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Sensitive Voltammetric Determination of Dopamine at Salicylic Acid and TX-100, SDS, CTAB Modified Carbon Paste Electrode

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A sensitive electrochemical method for the determination of dopamine (DA) was developed by using salicylic acid (SA) and TX-100, SDS, CTAB surfactants modified carbon paste electrode at phosphate buffer solution pH.7. This kind of modified electrode showed excellent electrocatalytic activity towards the oxidation of DA by the influences of different kinds of surfactants on the electrochemical signals of dopamine. Some parameters such as pH, scan rate, concentration and effect of surfactants of dopamine were optimized. This approach is so easy, low detection limit, fast response, high reproducibility, low cost and simplicity

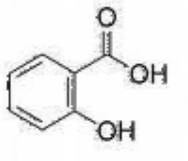
Keywords: Dopamine, Salicylic acid, carbon paste electrode, TX-100, SDS, CTAB, cyclic voltammetry

1. INTRODUCTION

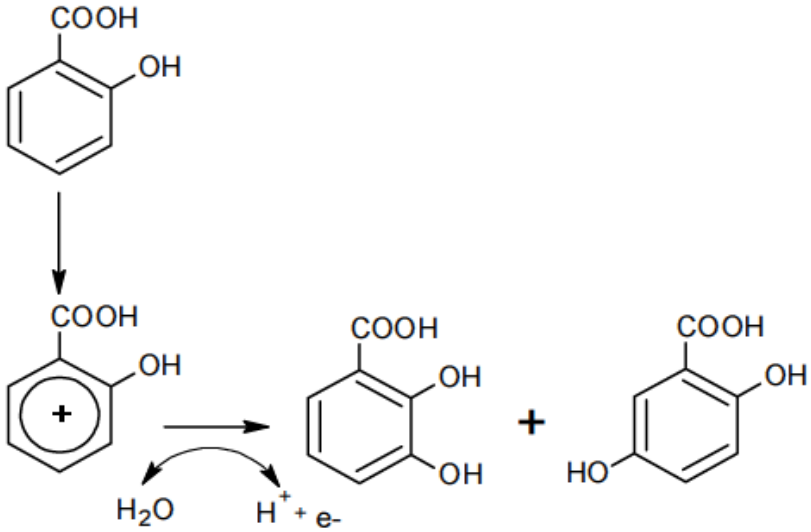
Salicylic acid(SA) is a beta hydroxy acid. This colorless crystalline organic acid is widely used in organic synthesis and functions as a plant hormone. It is derived from the metabolism of salicin. In addition to being a compound that is chemically similar to but not identical to the active component of aspirin (acetylsalicylic acid), it is probably best known for its use in anti-acne treatments. The salts and esters of salicylic acid are known as salicylates, The possible scheme of oxidation of SA is shown in scheme.2 [1].

It is well known that dopamine (DA), one of the neurotransmitters in the brain, plays an important role in regulating the body movements and mental activity. Psychomotor stimulants and neuroleptics exert multiple effects on dopaminergic signaling and produce the DA-related behaviors of

motor activation and catalepsy, respectively[2]. On the other hand, some types of neurodementia such as Pakinson's disease (PD), Alzheimer's disease (AD) and dialysis encephalopathy (DE) are believed to relate to an abnormally high level of aluminum (Al III) in the brain[3-4]. Therefore, the study of DA in the nerve center system and its interaction with Al III are of great significance to biomedicine for the treatment of neuropathic disease and exploitation of the relevant drugs.



Scheme 1. Structure of Salicylic acid



Scheme 2. The possible scheme of oxidation of SA

One of the most common routes is to use a modified carbon paste electrode which has the ability to eliminate the interfering substances from DA determination. The modification can be done by adding different types of modifiers. One of the modifiers chosen for the determination of electrochemical response of DA is salicylic acid and it is immobilized with TX-100, SDS, CTAB surfactants.

Surfactant is a liner molecule with a hydrophilic (attracted to water) head and a hydrophobic (repelled by water) end. Due to its unique molecular structure, surfactants have been extensively used in the fields of electrochemistry and electroanalytical chemistry 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 [5]. 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 electro generated intermediates or electrochemical products [6-11]. Related work has been done our research group [12-21]

The aim of the work was to establish a simple and sensitive electrochemical method for the determination of dopamine by salicylic acid and TX-100, SDS, CTAB, surfactants modified CPE.

2. EXPERIMENTAL PART

2.1. Reagents and chemicals

Salicylic acid received from Sigma Aldrich India, Bangalore, TX-100, SDS, CTAB, potassium ferrocyanide (K_4Fe (CN) $_6$) was dissolved in double distilled water stock solution of dopamine was prepared in 0.1 m perchloric acid. All other chemicals were of analytical grade quality and were used without further purification. In all the measurements, the supporting electrolyte used was 1M KCl and 0.2M phosphate buffer solution.

2.2. Apparatus and procedure

Cyclic voltammetry (CV) was performed in a model EA-201 Electro Analyser 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 potassium chloride (KCl) saturated calomel reference 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 was then packed into the cavity of a home made carbon paste electrode and smoothed on a weighing paper. Similarly the modified carbon paste electrode was prepared by grinding different concentration of SA along with graphite powder.

3. RESULTS AND DISCUSSION

3.1. Electrochemical behavior of K_4Fe (CN_6) at a SAMCPE

Potassium ferrocyanide was selected as a probe to evaluate the performance of the BCPE and the SAMCPE. Fig. 1 showed electrochemical responses of the BCPE(solid line) and the SAMCPE(dashed line) in 1m KCl containing 1mM mol L^{-1} $K_4[Fe(CN)_6]$ solution.At the BCPE, the peak potential occurs at 249 and 170 mV, corresponding to a electron transfer process, While at the SAMCPE, the peak potential was increased to 253 and 174 mV, indicating a electron transfer process. Furthermore, the peak currents of K_4 [Fe (CN) $_6$] at the SAMCPE were much bigger than that at the BCPE. Above experimental results showed the superiority of SAMCPE to BCPE in terms of improving reversibility and enhancing sensitivity. All these were attributed to the use of SA as a

modifier. Therefore, SA played an important role in improving the electrochemical performance of the SAMCPE.

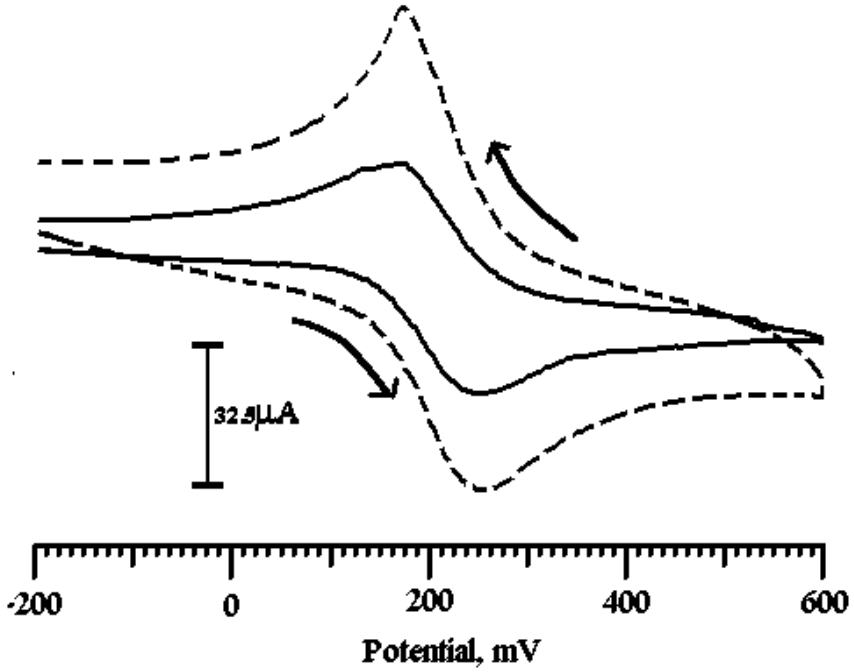


Figure 1. Electrochemical response of $1X10^{-3}M$ K_3Fe (CN_6) at SA modified carbon paste electrode(dashed line) and bare carbon paste electrode (solid line).

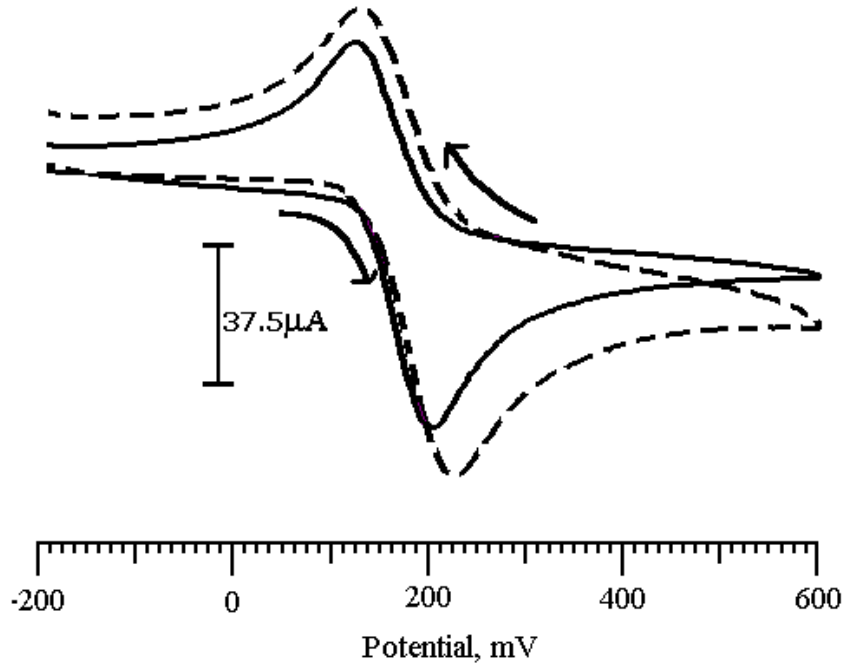


Figure 2. Cyclic voltammogram of $1X10^{-3}$ M DA in 0.2 M phosphate buffer solution of pH 7.0 at bare CPE (solid line) and SAMCPE (dashed line).

3.2. Study of electrochemical behavior of dopamine at a SAMCPE

Fig.2 shows the cyclic voltammograms obtained for the electrochemical response of $1X10^{-3}$ DA at the SAMCPE (dashed line) and bare CPE (solid line) in 0.2 M phosphate buffer solution pH 7.0. At bare CPE, the oxidation and reduction peak potentials occur at 203 V and 122 V respectively. Under identical conditions, the salicylic acid modified CPE produces increased peak current and a more quasireversible electron process of DA with the oxidation and reduction peak potentials at 225 mV and 129 mV respectively. The remarkable enhancement of peak current provides clear evidence of the catalytic effect of salicylic acid modified CPE.

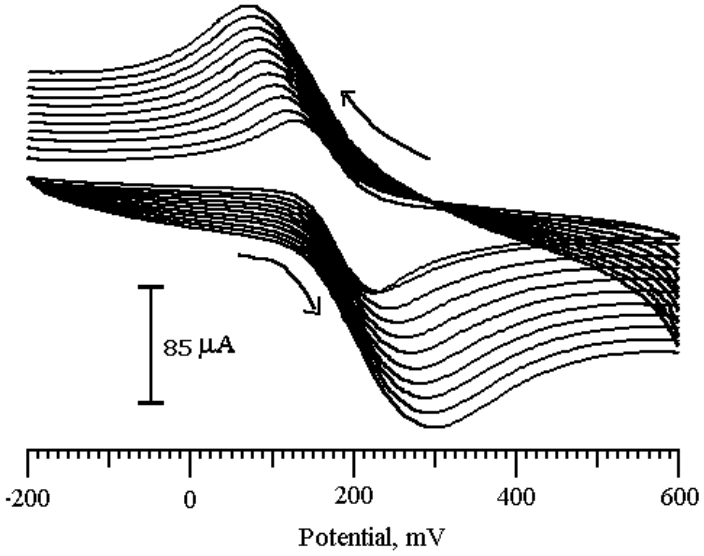


Figure 3a. Variation of scan rate for DA at SAMCPE ($100mVs^{-1}$ to $600mVs^{-1}$).

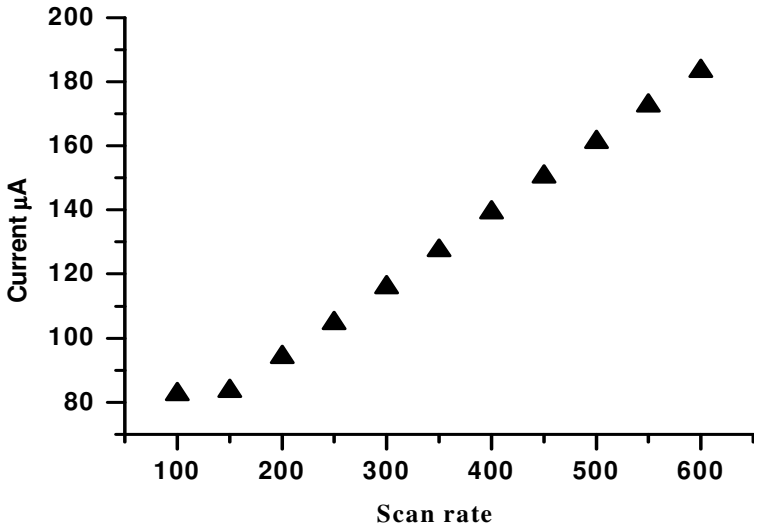


Figure 3b. Graph of current vs. scan rate.

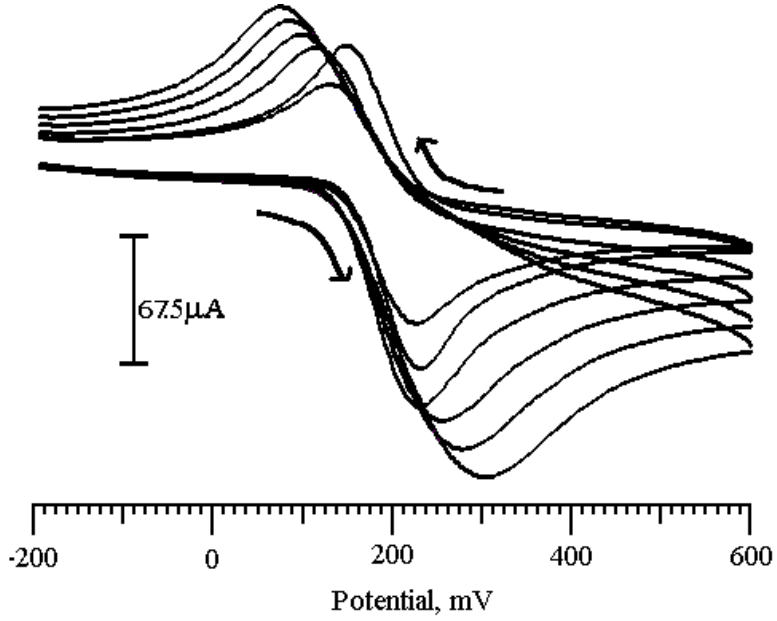


Figure 4a. Cyclic voltammogram of DA at different concentration ($1X10^{-3}$ M, $1.5X10^{-3}$ M, $2X10^{-3}$M, $2.5X10^{-3}$ M, $3\ X10^{-3}$ M, $3.5X10^{-3}$ M)

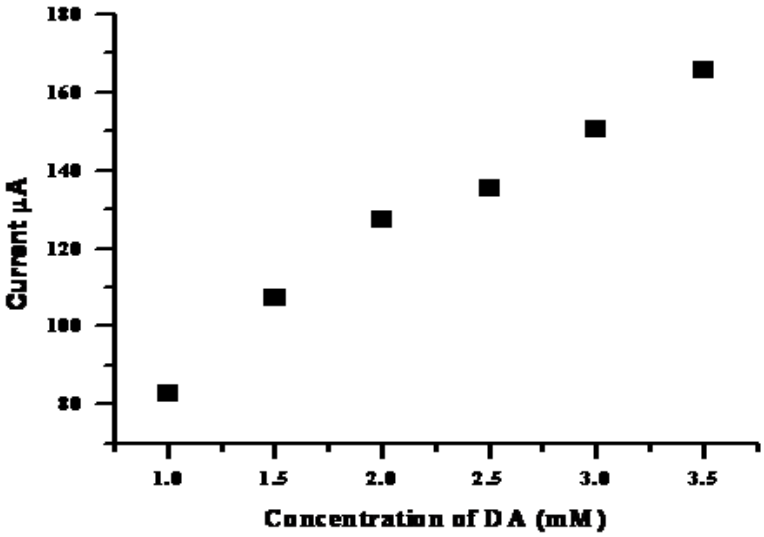


Figure 4b. Graph of current vs. concentration of DA

3.3. Effect of scan rate on the peak currents of dopamine

The effect of scan rates on the electrochemical response of dopamine at SAMCPE was studied and the cyclic voltammograms are shown in Fig. 3a. It was found that with the increase of the scan rate, the oxidation peak current increased gradually and the oxidation peak potential shifted towards

more positive potential. A linear relationship of oxidation peak current with the scan rate in the range from 100 to 600 mV s^{-1} was established with correlation coefficient $r_{=}$ 0.996). The results indicated that the electrode process was adsorption controlled (fig.3b)

3.4. Effect of dopamine concentration.

The charging current contribution to the background current, which is a limiting factor in the analytical determination. Cyclic voltammetry was used to estimate the lower limit of detection and the linear range of DA. The effects of increasing the concentration of DA in the range of $1x10^{-3}$ to $3.5\ x10^{-3}$ on the voltammograms are presented in Fig. 4a. The correlation coefficient $r_{=}$ 0.9886 is observed in fig. 4b.

3.5. Effect of pH

Cyclic voltammetry was used to investigate the effects of pH value in the determination of DA at the salicylic acid modified electrode. The effect of variation of pH was studied in the range from 5.0 to 10.0 in 0.2M phosphate buffer solution at a scan rate of 100mV/s. The peak potential was very high at pH. 7.0 and then later there was a gradual decrease in the anodic peak potential up to pH 8.0 as shown in Fig .5a (22,23).

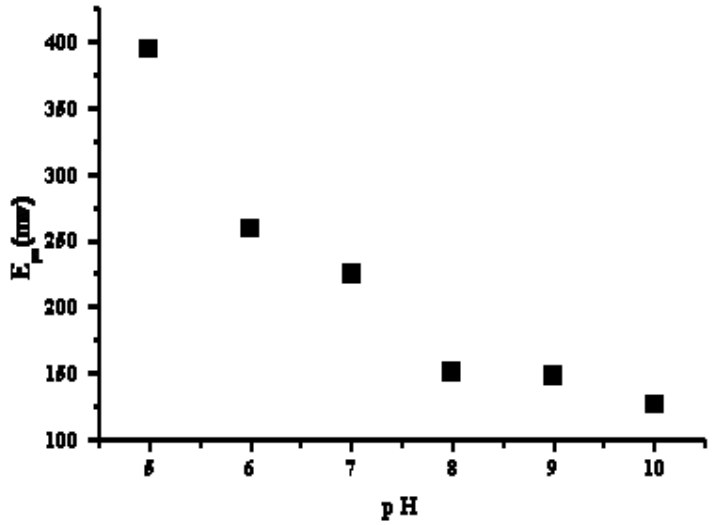


Figure 5a. Graph of the Effect of pH(EPA vs.pH)

3.6.Electrode modified with surfactants

The electrochemical responses of dopamine at SA modified carbon paste electrode in the presence of trace amount of SDS, TX-100 and CTAB surfactants, surface is immobilized form were

studied in 0.2M phosphate buffer solution at 100 mV/s. The low signal (solid line) is the cyclic voltammogram of dopamine for bare carbon paste electrode, SA modified carbon paste electrode (dashed line), surfactant immobilized SA modified carbon paste electrode (dotted line) . However the voltammetric response is apparently improved in the presence of 5µL of SDS, CTAB and TX-100 surfactants (Fig.6a,6b,6c) in immobilized forms respectively. When the anionic surfactant SDS, cationic surfactant CTAB, non-ionic surfactant TX-100, were used, there was increase in both oxidation as well as reduction peak currents.

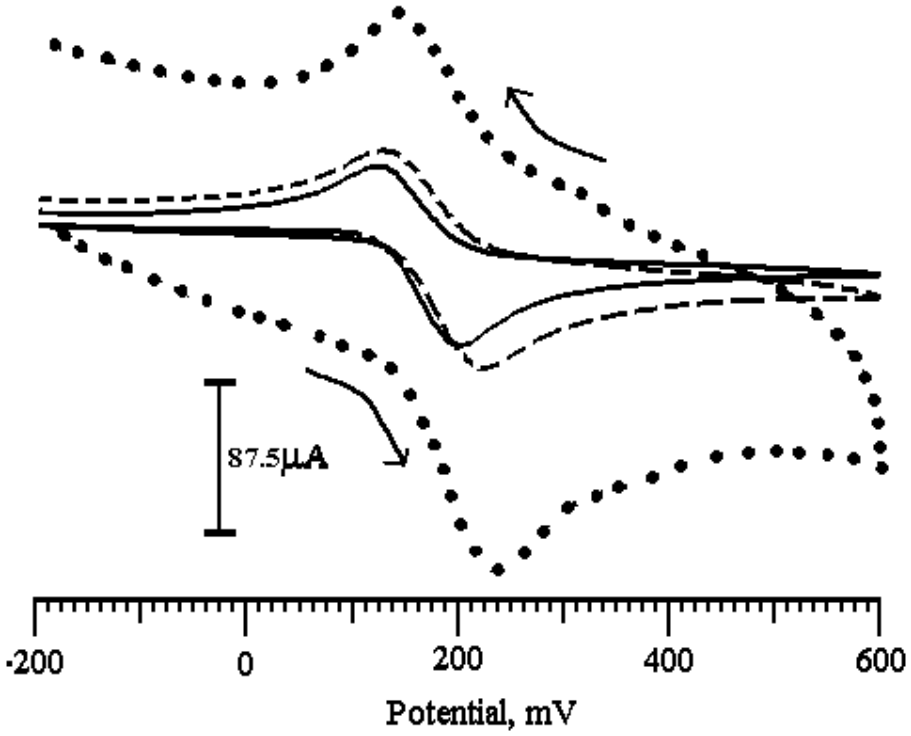


Figure 6a. Effect of surfactant [Bare(solid line) ,SAMCPE(dashed line) SDS / SAMCPE(dotted line)]

3.7. Effect of surfactants concentration

Fig.7a, 7b, 7c clearly shows that the concentration of surfactants 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 SDS, CTAB, TX-100. The oxidation and reduction peak current increases greatly as surfactants concentration was increased from 5uL to 30 uL, the background current gradually increases while increasing the surfactants concentration. The graph of concentration vs current shows very good linearity with correlation coefficient, SDS=0.942, CTAB=0.987, TX-100=9951 observed in fig.8a, 8b, 8c.

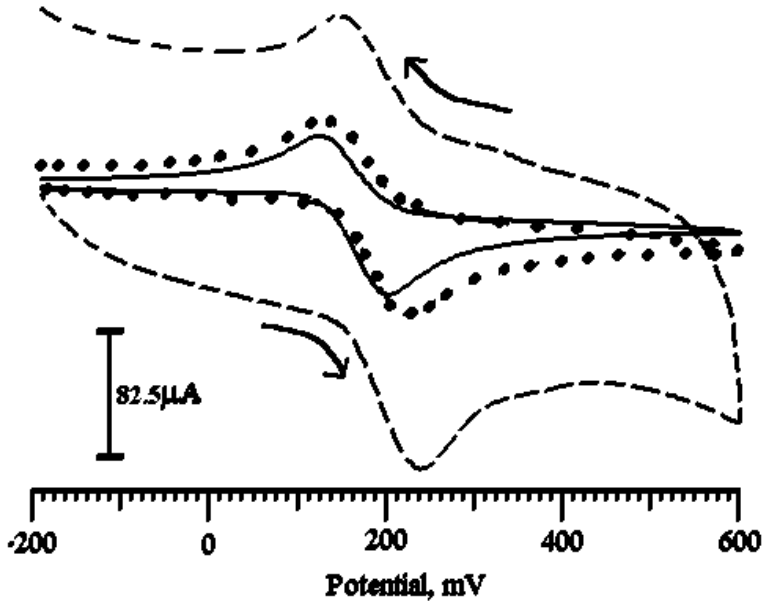


Figure 6b. Effect of surfactant [Bare(solid line) ,SAMCPE(dashed line)CTAB/ SAMCPE(dotted line)]

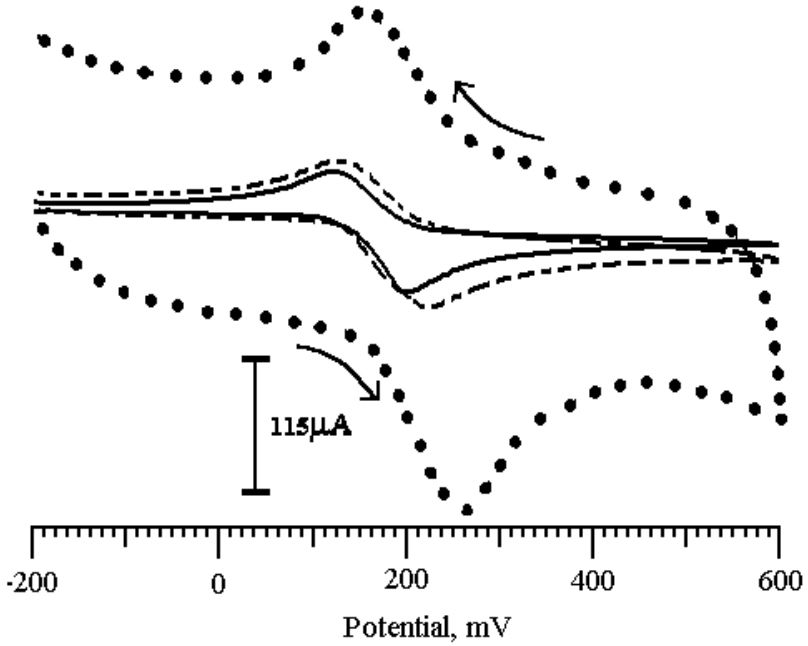


Figure 6c. Effect of surfactant [Bare(solid line) ,SAMCPE(dashed line) TX-100/ SAMCPE(dotted line)]

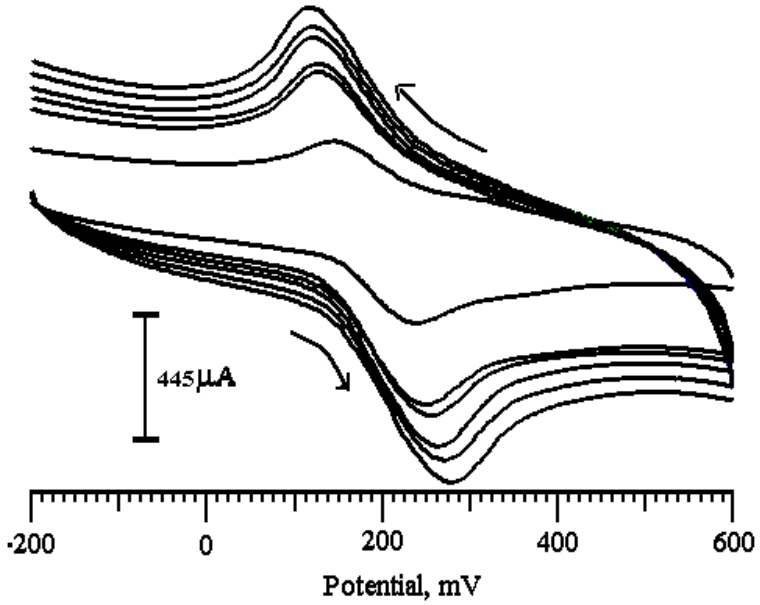


Figure 7a. Cyclic voltammogram of SDS surfactant different concentration (5µL-30µL)

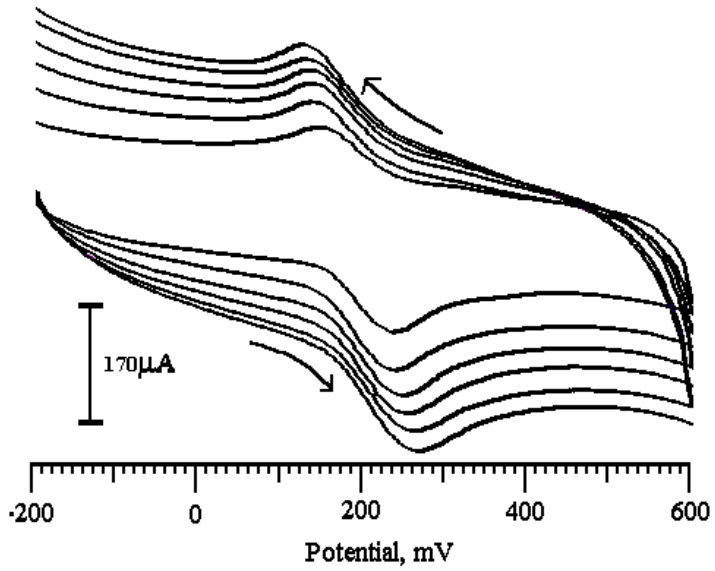


Figure 7b. Cyclic voltammogram of CTAB surfactant different concentration (5µL-30µL)

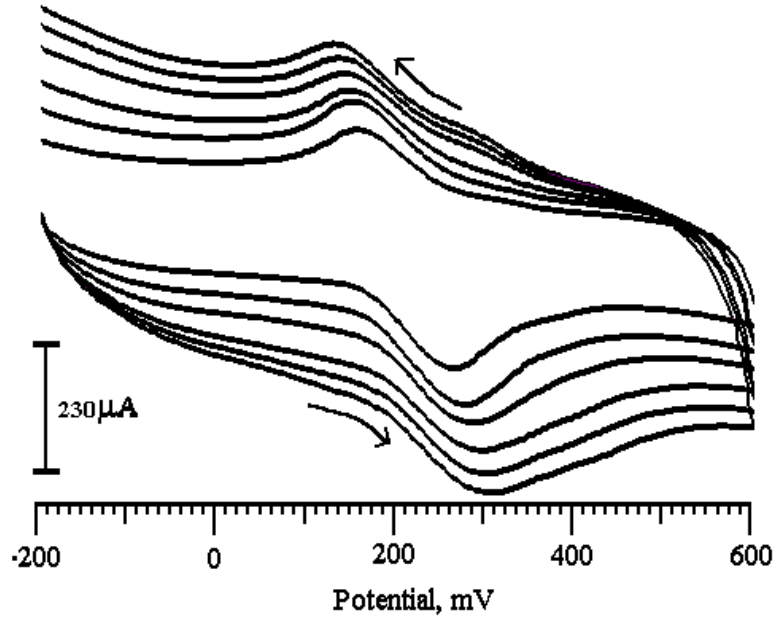


Figure 7c. Cyclic voltammogram of TX-100 surfactant different concentration (5µL-30µL)

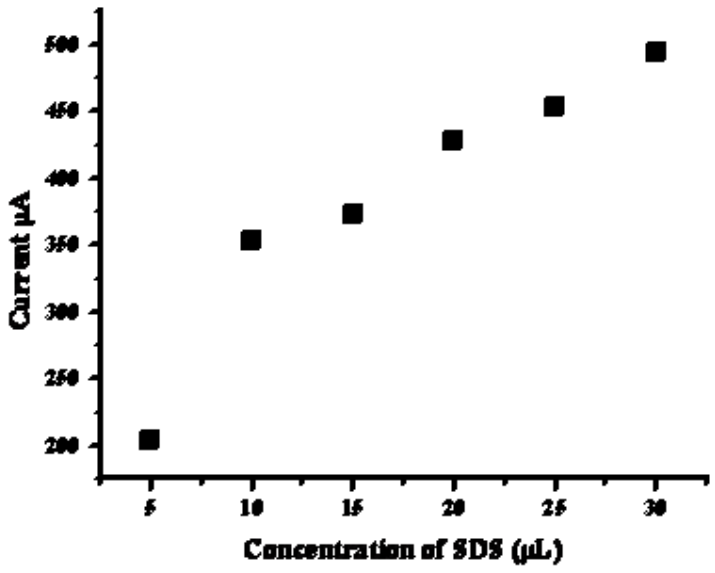


Figure 8a. Graph of the current vs. log of concentration SDS.

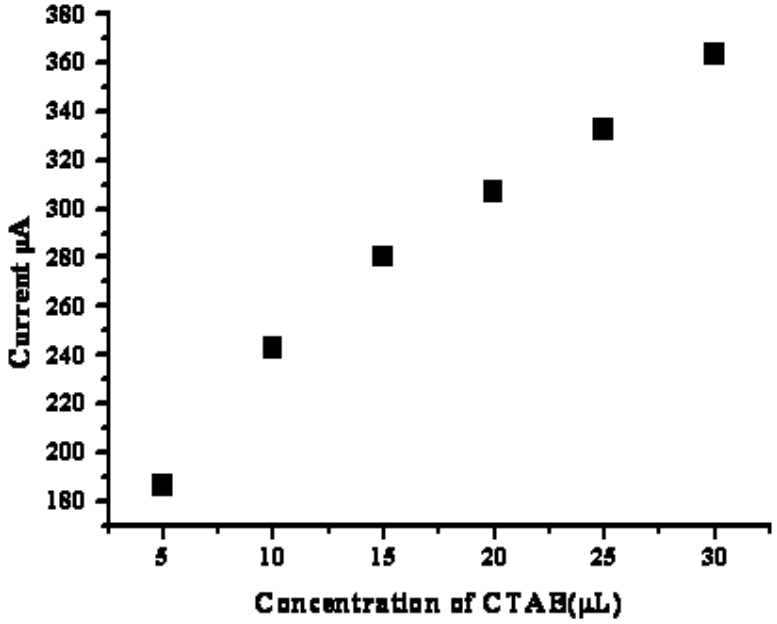


Figure 8b. Graph of the current vs. log of concentration CTAB.

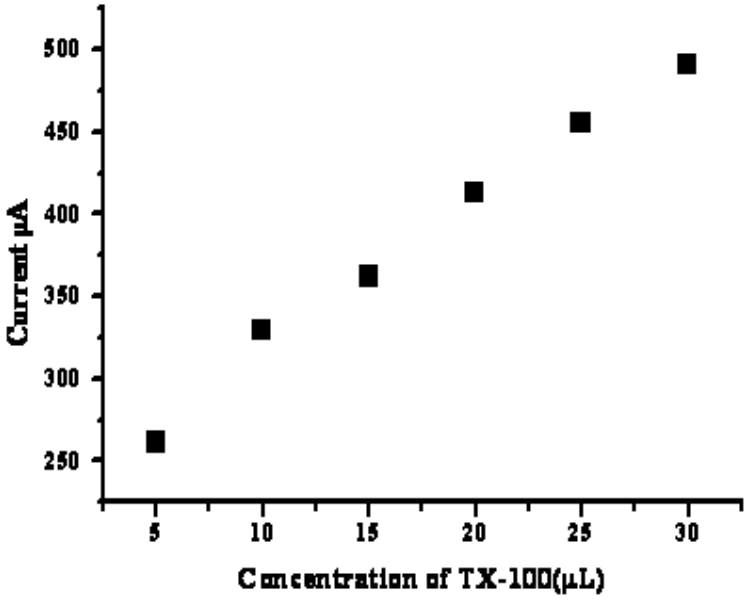


Figure 8c. Graph of the current vs. log of concentration TX-100.

4. CONCLUSIONS

In this work, chemically modified salicylic acid carbon paste electrode acts as a good sensor, and exhibited strong promoting effect and stability towards the electrochemical oxidation of potassium ferrocyanide in KCl solution and dopamine at pH 7 in 0.2 M phosphate buffer solution (PBS). TX-100, CTAB, SDS surfactants showed very good electrocatalytic effect on the salicylic acid modified carbon paste electrode. With its low cost and easy of preparation, the salicylic acid, surfactant modified carbon paste electrode seems to be at great utility for further sensor development.

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