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Determination of Dopamine in presence of Ascorbic Acid at Eriochrome Black T Modified Carbon Paste Electrode : A Voltammetric Study

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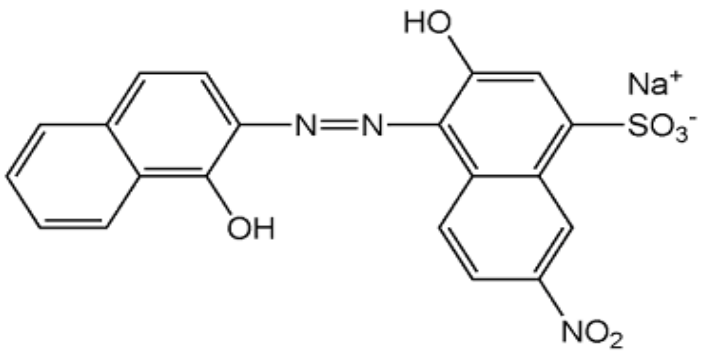
In this investigation the modification of carbon paste electrode was done by adding Eriochrome Black T (EBT) to the mixture of dry graphite powder and silicon oil of ratio 70:30 percent respectively. The voltammetry of EBT modified carbon paste electrode (EBTMCPE) was investigated with standard potassium ferricyanide solution shows reversible voltammogram. The electrochemical study shows catalytic oxidation of dopamine (DA) was better sensitive at EBTMCPE in 1M KCl solution as supporting electrolyte. The effect of concentration and scan rate were studied. The electrode process was found to be diffusion-controlled. The EBTMCPE shows selective enhancement of oxidation peak current for DA in the presence of ascorbic acid (AA). DA was also detected by using differential pulse voltammetry (DPV). In the presence of AA, DA-AA shows peak potential separation of 163mV. The concentration effect of both AA and DA were studied by using DPV.

Keywords: Eriochrome black T, dopamine, ascorbic acid, electrocatalytic oxidation, modified carbon paste electrode

1. INTRODUCTION

DA is one of the naturally occurring catecholamine and very important neurotransmitter in mammalian central nervous systems and has been a matter of great interest to neuroscientists and chemists, since its discovery in 1950s [1]. It plays an important role in the function of central nervous, renal hormonal and cardiovascular system [2]. Serious diseases such as Schizophrenia and Parkinsonism may result by loss of DA-containing neurons [3-6]. Patient with this disease shows a low level of DA. So, detection of DA contained samples plays an important part in the study of physiology mechanism and clinical diagnoses. Many methods such as spectroscopy, chromatography and

electrochemistry [7-10] were introduced to determine DA. Since DA is an oxidizable compound, it can be easily detectable by electrochemical methods based on anodic oxidation [6,11]. However, the major problem encountered with the voltammetric detection of DA in real samples is the coexistence of interfering compounds such as ascorbic acid (AA). AA is a vital vitamin in the diet of humans and is present in mammalian brain in the presence of several neurotransmitters including DA. AA has been used for the prevention and treatment of common cold, mental illness, infertility, cancer and AIDS [12]. AA exists at much higher concentration than that of DA. Both DA and AA oxidize at near potential, results in overlapping of voltammetric response at bare carbon paste electrode [12-15]. This becomes a major target to resolve this problem in electroanalytical research. 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 study of electrochemical determination with different modified electrode for sensitive and selective determination of DA has been reported [16-20]. The modification can be done by adding different types of modifiers. One of the modifiers we chosen for the determination of electrochemical response of DA is EBT, which is one of the metallochromic indicators used in complexometric titration (Scheme. 1) is basically water-soluble.



Scheme 1. Structure of Eriochrome Black T.

This is the ionochromic dye containing, C=C and N=N groups. Many electrochemical experiments have been done by electropolymerizing this EBT indicator and discussing their voltammetric behavior by modifying with glassy carbon electrode [21-23]. The Poly (Eriochrome Black-T) Modified Carbon Paste Electrode was prepared for simultaneous study of DA in presence of AA and electrochemical studies of EBT was studied at carbon paste electrode the by our group [24, 25].

In the present work, an approach was made to over come the problem of DA determination in presence of AA at EBTMCPE. The EBT was uniformly distributed in the carbon paste and not only improved the electrocatalytic oxidation of DA, but also changed the overlapping anodic of DA and AA peaks into two well defined peaks. The anodic peak currents increased linearly with the concentration of dopamine in the range of 1 X 10^{-5} M to 7 X 10^{-5} M by DPV. Moreover, in this concentration range, the coexistence of AA does not interfere with the voltammetric sensing of DA. The separation between DA-AA was found to be 107mV by CV and 163mV by DPV.

2. EXPERIMENTAL PART

2.1. Reagent and Chemicals

10mg of Eriochrome Black T was used as modifier. Potassium ferricyanide ($K_3Fe(CN)_6$) and AA solutions were prepared by dissolving in double distilled water. DA was prepared by dissolving in 0.1M perchloric acid ($HClO_4$) solution. 1M potassium chloride (KCl) was used as supporting electrolyte for all analyte. Chemicals mentioned above were all purchased from Fluka and were analytical grade.

2.2. Apparatus and Procedure

The electrochemical experiments were carried out using a model-201 Electroanalyser (EA-201 chemilink system). All experiments were carried out in a conventional three-electrode system. The electrode system contained a working carbon paste electrode, home made cavity of 3mm diameter, a platinum wire as counter electrode and saturated calomel electrode as reference electrode. EBTMCPE was prepared by grinding the 10mg of EBT indicator with 70% graphite powder (50μm particle size was purchased from Loba Chemie) and 30% silicon oil (Himedia) in an agate mortar by hand mixing for about 30 minute to get homogenous EBTMCPE. The paste was packed into the cavity CPE and smoothened on weighing paper. The bare CPE was prepared without adding modifier.

3. RESULTS AND DISCUSSION

3.1. Electrochemical characterization of EBTMCPE

EBT is a metallochromic indicator used as a modifier in the preparation of EBTMCPE. The characterization of EBTMCPE was investigated by using cyclic voltammetric technique.

Fig.1a shows the cyclic voltammogram of $1X10^{-3}$ M $K_3Fe(CN)_6$ at bare CPE and EBTMCPE in the potential range from 600 mV to –200 mV at 50 mVs^{-1} scan rate in 1M KCl supporting electrolyte. The voltammogram of 1 mM $K_3Fe(CN)_6$ at both bare CPE and EBTMCPE showed identical reversible cycles. The EBTMCPE showed very good electrochemical response when compared to bare CPE. The dashed line shows the electrochemical response of bare CPE having the cathodic peak potential (Epc) 207 mV and anodic peak potential (Epa) 287 mV with less sensitivity. After modification with 10 mg of EBT the electrode shows improvement in enhancement of both electrochemical cathodic and anodic peak current, this was shows in solid line.

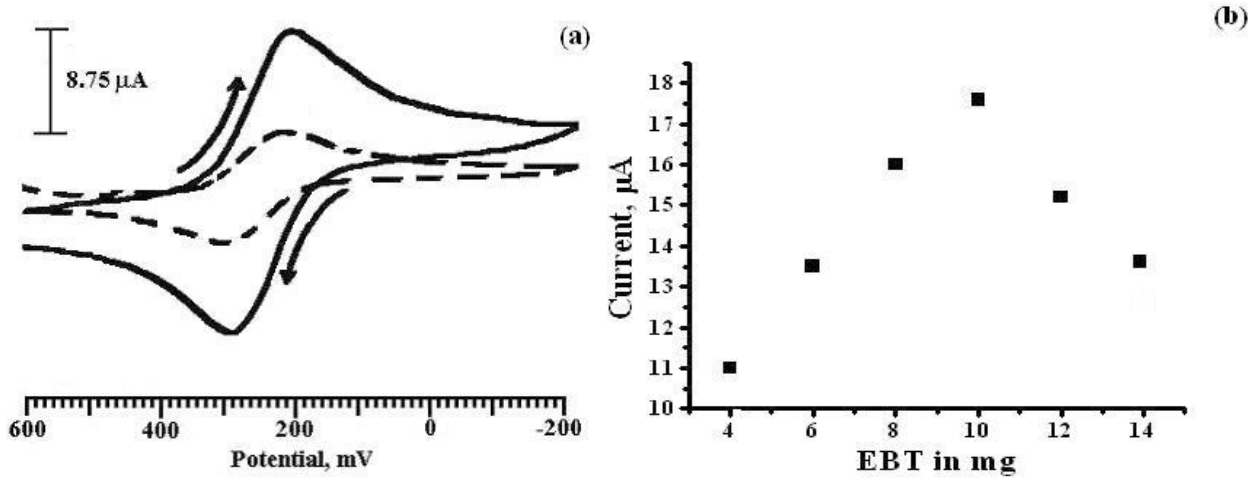


Figure 1. a)Cyclic voltammogram for 1 mM $K_3Fe(CN)_6$ at bare CPE (dashed line) and EBTMCPE (solid line), at 50mVs^{-1}; b)Graph of current vs quantity of EBT in carbon paste electrode.

EBTMCPE was prepared of different ratio by adding different amount of EBT. By increasing the quantity of EBT in the modification, the electrochemical cathodic and anodic peak current (I_{pa}) goes on increasing. EBTMCPE from 4 mg to 10 mg shows the cathodic peak current (I_{pc}) was increased with negligible change in redox peak potentials (Fig. 1b). Further increase in the quantity of EBT the both I_{pa} and I_{pc} were decreased. So, the 10 mg EBT as modifier was fixed for further investigation with DA.

3.2. Electrocatalytic response of DA at EBTMCPE

DA being an easily oxidizable catecholamine, its voltammogram was recorded in the potential range from 0 to 800mV with supporting electrolyte 1 M KCl at 50 mVs^{-1} scan rate. Fig.2a shows a pair of redox peak for 5X10^{-5} M DA at bare CPE (dashed line) with Epa at 482 mV and Epc 269 mV (vs. SCE) in 1 M KCl as supporting electrolyte. The peak to peak separation (ΔEp) was found to be 213 mV and the ratio of redox peak current (I_{pa}/I_{pc}) was 1.66, which were the characteristics of quassireversible electrode process. However, for the EBTMCPE a pair of redox peaks is obtained with strong increase in both anodic and cathodic peak current (solid line). The Epa was located at 477 mV, and the corresponding cathodic peak potential was located at 256 mV (vs SCE). The ΔEp was 221 mV and the value of I_{pa}/I_{pc} was about 1.7. So, the voltammogram obtained for EBTMCPE was also quassireversible with good improvement in enhancement of oxidation and reduction peak currents. The voltammogram shows increase in the both Ipa and Ipc of the DA with increase in scan rate (Fig. 2b) at the modified electrode. The graph of current (Ipa) vs square root of scan rate ($\nu^{1/2}$) were plotted. The graph obtained was nearly straight line (Fig. 2c). In the range from 50mV s^{-1}- 300mV s^{-1} the redox peak currents were proportional to the square root of scan rate ($\nu^{1/2}$) with correlation coefficient 0.9991. This indicates that, the electrode transfer reaction was diffusion controlled.

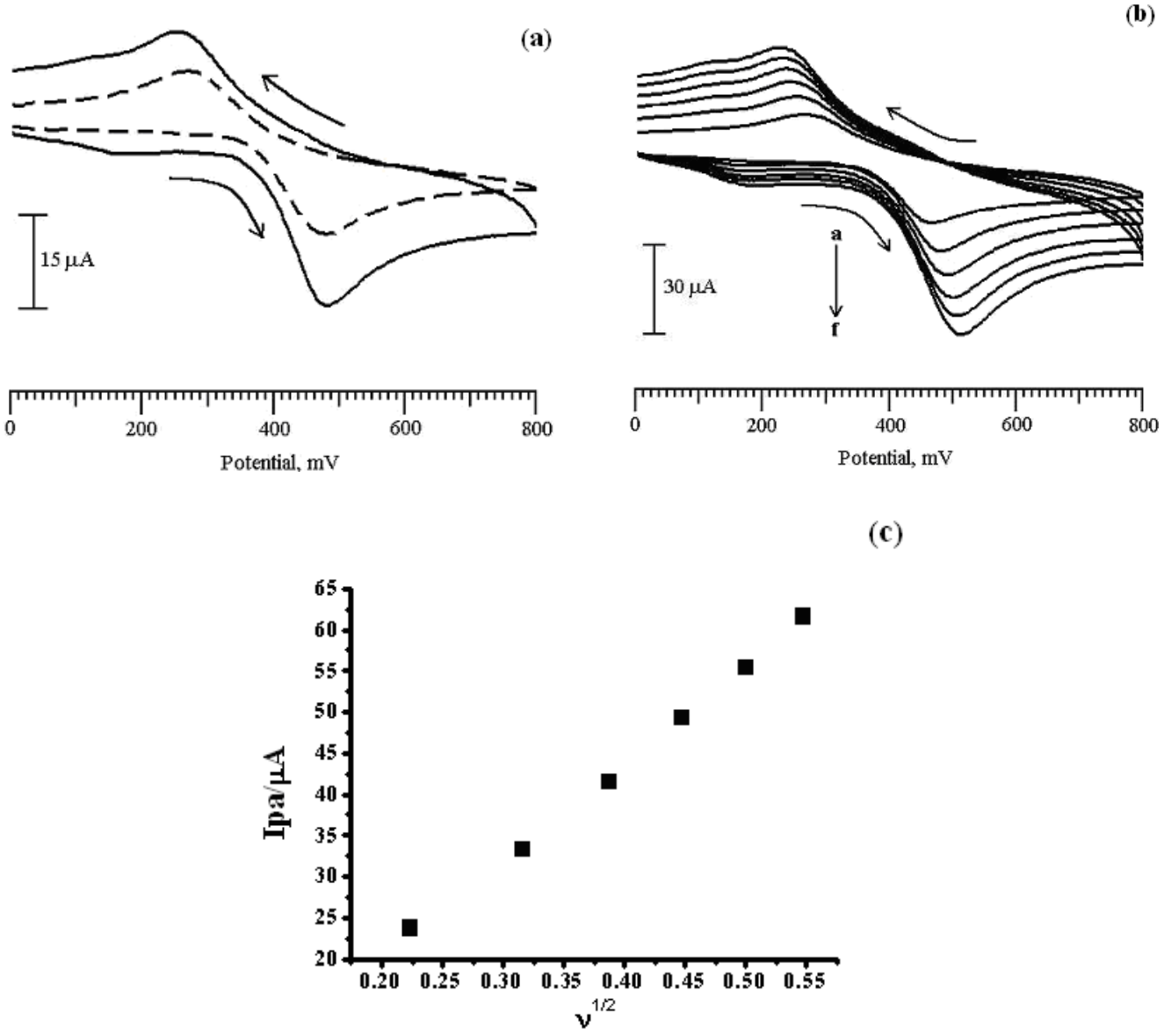


Figure 2. a)Cyclic voltammogram of $5X10^{-5}$M DA in 1M KCl at bare CPE (dashed line) and EBTMCPE (solid line), at $50mVs^{-1}$; b)Cyclic voltammogram of 0.5 mM DA at different scan rate (a-f; 50 mVs^{-1}, 100 mVs^{-1}, 150 mVs^{-1}, 200 mVs^{-1}, 250 mVs^{-1}, 300 mVs^{-1}; c)Graph of current vs square root of scan rate.

3.3. Effect of DA concentration

The electrocatalytic oxidation of DA was carried out by varying the concentration at EBTMCPE (Fig.3a). By increasing the concentration of DA, the Ipa and Ipc goes on increasing with shifting Epa towards positive and Epc with negligible shifting.

DA from $5X10^{-5}$M to $9X10^{-5}$M concentrations shows the Epa was shifted from 477mV to 549mV. The graph of Ipa vs concentration of DA was plotted, shows increase in electrochemical peak

current, (Fig. 3b). The graph obtained linearly increase in peak current with increase in the DA concentration and Ipa is proportional to concentration of DA.

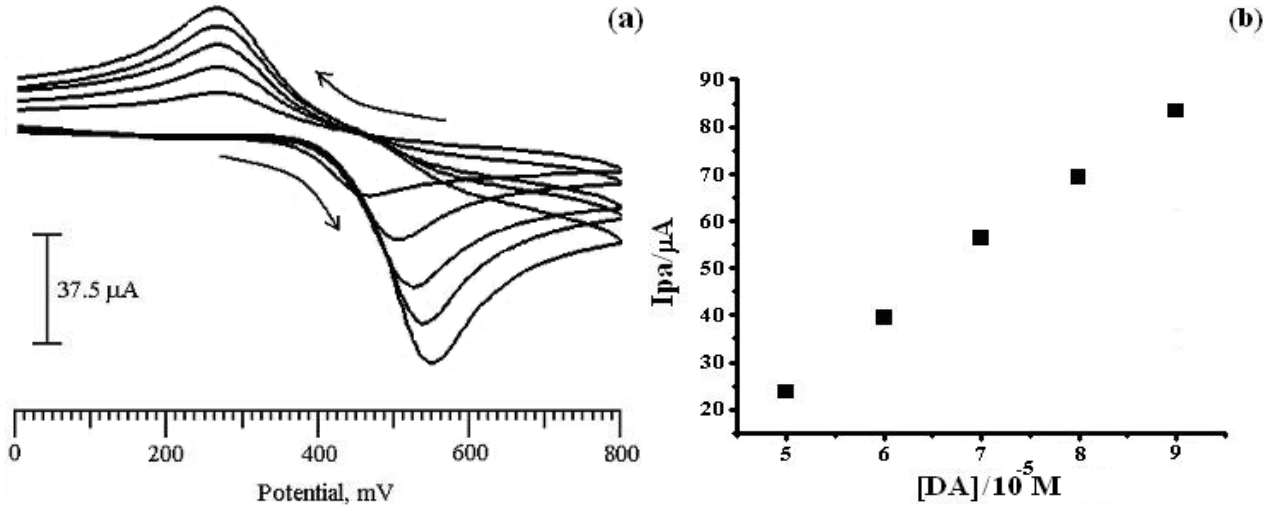


Figure 3. a)Cyclic voltammogram for different concentration of DA (a) $5X10^{-5}$M, (b) $6X10^{-5}$M, (c) $7X10^{-5}$M, (d) $8X10^{-5}$M and (e) $9X10^{-5}$M at EBTMCPE with scan rate $50mVs^{-1}$; b)Graph of current vs concentration of DA.

3.4. Simultaneous determination of DA and AA by cyclic voltammetry

AA is present along with DA in mammalian brain. The concentration of AA is much higher than that of DA. Since, the oxidation potential of AA is very close to that of DA results in overlapping response of peak potential at bare CPE. However, the EBTMCPE has ability to separate the oxidation peak potential of AA and DA.

Previously the voltammogram was recorded for $10X10^{-5}$M AA only in the potential range 0 to 600mV (Fig. 4a). The AA shows the electrochemical anodic peak potential at 254mV in 1M KCl system at bare CPE (dashed line). At EBTMCPE (solid line) the AA shows the anodic peak potential at 345mV. The electrode process could be found diffusion controlled with correlation coefficient 0.9950.

The Fig. 4b shows the voltammogram for solution containing mixture of both $5X10^{-5}$M DA and $10X10^{-5}$M AA in 1M KCl system. The bare CPE shows only one broad anodic peak without giving reduction peak (dashed line) for the sample mixture. The anodic peak potential of AA is nearly same as that of DA result in an overlapped voltammetric response at bare CPE. The anodic peak potential was occurred at 329mV. The EBTMCPE has able to separate the oxidation peaks of both AA and DA (solid line). The electrochemical response of AA shows oxidation peak potential at 359 mV at EBTMCPE. For DA the electrochemical response at EBTMCPE, the oxidation peak potential was observed at 466 mV and reduction peak potential was at 345 mV. After modification, EBTMCPE shows the selective determination of DA in the presence of AA and acts as sensor for the detection of DA in low concentration.

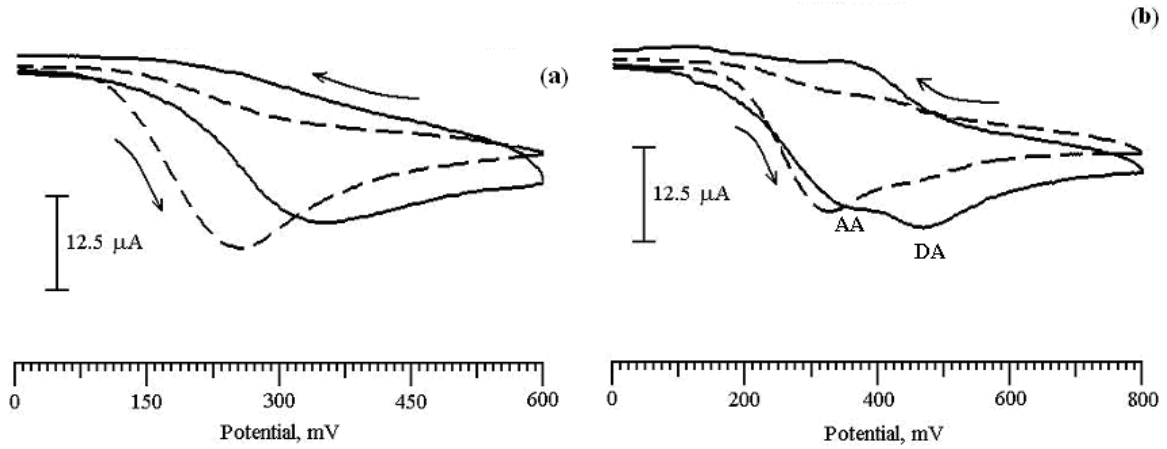


Figure 4. a)Cyclic voltammogram of $10X10^{-5}$M AA at bare CPE (dashed line) and EBTMCPE (solid line) with scan rate of $50mVs^{-1}$; b)Cyclic voltammogram for simultaneous determination of (a) AA and (b) DA at bare CPE (dashed line) and EBTMCPE (solid line) with the scan rate of $50mVs^{-1}$.

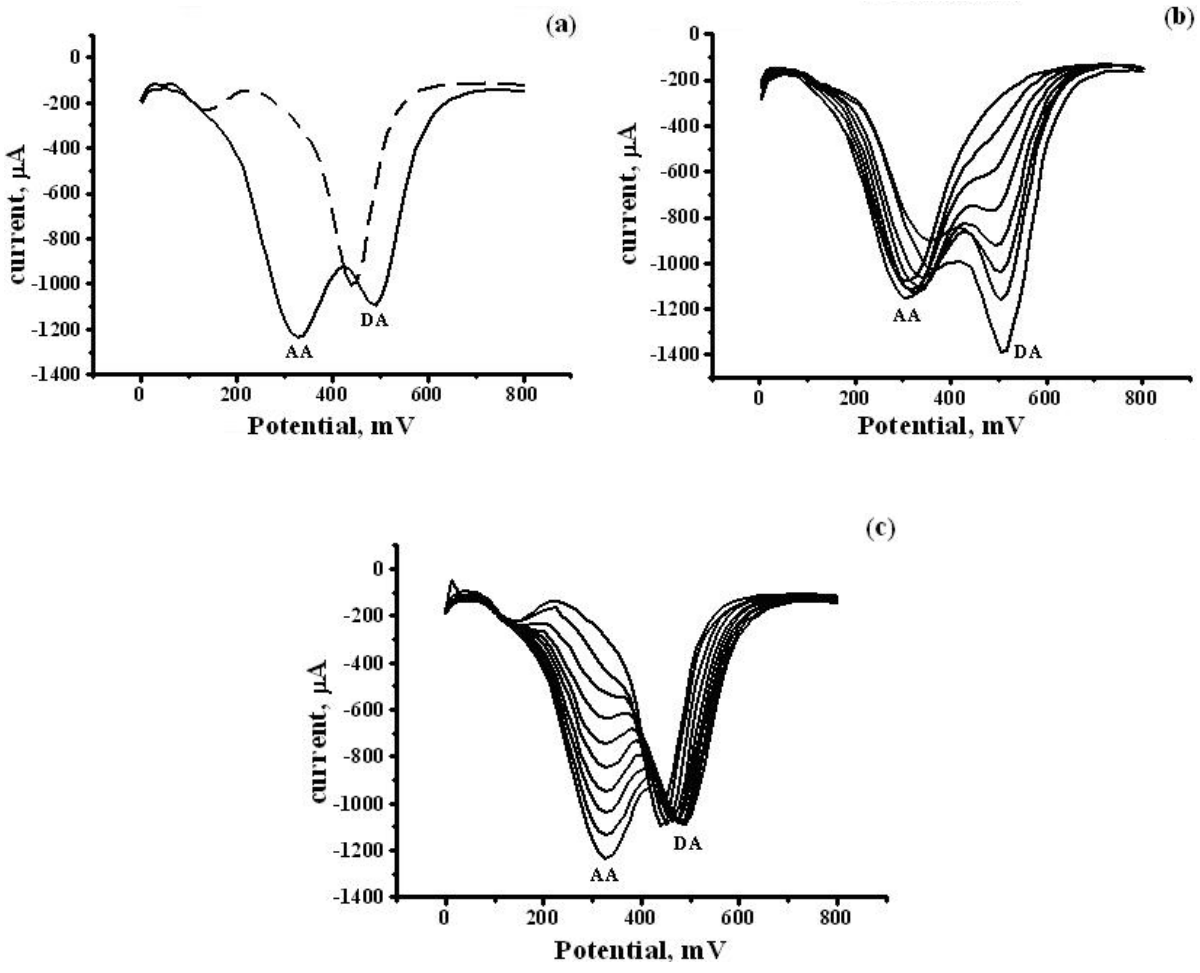


Figure 5. a)Differential pulse voltammogram for simultaneous detection of $5X10^{-5}$M DA and $10X10^{-5}$M AA at EBTMCPE (solid line) and at bare CPE (dashed line); b)DPV graphs of (a) 0 M, (b) $1X10^{-5}$M, (c) $2X10^{-5}$M, (d) $3X10^{-5}$M, (e) $4X10^{-5}$M, (f) $5X10^{-5}$M, (g) $6X10^{-5}$M and (f) $7X10^{-5}$M DA in 1M KCl in the presence of $10X10^{-5}$M AA at EBTMCPE; c)DPV graphs of (a) 0 M, (b) $1X10^{-5}$M, (c) $2X10^{-5}$M, (d) $3X10^{-5}$M, (e) $4X10^{-5}$M, (f) $5X10^{-5}$M, (g) $6X10^{-5}$M, (h) $7X10^{-5}$M, (i) $8X10^{-5}$M and (j) $9X10^{-5}$M AA in 1M KCl in the presence of $5X10^{-5}$M DA at EBTMCPE.

3.5. Simultaneous determination of DA and AA by differential pulse voltammetry

DPV was used for the determination of DA and AA at EBTMCPE because of its higher current sensitivity and better resolution than CV. The simultaneous study was carried out in the potential range from 0 to 800 mV (Fig. 5a). The DPV shows the simultaneous determination of DA and AA with well separated two anodic peaks corresponding to their oxidation could be possible at EBTMCPE (solid line), where as the bare CPE shows only one oxidation peak for the mixture of DA and AA (dashed line). The $10X10^{-5}$ M AA shows its Epa at 341 and $5X10^{-5}$ M DA was at 504mV. The peak separation between DA and AA was 163 mV which was very large when comparing to peak separation occurred by CV.

The simultaneous determination of DA and AA in the mixture was carried out at EBTMCPE when concentration of one species changed, whereas another one remained kept constant. From the Fig. 5b, it can be seen that the peak current of DA was proportional to its concentration, which was increased from 0 M to $7X10^{-5}$M when keeping the concentration of AA $10X10^{-5}$M constant. There was no change in the peak current and peak potential occurred for AA. Similarly in the Fig. 5c keeping the concentration of DA constant at $5X10^{-5}$M, the AA concentration was varied from 0 M to $9X10^{-5}$M. The oxidation peak current of AA increases with increase in its concentrations. The limit of detection of DA and AA was found to be $1.8X10^{-7}$M and $2.7X10^{-7}$M respectively.

4. CONCLUSION

In this work, we chose EBT, a metallochromic indicator as a modifier to study the electrochemical response of an interesting neurotransmitter DA. The EBTMCPE enhanced both anodic and cathodic peak current. The increase in the concentration of DA results in greater the enhancement of electrochemical anodic and cathodic peak currents. The modification shows high selective and electrocatalytic activity towards the oxidation of DA and AA in a mixed sample with low detection limit. The DPV results show there is no influence of AA towards the oxidation peak of DA at EBTMCPE. Hence this electrode is very good for practical analysis of neurotransmitter.

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