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Detection of Epinephrine in Presence of Serotonin and Ascorbic Acid by TTAB Modified Carbon Paste Electrode: A Voltammetric Study

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The Tetradecyltrimethyl ammonium bromide (TTAB) surfactant immobilized carbon paste electrode (TTABMCPE) has been proposed for simultaneous investigation and determination of epinephrine (EP) and serotonin (5-HT) in presence of ascorbic acid (AA) by voltammetric techniques, in phosphate buffer solution (PBS) at pH 7.4. The anodic peaks of EP, 5-HT and AA were observed at 198 mV, 363 mV and -17 mV respectively at a scan rate 50 mVs^{-1}. At the TTABMCPE peak currents of all electroactive molecules were increased. It is found that EP and 5-HT could be simultaneously determined with good sensitivity even in the presence of higher concentration of AA. The interference studies showed that the modified electrode had excellent selectivity for the determination of EP in the presence of large excess of AA and 5-HT. The differences of the oxidation peak potentials for EP–AA and EP–5-HT were about 215 and 165 mV, respectively. The voltammetric resolution is large enough to determine AA, EP and 5-HT individually. Detection limit of the modified electrode was found to be 0.12 μM by differential pulse voltammetric technique. The developed method has been applied to the determination of EP in synthetic samples with satisfactory results.

Keywords: Epinephrine, Simultaneous analysis, Cyclic Voltammetry, Tetradecyltrimethyl ammonium bromide, Surfactant modified electrode.

1. INTRODUCTION

Epinephrine is an important monoamine neurotransmitter in the mammalian central nervous system [1]. Many life phenomena are related to the concentration of epinephrine in blood [2]. Medically, it was used as a common emergency healthcare medicine [1], apart from this epinephrine

drug used to treat hypertension, organic heart disease and is used in cardiac surgery and myocardial infarction [3, 4].

Serotonin in presence of neurotransmitters play important role in the control and regulation of the central and peripheral nervous system. The physiological functions such as, sleep, thermoregulation, food intake, and sexual activity, as well as in psychopathological states such as depression, anxiety, alcoholism, and drug dependency were directly related to the concentration of serotonin [5]. Serotonin was highly unstable and easily metabolized to its major metabolite, 5-hydroxyindoleaceticacid and other compounds [6]. Therefore in the recent year's considerable interested was devoted to electrochemical techniques for measurement of monoamine neurotransmitters such as epinephrine and serotonin (5-HT).

Ascorbic acid was one of the essential water soluble vitamins present in the mammalian diet. It had pH regulation and antioxidant property hence it was added pharmaceutical ingredients [7]. AA has been used for the prevention and treatment of common cold, mental illness, infertility, cancer and AIDS [8]. So, the determination of NE, 5-HT and AA is an important topic in clinic medicine. NE is an electroactive compound and its electrochemical behavior has been studied extensively.

However, it is almost impossible to detect this component electrochemically by direct oxidation on a conventional electrode (i.e., bare glassy carbon, graphite, Au, Pt) because of its high overpotential, electrode fouling property, poor reproducibility and poor sensitivity. Thus the development of epinephrine sensor has been major electroanalytical research goal for in vivo monitoring. The successful route to overcome the problems of selectivity is to modify the electrode surface, because the modified electrode could decrease the overpotential, improve the mass transfer velocity and effectively enrich the substance [9, 10]. In recent years, carbon based electro chemical sensors have gained attention to attend to the growing demand for rapid, reliable, and inexpensive sensors [7-14]. Various modified materials have been modified on various base electrodes to investigate and detect epinephrine [11-15]. Now-a-days voltammetric techniques are getting much attention in the electro analytical field [16-20].

There are several surfactant modified electrodes have been reported previously. Jianbin Zheng et al. developed sensor for some neurotransmitter by using sodium do decyl sulphate and they successfully over come the problems of selectivity [21]. Svancara et al.[22] also reported a carbon paste electrode modified with cationic surfactants, which was used to determine chromate based on synergistic pre-concentration of the chromate anion at modified electrode. Chen and Chzo [23] have studied the simultaneous voltammetric detection of dopamine and ascorbic acid using didodecyl dimethyl ammonium bromide (DDAB) film modified electrodes. Some less soluble surfactants were employed in the immobilization of macromolecules or other functional materials, the applications of surfactants in the immobilization of biomolecules were also reported [24–26]. Corona-Avendano et al. studied the electrochemistry of dopamine by using CTAB modified carbon paste electrode [27]. Kalimuthu and John developed ultrathin polymer film of 5-amino-1,3,4-thiadiazole-2-thiol modified electrode and successfully used for the Simultaneous Voltammetric Determination of epinephrine, uric acid and xanthine in the presence of ascorbic acid [28]. A.A. Ensafi et al fabricated poly (p-xylenolsulfonephthalein) modified glassy carbon electrode and applied it for the electrocatalytic oxidation and determination of norepinephrine in the presence of ascorbic and uric acids by differential

pulse voltammetry [29]. Sun et al. have fabricated sutriazole self-assembled monolayer on the surface of gold electrode (TA SAM/Au) for the selective detection epinephrine [30].

Surfactant belongs to a class of molecules with surface active properties. Ionic surfactants generate the charge on the surface of the electrodes. As the concentration of surfactant was increased, the attractive and repulsive forces between the molecules cause self-aggregation to occur resulting in the formation of monolayer or micelles [31]. Cationic surfactants like CTAB used in voltammetry for detection of molecules like ascorbic acid [32], 4-chlorophenol [33, 34]. The cationic surfactant TTAB has close structural resemblance to CTAB and it was widely used in the synthesis of nanoparticles [35] and electrophoretic separation [36]. In recent years, our group has fabricated many kinds of modified carbon paste electrodes for the analysis of neurotransmitters [37– 41].

In this paper, the work involved the fabrication of carbon paste electrode and its surface modification by tetradecyltrimethyl ammonium bromide (TTAB) through surface immobilization method. TTAB is a cationic surfactant forms cationic monolayer on the surface of the electrode. The modified electrode resolved the overlapped voltammetric responses of epinephrine, serotonin and ascorbic acid into three well defined cyclic voltammetric peaks. The modified electrode used for the commercial sample analysis of epinephrine and 5-HT with satisfactory result.

2. MATERIALS AND METHODS

2.1. Reagents and Chemicals

Tetradecyltrimethyl ammonium bromide, epinephrine, ascorbic acid and serotonin were obtained from Himedia chemical company. 1 mM potassium Ferro cyanide K_4 [Fe (CN) $_6$] was prepared in double distilled water. In all the measurements, the supporting electrolyte used was 0.2 M phosphate buffer solution. TTAB 1 mM stock solution was prepared by dissolving in double distilled water. All chemicals were of analytical grade quality and were used without further purification.

2.2. Apparatus and procedure.

Cyclic voltammetry (CV) was performed on Model EA-201 Electroanalyser (EA-201, Chemilink System). All the experiments were carried out in a conventional electrochemical cell. The electrode system contained a carbon paste working electrode (3.0 mm in diameter), a platinum wire counter electrode and a potassium chloride (KCl) saturated calomel reference electrode (SCE).

The carbon paste electrode was prepared as fallows 70 % graphite powder (particle size 50 mm and density is 20 g/100 ml) 30 % silicone oil were mixed by hand to produce a homogeneous carbon paste electrode. The carbon paste was then packed into the cavity of a homemade carbon paste electrode and smoothened on a weighing paper. Similarly modified carbon paste electrode was prepared by immobilizing 20 μL TTAB on the surface of the bare carbon paste electrode for 15 minutes.

3. RESULTS AND DISCUSSION

3.1. Electrochemical behavior of potassium ferrocyanide at TTABMCPE.

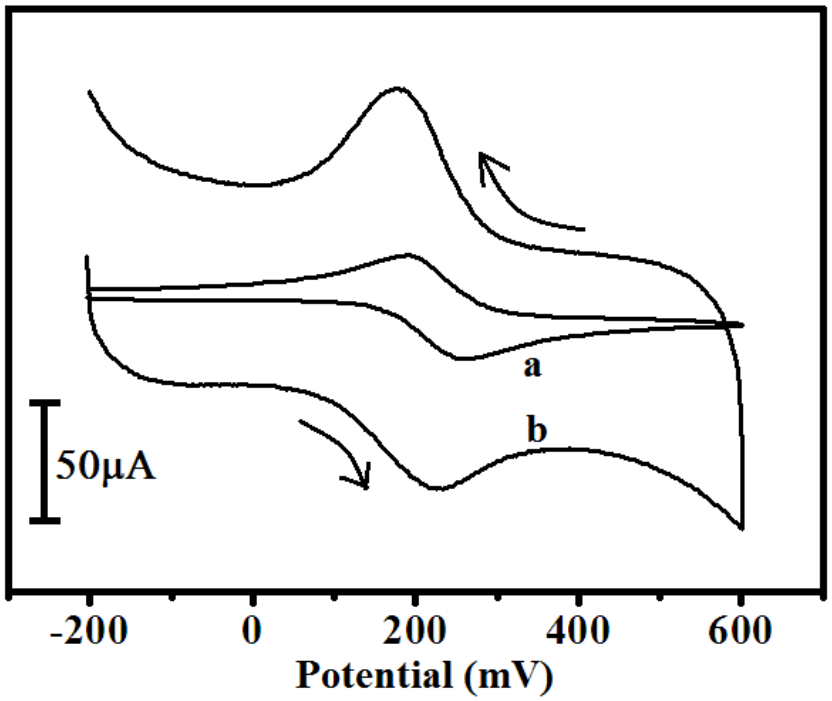


Figure 1a. Cyclic voltammograms for the electrochemical responses of $K_4[Fe(CN)_6]$ at bare (dotted line) and TTABMCPE (solid line) in 1 M KCl containing 1mM $K_4[Fe(CN)_6]$ at scan rate 50 mVs^{-1}.

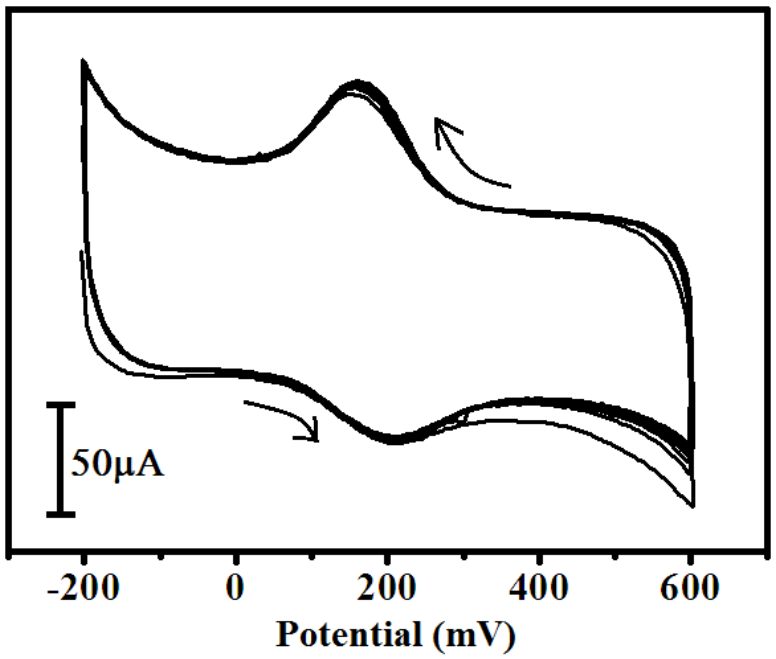


Figure 1b. Cyclic voltammograms for 20 multiple cycles of 1mM $K_4[Fe(CN)_6]$ at TTABMCPE in 0.2 M KCl solution at scan rate of 50 mVs^{-1}.

Fig. 1a.shows the cyclic voltammograms of bare carbon paste electrode (BCPE) and TTAB immobilized carbon paste electrode (TTABMCPE) in the presence of 1 mM potassium ferrocyanide in 1M KCl solution as supporting electrolyte. The curve 'a' represents the electrochemical response of 1 mM $K_4[Fe(CN)_6]$ at BCPE. The electrochemical cathodic peak potential (E_{pc}) was observed at 194 mV and anodic peak potential was at (E_{pa}) at 257 mV. At the MCPE back ground current and shape of the redox peaks were increased. At the MCPE (curve b) the $K_4[Fe(CN)_6]$ undergo oxidation at 210 mV and reduction at 150 mV. The peak to peak separation was found to be 60 mV. This indicates that the surface property of the modified electrode has been significantly changed. The reproducibility of the MCPE was shown in the fig 1b; the 10 successive voltammograms were taken to check the stability of 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 TTABMCPE towards the electroactive species.

3.2. Optimization of concentration and immobilization time of TTAB on voltammetric response of $K_4[Fe(CN)_6]$.

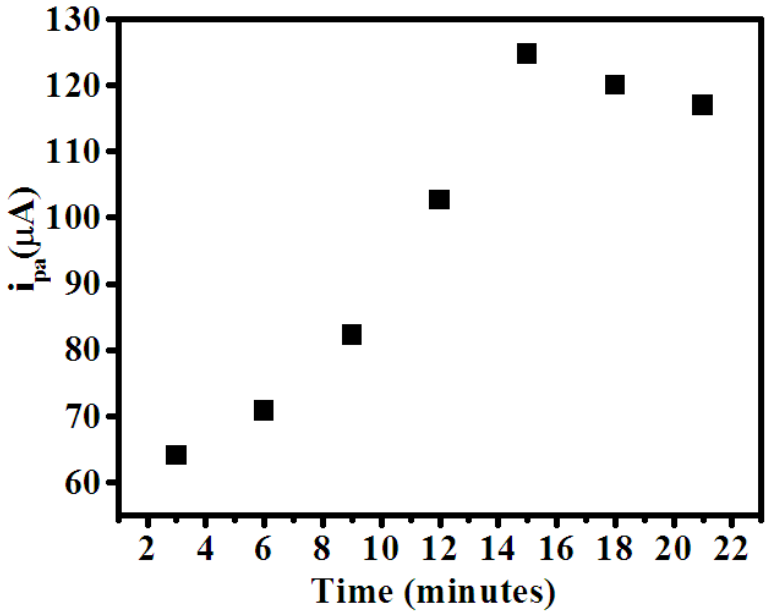


Figure 2a. The influence of TTAB concentration on the oxidation peak current of 1mM $K_4[Fe(CN)_6]$ at 50 mVs^{-1} scan rate .

Surfactant concentration and immobilization time are the main parameters which influence the catalytic activity of the modified electrode. Hence the effects of concentration and immobilization time were studied (fig 2a). When the immobilization time increases from 3 to 15 min, the oxidation peak current of $K_4[Fe(CN)_6]$ greatly increased. As increasing the immobilization time, more and more $K_4[Fe(CN)_6]$ was accumulated at the TTABMCPE surface under the strong adsorption ability of TTAB. Without a doubt, the oxidation peak current of $K_4[Fe(CN)_6]$ remarkably increases. However,

the oxidation peak current of $K_4[Fe(CN)_6]$ decreases slightly when the accumulation time extends from 18 to 20 min. Therefore the accumulation time is selected as 15 min in this work. As gradually increasing the concentration of TTAB, the oxidation peak current firstly increases sharply up to 20 µL, and then gradually decreases (fig 2b). It may be caused by the micellar effect of TTAB, i.e. the peak current changes abruptly around the critical micelle concentration (CMC) of the surfactants.

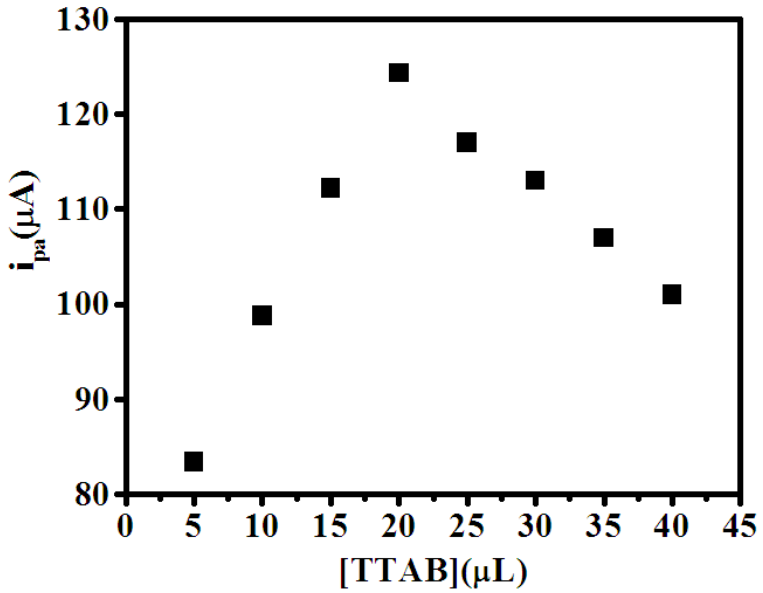


Figure 2b. Effects of immobilization time on the oxidation peak current of 1mM $K_4[Fe(CN)_6]$ at 50 mVs^{-1} scan rate .

Thus 20 µl TTAB was employed for the fabrication of modified electrode in the work.

3.3. Surface morphology of TTABMCPE.

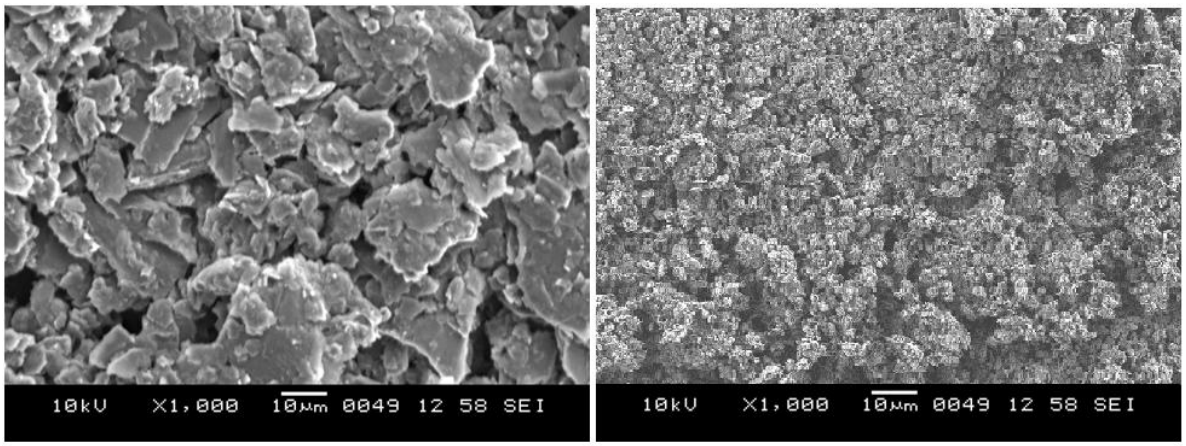


Figure 3. Scanning electron microscopic image of BCPE (A) and TTABMCPE (B).

Fig. 3 explains the surface morphology of BCPE and TTABMCPE using scanning electron microscopy. The surface of BCPE was irregularly shaped micrometer sized flakes of graphite. However after immobilization of the TTAB on BCPE has typical uniform arrangement of TTAB molecules on the surface of carbon paste electrode. This confirms that the surface morphology of carbon paste electrode was changed by TTAB monolayer.

3.4. Electrochemical behavior of epinephrine at TTABMCPE.

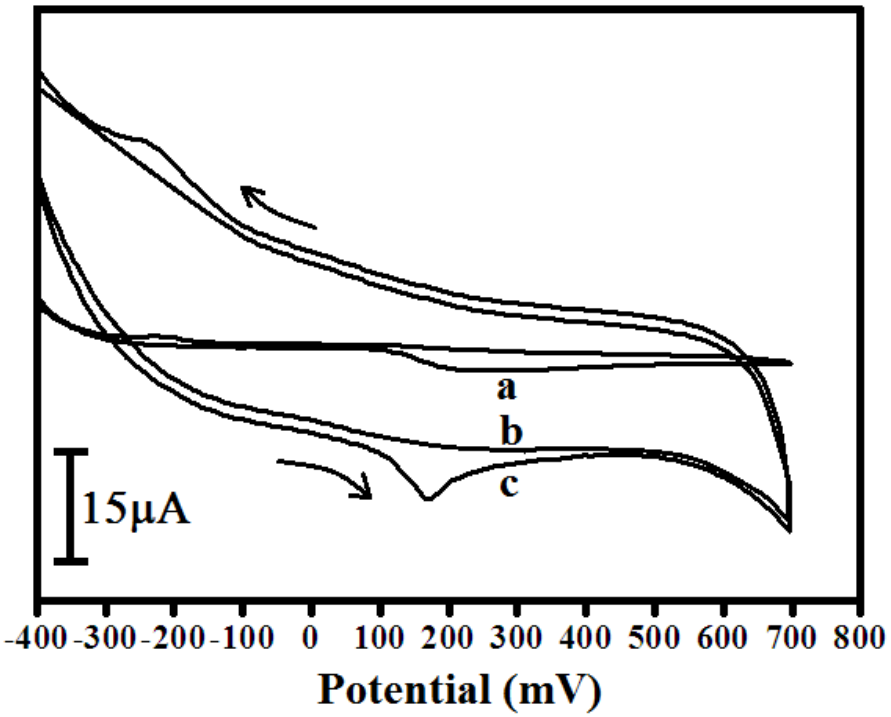


Figure 4a. Cyclic voltammograms obtained for PBS at TTABMCPE (b) and for 10 µM EP in 0.2 M pH 7.4 PBS at scan rate of 50 mVs^{-1} at BCPE (a) and TTAABMCPE (c).

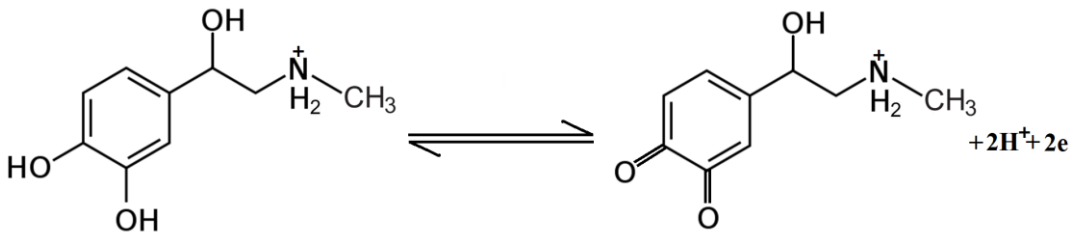
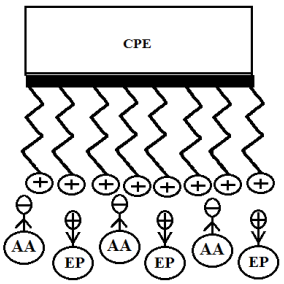


Figure 4b. Electrochemical oxidation mechanism of EP at TTABMCPE

Fig. 4a shows the voltammograms of 10 µM EP at the BCPE (curve a) and at TTABMCPE (curve c) in pH 7.4 PBS. At the BCPE, EP exhibited a poor electrochemical response. The oxidation peak (Epa) was located at 225 mV and redox peak (Epc) was at -218 mV in 0.2 M PBS of pH 7.4. But at the modified electrode, the peak current was increased considerably. The anodic peak potential

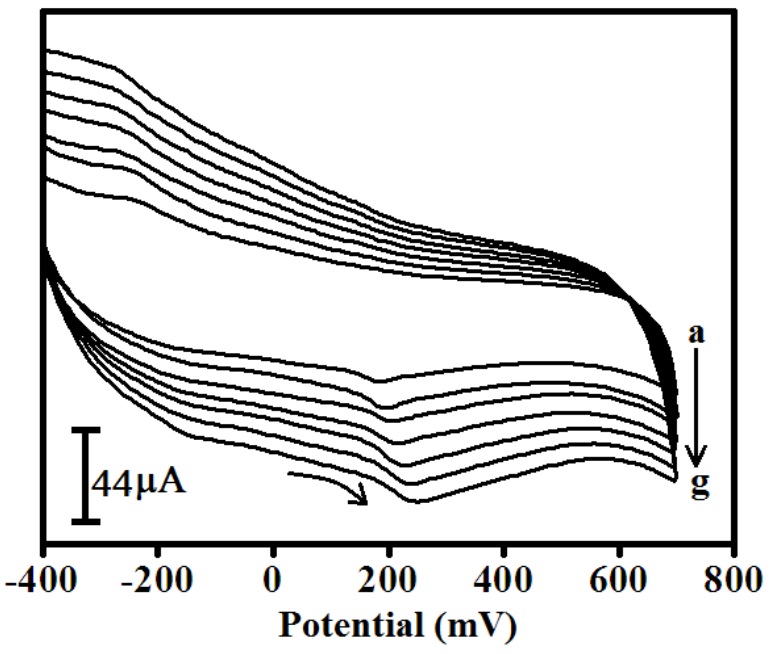
(Epa) was located at 171 mV and cathodic peak potential (Epc) at -248 mV. Further the same experiment was carried out without taking any EP with buffer solution (blank). No peaks were obtained for the modified electrode (curve b). The above results revealed that the TTABMCPE exerted very good electrocatalytic effect on EP. The electrochemical oxidation mechanism of EP on the surface of TTABMCPE is out-lined in Fig. 4b.



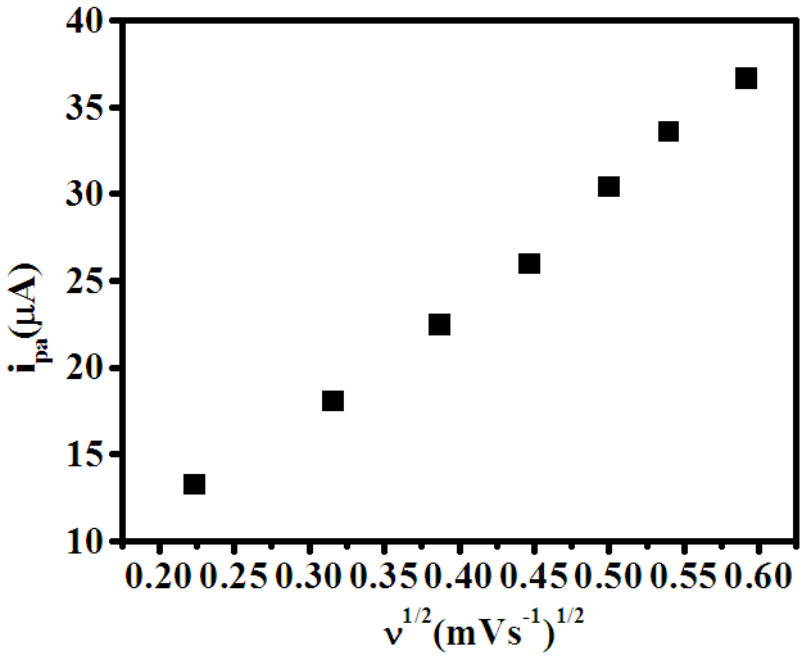
Scheme 1. Interactions of AA and Ep with TTABMCPE.

A positive electric field exists around the modified electrode surface. The monolayer adsorption of TTAB on the CPE surface is similar to the adsorption character of CTAB on the graphite surface. At 7.4 pH the amine group in EP molecule was electropositive. The positively charged TTAB monolayer interacts with the positively charged EP by repulsive force (scheme.1). Therefore electropositive EP is repelled electrostatically to the monolayer and can be oxidized at relatively low potentials.

3.5. Effect of scan rate TTABMCPE.



A



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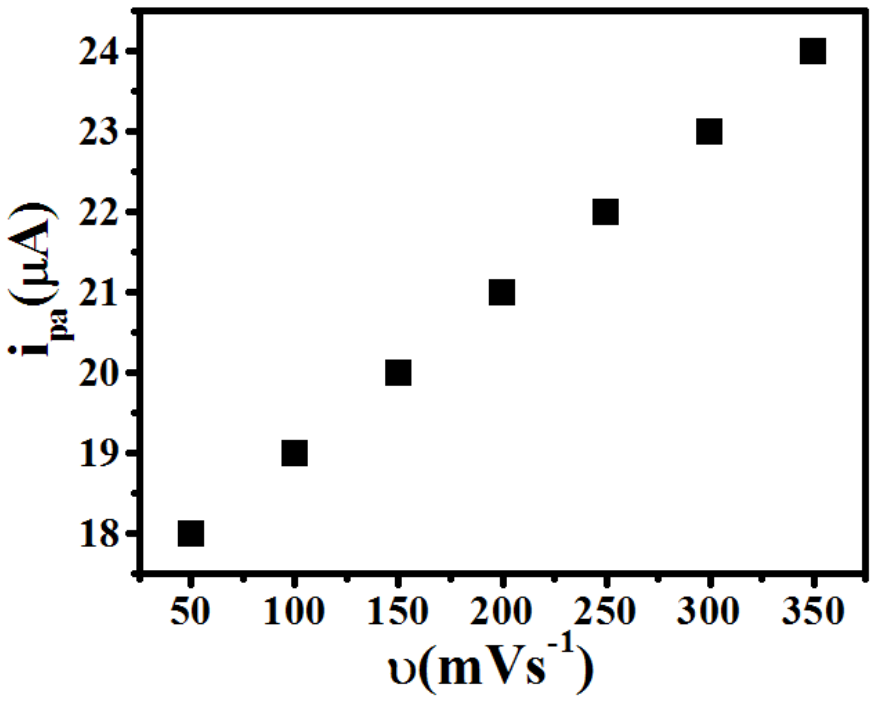

C

Figure 5. (a) Cyclic voltammograms of 10 μM EP on the TTABMCPE at different scan rates (a–g: 50, 100, 150, 200, 250, 300, 350 mVs^{-1}) in 0.2 M PBS of pH 7.4, (b) is the plot of the redox peak current versus the scan rate and (c) is the plot of the redox peak current versus the square root of scan rate.

The effect of scan rate for 10 μM EP was studied by CV at TTABMCPE. It showed increase in the oxidation peak current with increase in scan rate from 50 to 250 mVs^{-1} (Fig.5a).

The graph of current (*I*pa) vs scan rate (ν) was plotted and it was good linearity between the scan rate and *I*pa (Fig.5b). In the range from 50 – 350 mVs^{-1} the redox peak currents were proportional to the scan rate (ν). The correlation coefficient was 0.9879, the corresponding linear regression equation is expressed as follows ip (μA) = 0.167+ 0.221ν (mVs^{-1}) which indicate the electrode transfer reaction was adsorption controlled. Further the graph of current (Ipa) versus square root of scan rate was plotted (fig 5c).

The graph obtained results with good linearity in the range 50-350 mVs^{-1} with correlation coefficient 0.99753 and the linear regression equation is Ip (μA) = -0.214+6.49 $\nu^{1/2}$ $(mVs^{-1})^{1/2}$, which indicates a diffusion controlled process occurring at the TTABMCPE. From the above observation it is clear that the electrode process was controlled by both adsorption and diffusion process simultaneously.

3.6. Effect of concentration of EP.

The electrocatalytic oxidation of EP was carried out by varying its concentration at TTABMCPE. By increasing the concentration of EP, the electrochemical anodic peak and cathodic peak current goes on increasing with negligible shifting in redox peak potentials. The graph of anodic peak current vs concentration of EP was plotted, the EP from 0.15 μM to 2.5 μM concentrations was proportional to electrochemical peak current, (Fig.6) The linear regression equation has been obtained as i_{pa} (μA) = 0.0668 + 0.4006 $(C)_{DA}$ μM/L and correlation coefficient (r) was found to be 0.992. The limit of detection (LOD) was calculated by suing the formula (1) [42, 43] and it was found to be 0.12 μM. The performance of modified electrode was compared with other reported modified electrodes and given it in the table 1.

Table 1. Comparison of TTABMCPE with other reported modified electrodes

Electrode	Detection limit	Linear range	Method	Reference
Pen SAM-MAuE	0.1μM	100 μM to 0.1 μM	CV	[45]
2PHCMCNPE	9.4 nM	0.05 μM to 550 μM	SWV	[56]
P(1-methylpyrrole)GCE	0.168 μM	0.75 μM to 200 μM	SWV	[47]
p (taurine)ME	0.3 μM	2 μM to 600 μM	DPV	[48]
FCDMCNPE	35nM	0.05 μM to 450 μM	DPV	[49]
FePc-ME	0.5 μM	1 μM to 300 μM	CV	[50]
poly(caffeic acid)MGCE	0.6 μM	2 μM to 300 μM	CV	[51]
TTABMCPE	0.12 μM	0.15 μM to 30 μM	DPV	This work

LOD = 3S/M (1)

Where S is standard deviation and M is slope

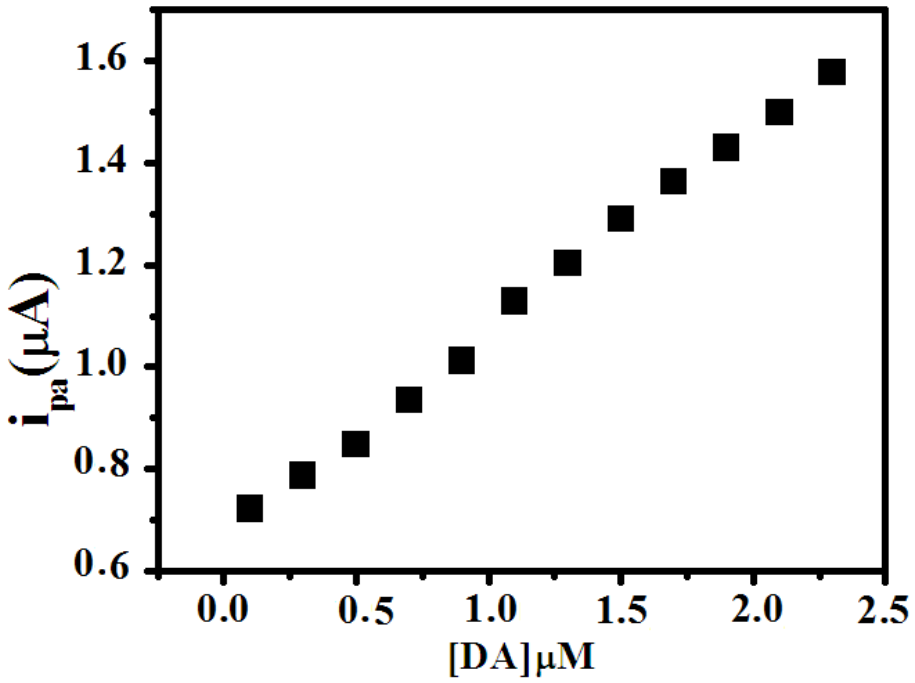

Figure 6. Graph of Ipa versus concentration of EP in μM on TTABMCPE in pH 7.4 PBS with scan rate 50 mVs^{-1}.

3.7. Effect of pH.

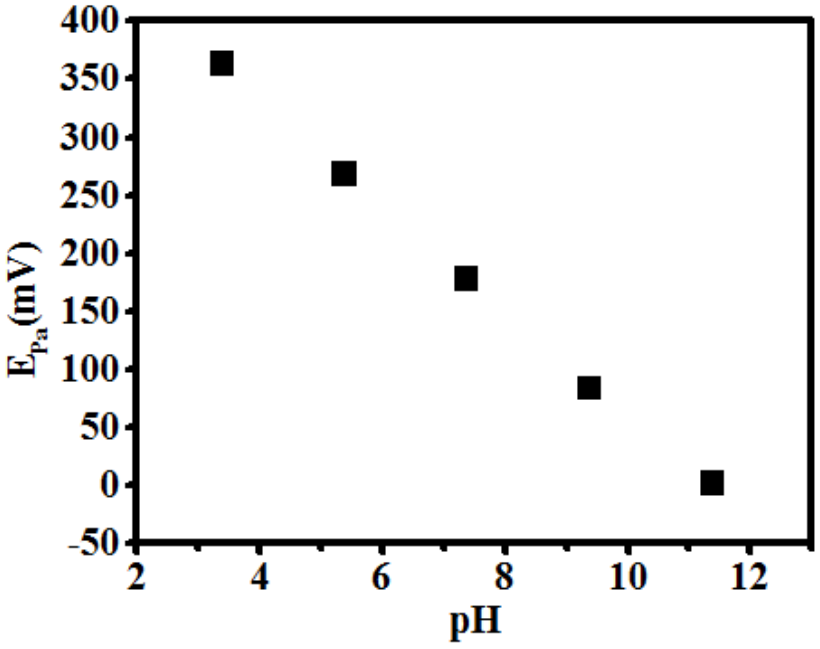

Figure 7a. Relationship of Epa with different pH values of PBS at a scan rate of 50 mVs^{-1}.

The electrochemical response of EP at TTABMCPE was generally pH dependent. The both anodic and cathodic peak potentials were shifted to less positive side with increasing in the pH values. The anodic peak potential of EP shifted from 382 mV to 62 mV with respect to the pH from 3.4 to 11.4, as shown in the Fig.7a. The graph has good linearity with a slope of 61 mV/pH this behavior is nearly obeyed the Nernst Equation for equal number of electron and proton transfer reaction [44]. Fig.7b shows the graph of anodic peak current vs. pH of the solution, from the graph it is very clear that the maximum sensitivity was obtained at 7.4 pH.

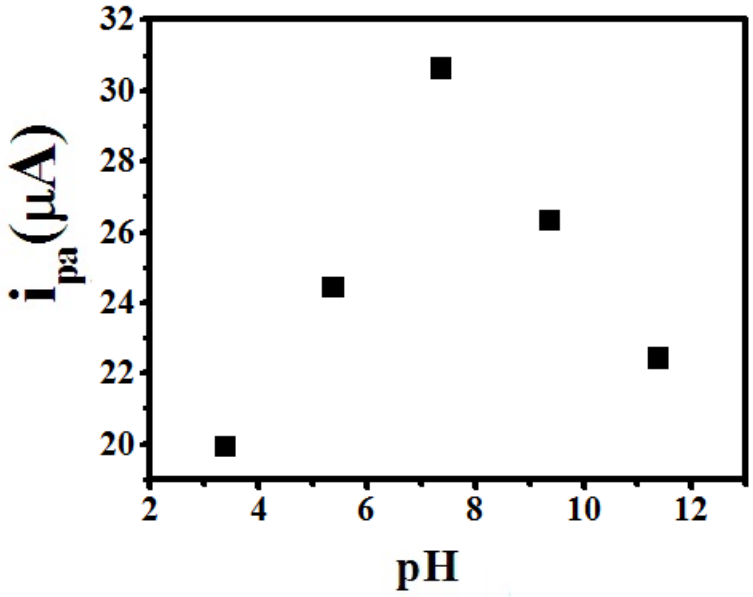

Figure 7b. Plot of i_{pa} with different pH values of PBS at scan rate of 50 mVs^{-1}.

3.8. Electrochemical oxidation of serotonin at TTABMCPE.

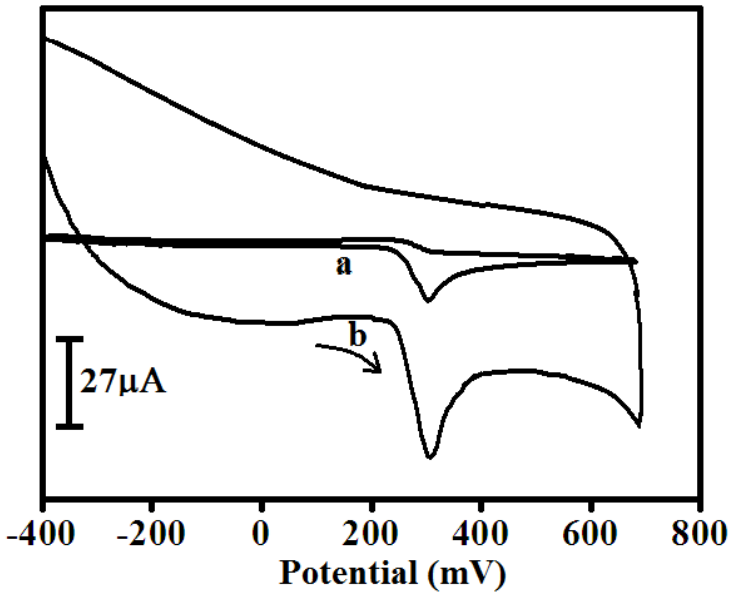

Figure 8. CVs of for 100 μM 5-HT at BCPE (a) and at TTABMCPE (b) in PBS of pH 7.4 at sweep rate of 50 mVs^{-1}.

The fig 8 represents the cyclic voltammogram of 100 μM serotonin in the PBS of pH 7.4 at a scan rate 50 mVs^{-1}. The cyclic voltammograms of 5-HT in the PBS produced a single irreversible oxidation peak in both TTABCPE and BCPE. The oxidation of 5-HT in PBS of 7.4 was occurred at around 312 mV at the BCPE and at the TTABMCPE it was at 306 mV.

While increasing the scan rate, the oxidation peak potential shifted to more positive potential which was in line with the characteristic irreversible electrochemical process. A good linear relationship was observed between Ipa and ν, Ipa and $\nu^{1/2}$ within the range of 50 to 300 mVs^{-1}. These results revealed that the reaction at TTABMCPE was controlled by both adsorption and diffusion simultaneously. The effect of pH on electrochemical reaction of 5-HT at TTABMCPE was also examined. With pH increasing from 3.2 to 11.4, the Epa shifted toward more negative potential and pH was 7.4 maximum Ipa was obtained suggesting that pH 7.4 should be selected as a optimum protocol for determination of 5-HT.

3.9. Electrochemical oxidation of ascorbic acid at TTABMCPE.

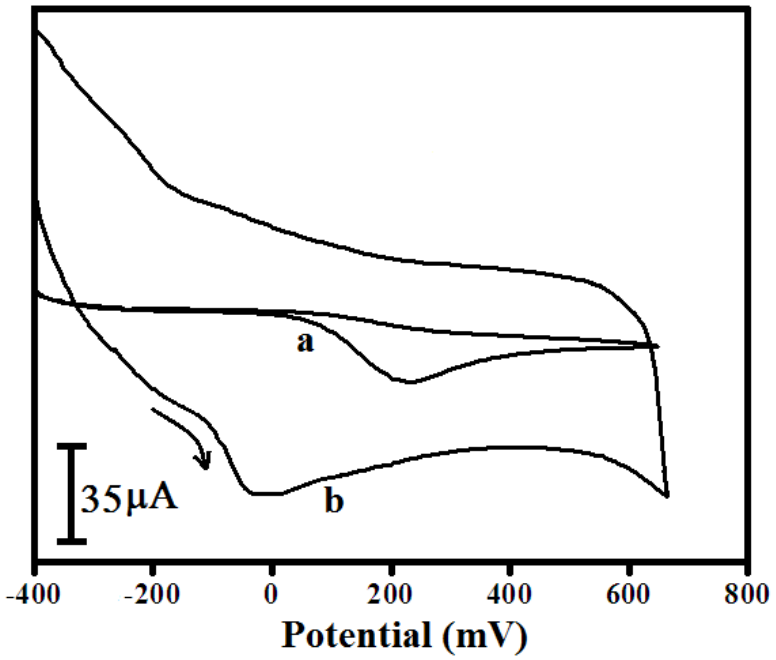

Figure 9. Cyclic voltammograms of 1.0 mM AA at a BCPE (a) at a TTABMCPE (b) in pH 7.4 PBS at scan rate of 50 mV s^{-1}.

The fig 9 represents the cyclic voltammogram of 1 mM AA in the PBS of pH 7.4 at 50 mV^{-1} scan rate. Since ascorbic acid was present in the mammalian cell with the dopamine, its voltammetric behavior at the TTABMCPE was studied. The cyclic voltammograms of ascorbic acid in the PBS produced a single irreversible oxidation peak in both TTABCPE and BCPE. The oxidation of AA occurred at 220 mV at the BCPE and at the TTABMCPE it was -10 mV in PBS of pH 7.4. Reason for this negative shifting may due to the attractive force between the positively charged monolayer of the

TTABMCPE and anionic form of AA. This result reveals that, TTABMCPE has an effective electrocatalysis for the oxidation of ascorbic acid.

3.10. Simultaneous detection of epinephrine, serotonin and ascorbic acid at TTABMCPE.

Based on the electrocatalytic action of TTABMCPE to EP, AA and 5-HT, it was supposed that the TTABMCPE could conspicuously improve the voltammetric resolution of EP, AA and 5-HT. To ascertain the presumption, the cyclic voltammograms of mixture solution containing 10 μM EP, 1 mM AA and 100 μM 5-HT in PBS of pH 7.4 were recorded with the scan rate of 50 mVs^{-1} at BCPE and TTABMCPE.

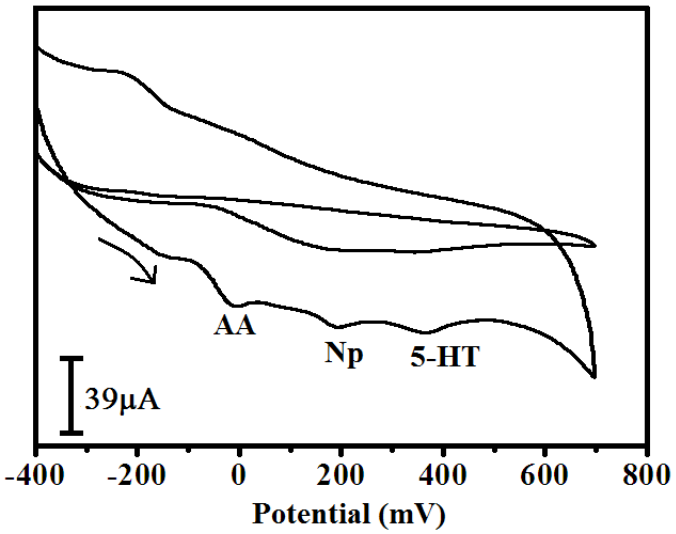

Figure 10a. CVs at BCPE (a) and TTABMCPE (b) in 0.2 M PBS (pH 7.4) containing 1mM AA, 10 μM EP and 100 μM 5-HT. Scan rate: 50 mVs^{-1}.

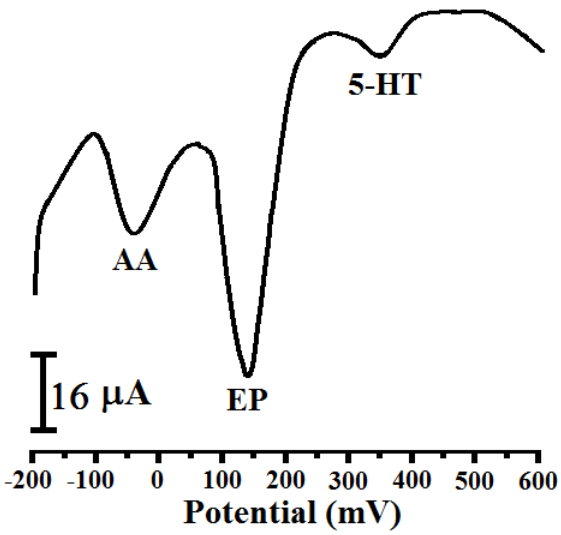

Figure 10b. DPV for 1mM AA, 10 μM EP and 100 μM 5-HT at the TTABMCPE in PBS solution at pH 7.4, with a 20 mVs^{-1} scan rate, 50 mV pulse amplitude, and 50 ms pulse width.

As shown in the fig.10a the voltammograms at the BCPE appeared the seriously overlapped peaks at the anodic potentials of 240 mV, while three separated oxidation peak can be found at the TTABMCPE. The oxidation peak of AA was found at -8 mV, EP was found at 198 mV and that of 5-HT was located at 363 mV. The cathodic peak of EP was at -240 mV.

The difference of the oxidation peak potential for EP-AA, EP-5-HT was 206 mV and 165 mV respectively, which were enough large separation to allow the simultaneous determination of EP, AA and 5-HT in a mixture. Further, the separation study was moved to DPV (Fig 10b) because of its higher current sensitivity and better resolution than cyclic voltammetry. The anodic peak potentials for EP, AA and 5-HT were at 171 mV, -17mV and 366 mV respectively. The peak to peak separation for EP-AA and NP-5-HT were 188 mV and 195 mV, respectively. It further identified that TTABMCPE possessed higher active surface area and excellent electrocatalytic activity for the oxidation of EP, AA and 5-HT.

3.11. Interference study

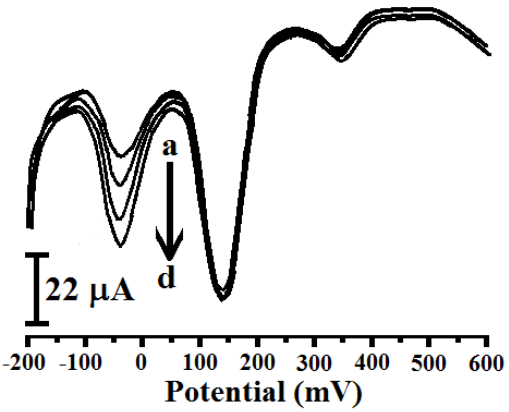

Figure 11a. Differential pulse voltammograms of EP in the presence of 1mM AA and 100 µM 5-HT in 0.2 M PBS (pH 7.4). DA concentrations (from a to e); [EP] 10,12,14,18 and 20 µM.

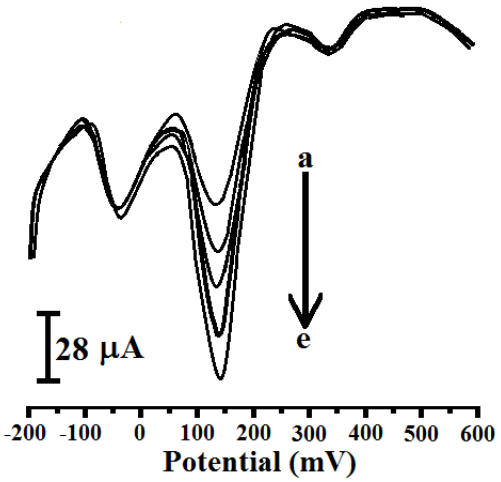

Figure 11b. Differential pulse voltammograms of AA in the presence of 10 µM EP and 100 µM 5-HT in 0.2 M PBS (pH 7.4). AA concentrations (from a to d) [AA]: 1, 2, 3, and 4 mM.

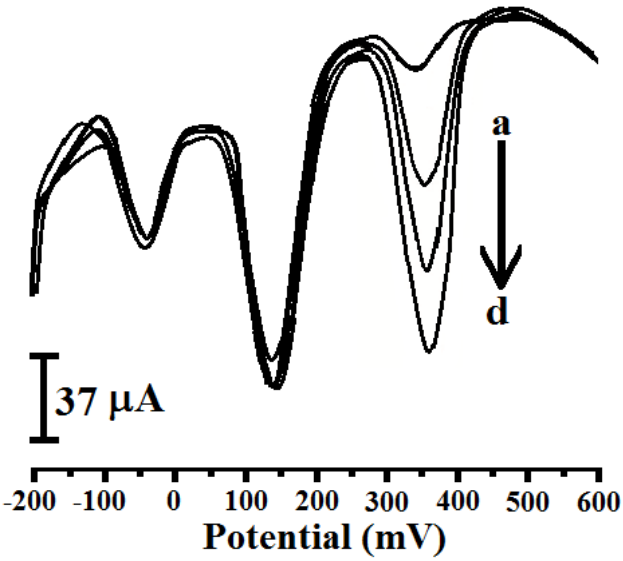

Figure 11c. Differential pulse voltammograms of 100 μM 5-HT in the presence of 10 μM EP and 1 mM AA in 0.2 M PBS (pH 7.4). 5-HT concentrations from (a to d) [5-HT]: 100,110,120 and 130 μM.

The electrochemical behavior of EP with different concentration in presence of 1 mM AA, and 100 μM 5-HT at TTABMCPE was studied by DPV. The EP concentration was varied from 10 to 18 μM (Fig. 11a). The anodic peak current of EP were increased with respect to concentration of EP. Likewise the other two species AA was increased from 1mM to 0.4 mM and 5-HT was from 100 to 120 μM (Fig. 11b and Fig. 11c respectively). The experimental results showed that there was no shift in anodic peak potentials of all electroactive species. The TTABMCPE was able to determine EP in the presence of higher concentration of AA and 5-HT. The obtained result could explain the oxidation peaks of EP, AA and 5-HTexisted independently. At the same time oxidation of dopamine undergoes at 180 mV and that of uric acid at 308 mV at the TTABMCPE. So the interference of dopamine - epinephrine and uric acid - 5HT can't resolve by using this modified electrode.

3.12. Stability and reproducibility of the TTABMCPE

The stability of the electrochemical sensor was investigated by recording a cyclic voltammograms of TTABMCPE in 0.2 M PBS (pH 7.4). After 50 successive potential scan the anodic and cathodic peak current of EP at the TTABMCPE decreased only by 4.1%. The storage stability of TTABMCPE was tested after stored it in 0.2 M PBS (pH 7.4) for two weeks and it retained 94% of the initial response. The background current variation of the TTABMCPE surface at five newly prepared TTABMCPE was less than 4% which validates the reproducible nature of the TTABMCPE. The results suggests that the TTABMCPE posses good stability and reproducibility. However as the procedure for electrode preparation is easy and rapid it is not so important for the electrode to be stable for prolonged period. Therefore it can be prepared easily for instant use.

3.13. Analytical applications

The modified electrode was applied to the determination of Epinephrine (adrenalie tartrate from HINDUSTAN PHARMACEUTICALS INDIA LTD,1mg/ml). Using the proposed methods described above, the injection of Epinephrine tartrate was analyzed by standard addition method and the results are shown in Table 2.

Table 2. Determination of EP in adrenaline tartrate injection sample by TTABMCPE

Sample	Added (μM)	Found (μM)	RSD(%)	Recovery (%)
1	10	9.81± 0.070	0.91	98.1
2	10	9. 63 ± 0.062	1.82	96.3
3	10	9.58 ± 0.078	1.98	95.8

It demonstrated a good performance of the TTABMCPE with satisfactory reproducibility and the recoveries were acceptable, showing that the proposed methods could be efficiently used for the determination of EP in its injection samples.

4. CONCLUSION

BCPE can be modified by several surfactants; TTAB was used to modify and characterize the BCPE. CV results show that TTAB cationic monolayer formed on the BCPE can promote and accelerate the electrochemical reaction of EP even in presence of 5HT and AA. There are good linear relations between ipa in the range of 0.15 μM to 2.5 μM. The detection limit was calculated as 0.12μM by differential pulse voltammetry. Therefore TTABMCPE is fit for the quantitative determination of EP in its injection sample. In the mean-time, the peak potentials of AA, 5-HT and EP can be separated successfully at TTAB by both CV and DPV at pH 7.4 in PBS; it is possible that TTABMCPE can be used for simultaneous determination of EP, 5HT and AA.

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