH 7.0. The phosphate buffer of pH 7.0 was selected to get the maximum bioactivity and optimal sensitivity at 50 $mVs^{-1}$. Figure 4b shows a decrease in the oxidation peak potential with increase in pH. There is a linear relationship between the anodic peak potential and pH of the solution in the range 5.0 – 9.0. The linear regression equation is

$$Epa\,(\mathrm{mV}) = 312.214 - 58.02\,\mathrm{pH} \qquad (R = 0.99634)$$

The number of electrons and protons are equal in the electrochemical oxidation of EN at SAOS modified carbon paste electrode is indicated by negative slope of 58.02.

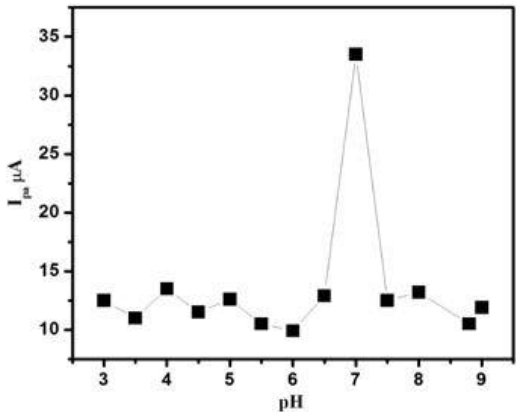



**Figure-4a: Plot of anodic peak current vs. pH at SAOS modified CPE.**

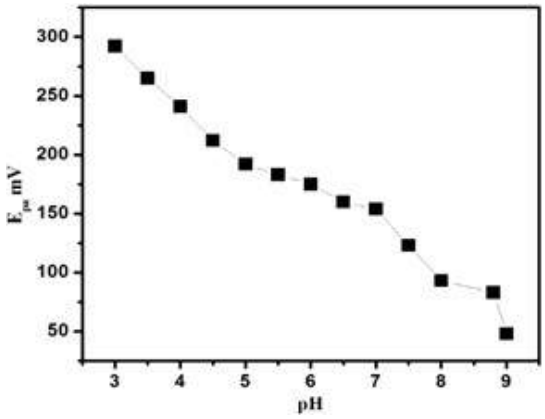


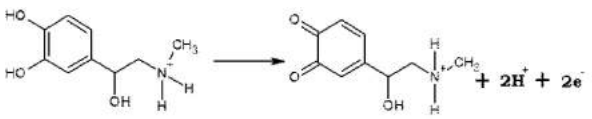

**Fig. 4b. Plot of anodic peak potential vs. pH at SAOS modified CPE.**

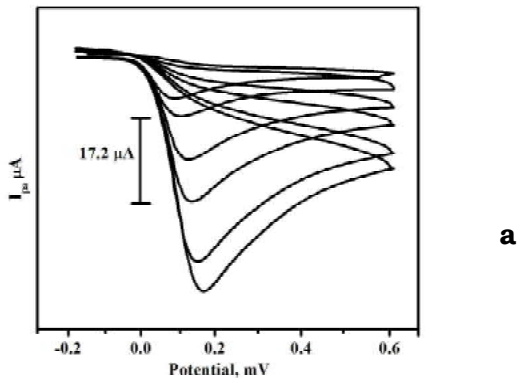
## Effect of scan rate

The effect of scan rates on the electrochemical response of epinephrine at SAOS modified CPE was studied. With increase in the scan rate (γ) in the range 30, 40, 50, 60, 70 and 80 $mVs^{-1}$ there is a linear increase in the redox peak current. Figure 5a shows the cyclic voltammograms of scan rate (γ) in the range 30-80 $mVs^{-1}$. A linear relationship was obtained between the peak current and scan rate in the range of 30-80 $mVs^{-1}$ with a correlation coefficient of R= 0.9982 (Fig. 5b). Figure 5c shows the plot of square root of scan rate vs. the anodic peak current. The linearity was obtained with a correlation coefficient of 0.99842 which revealed a diffusion-controlled process occurring at the SAOS modified CPE. By plotting the logarithm of anodic peak current vs.

logarithm of scan rate (Fig. 5d), the relationship between the anodic peak current and scan rate was explained by the relation: $\log_{ipa} = 0.478\log\tilde{o} + 1.385$; R= 0.99432.

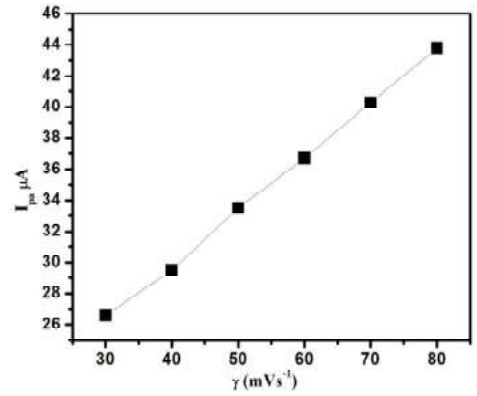
By Laviron's theory [16] the slope is equal to RT/ ánáF. The ná was calculated as 1.90 for a totally irreversible electrode reaction which indicated that two electrons are involved in the oxidation process of epinephrine at the SAOS modified CPE. Equal number of protons and electrons are taking part in the electrochemical oxidation process of epinephrine [17]. Therefore, the electrochemical reaction process for epinephrine at SAOS modified carbon paste electrode can be summarized as below.



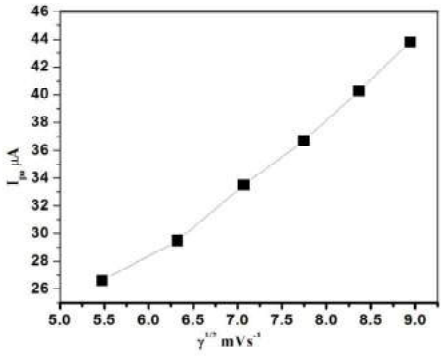

a

**Figure 5a: Cyclic Voltammograms of different scan rate were 30 $mVs^{-1}$ to 80 $mVs^{-1}$ of 1mM EN at SAOS modified CPE.**



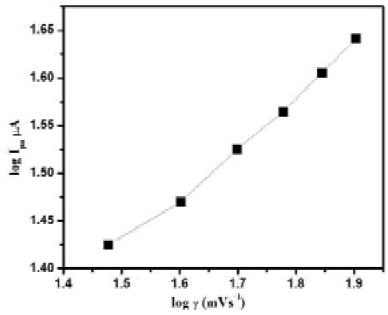

b

**Fig. 5b: Plot of anodic peak currents vs. scan rates at SAOS modified EN modified CPE.**




c

**Fig. 5c. Plot of anodic peak current of EN vs. square root of scan rates at SAOS modified CPE.**




d

**Fig. 5d. Plot of logarithm of anodic peak current of EN vs. logarithm of scan rate at SAOS modified CPE.**

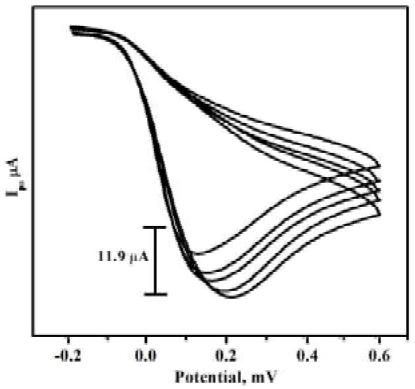
Effect of concentration of epinephrine

The effect of epinephrine concentration on the oxidation peak current in PBS (pH 7.0) at the scan rate of 50 $mVs^{-1}$ was studied under selected conditions by cyclic voltammetry. The oxidation peak current increases with increase in concentration of epinephrine under the optimum conditions. The linear relationship between the oxidation peak current (Ipa) with epinephrine concentration in the range $5\times10^{-4}$ M to $1\times10^{-3}$M are shown in Fig. 6a and Fig. 6b. The linear regression equation: Ipa (µA) = 0.688+ 33.621C (R = 0.99741). The following equation were used to calculate the LOD and LOQ from the peak current.

LOD = 3S/M, ….LOQ = 10S/M

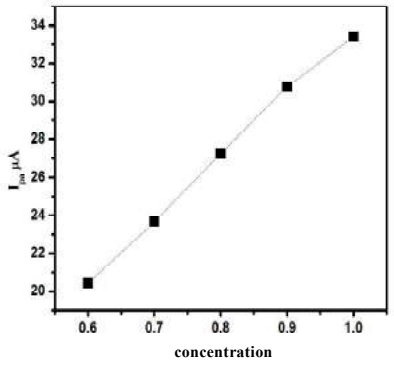
where M is the slope (Sensitivity) of calibration plot and S is standard deviation.

The limit of detection (LOD) and limit of quantification (LOQ) of epinephrine were found to be $0.6125\times10^{-5}$ M and $2.108\times10^{-5}$ M respectively.




a

**Fig.6a.Effect of variation of concentration of EN from $5\times10^{-4}$ M to $1\times10^{-3}$M on anodic peak current at a scan rate 50 $mVs^{-1}$ in pH 7.0 at SAOS modified carbon paste electrode.**




b

**Figure-6b: Plot of anodic peak current versus EN concentration ($5\times10^{-4}$ M to $1\times10^{-3}$M ) at SAOS modified CPE.**

## Conclusion

In this study, the electrochemical determination of epinephrine is done by SAOS surfactant modified carbon paste electrode based on the immobilization method. At SAOS modified carbon paste electrode oxidation peak current of epinephrine was improved. The reaction is irreversible, and is diffusion controlled.

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