

Simultaneous Determination of Dopamine, Uric Acid and Ascorbic Acid with CTAB Modified Carbon Paste Electrode

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A cation surfactant Cetyltrimethyl ammonium Bromide (CTAB) modified carbon paste electrode was fabricated and applied to simultaneous determination of ascorbic acid, dopamine and uric acid. The modified electrode resolved the overlapped voltammetric responses of ascorbic acid, dopamine and uric acid in to three well defined voltammetric peaks by cyclic voltammetry (CV). The results showed that the electrocatalytic activity of CTAB modified carbon paste electrode (CTABMCPE) was more excellent when compared to bare CPE. The scan rate and concentration effect were linear with anodic peak current of dopamine. The modified electrode showed good selectivity, stability and antifouling properties.

Keywords: CTAB, Carbon paste electrode, cyclic voltammetry, Dopamine, Uric acid, Ascorbic acid.

1. INTRODUCTION

Dopamine (DA) is one of the excitatory neurotransmitters that play an important role in several physiological events. It is involved in the functioning of renal, cardiovascular, hormonal and nervous systems. DA is also involved in neurological diseases such as Parkinson's [1], Alzheimer's disease [2] and Schizophrenia [3]. It has been also suggested that DA plays a role in drug addiction [4-7] and some manifestation of HIV [8, 9]. A major problem in DA determination is the resolution between DA and coexisting species such as uric acid (UA) and ascorbic acid (AA). UA is a primary product of purine metabolism in the human body [10]. Its abnormal concentration level causes many diseases, such as gout, hyperuricaemia and Lesch-Nyan disease [11]. Therefore, the research of UA determination is of great importance in reality [12]. AA is a water soluble vitamin, and is a compound that takes part in many important life processes. It is one of the most important vitamins, due to its antioxidant and pH regulator properties often being added to various food products and

pharmaceuticals [13]. UA and AA are both present in biological fluids such as blood and urine [14]. As reported, the concentration of AA is generally much higher than that of DA (100 to 1000 times) [15].

At traditional electrodes, AA and UA are oxidized at potentials close to that of DA, resulting in an overlapping voltammetric response [16-18]. Moreover, the unmodified electrodes very often suffer from the fouling effect due to the accumulation of oxidized products on the electrode surface, which results in rather poor selectivity and sensitivity in addition, oxidation of DA at the electrode surface in the presence of AA results in a homogeneous catalytic oxidation of AA. The regenerated DA returns to the electrode, resulting in an enhanced current [19]. Therefore, improvement of the selectivity of DA monitoring techniques has been the focus of much research, and simultaneous detection of neurotransmitters and coexisting species, especially AA and UA, is a problem of critical importance not only in the field of biomedical chemistry and neurochemistry but also in diagnostic and pathological research.

CTAB, a cationic surfactant with a hydrophilic head on one side and a long hydrophobic head on the other side, had been widely used in electrochemistry and electro analytical chemistry field for different purposes [20-23]. It is well known that surfactants not only endow the electrode/solution interface with different electrical properties, but also adsorb at electrode surface or aggregate into super molecular structures to change electrochemical process [24-27]. Electrochemical characterization of CTABMCPE was studied and mechanism was predicted to show adsorptive behavior of CTAB on carbon paste electrode [CPE]. They revealed that CTAB formed a compact monolayer on the electrode surface with high density of positive charges directed outside the electrode [28]. Recently surfactant modified carbon paste electrode was studied by our group [29-33].

In this work, the immobilisation of CTAB at carbon paste electrode was explored by cyclic voltammetry which might be able to explain the enhancement effects of surfactant in electroanalytical chemistry for Dopamine, uric acid, ascorbic acid. The results revealed not only the adsorptive behavior CTAB but also the influences of CTAB adsorption on the surface of the electrode interface and the redox reactions in solution. These results might be able to explain the enhancement effects of surfactants in electroanalytical chemistry.

2. EXPERIMENTAL PART

2.1. Reagents and Chemicals

Cetyltrimethyl ammonium bromide, Dopamine hydrochloride, Ascorbic acid, Uric acid was obtained from Himedia chemical company. CTAB was prepared $1 \times 10^{-3} \text{M}$ stock solution by dissolving in double distilled water. Dopamine, ascorbic acid and uric acid chemicals were of analytical grade and used without further purification. Dopamine was prepared $25 \times 10^{-4} \text{M}$ stock solution by dissolving in 0.1M perchloric acid solution ascorbic acid was prepared $25 \times 10^{-3} \text{M}$ stock solution by dissolving double distilled water and $25 \times 10^{-3} \text{M}$ stock solution of UA by dissolving in 0.1M sodium hydroxide solution. In all the measurements, the supporting electrolyte used was 7.4 phosphate buffer solution.

2.2. Apparatus and Procedure

Cyclic voltammetry (CV) was performed on Model EA-201 Electroanalyser (Chemilink System). All the experiments were carried out in a conventional three electrode electrochemical cell. The electrode system contained a carbon paste as working electrode (3.0mm in diameter), a platinum wire counter electrode and saturated calomel electrode as reference electrode (SCE). The carbon paste electrode was prepared as follows, 70% graphite powder and 30% silicone oil were mixed by hand in an agate mortar to produce a homogeneous paste. The paste was then packed into the cavity of a homemade carbon paste electrode and smoothed on a weighing paper. CTABMCPE electrode was prepared by immobilizing the CTAB solution on to the surface of bare CPE.

3. RESULTS AND DISCUSSION

3.1. Electrochemical characterization of the modified electrode

Cyclic voltammetry was used to estimate the electroactive surface of the modified electrode. Fig.1 represents the CVs of bare CPE (dashed line) and CTABMCPE (solid line), which were recorded in $1 \times 10^{-3} \text{M}$ $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution containing 1M KCl as supporting electrolyte at a scan rate of 50 mV/s. A well defined redox peak with great enhancement was observed at CTABMCPE when compared with bare CPE. This may be ascribed to the higher electrochemical activity of the CTABMCPE. Compared with the bare CPE the peak current at CTABMCPE increased and was 4.0 times of that on bare CPE. Due to increased peak current the modified electrode possesses the highest electrocatalytic activity.

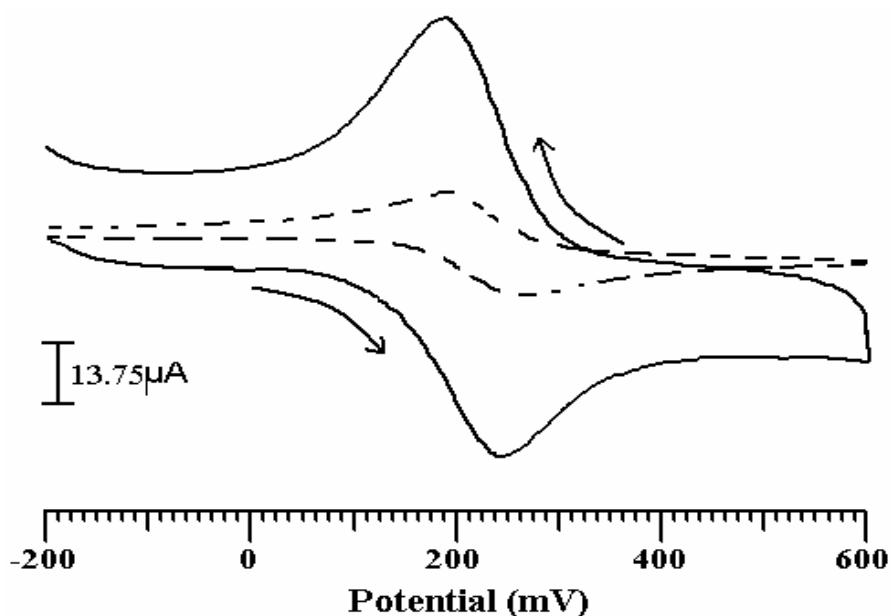


Figure 1. Cyclic voltammograms obtained for the electrochemical response of $1 \times 10^{-3} \text{M}$ $\text{K}_4[\text{Fe}(\text{CN})_6]$ at CTAB modified electrode (solid line) and bare CPE (dashed line) in 1M KCl. Scan rate 50 mV/s.

3.2. Electrocatalytic oxidation of DA at CTABMCPE

The electrochemical behavior of DA at the CTABMCPE was investigated using cyclic voltammetry and the cyclic voltammograms are shown in Fig.2 at the bare CPE (dotted line). The cyclic voltammogram of 1×10^{-4} M DA showed a pair of redox peaks in pH 7.4 PBS in the range from -300 to 600 mV. The CTABMCPE was scanned in the same range without adding DA in PBS of pH 7.4 (dashed line). A big background current was obtained at CTABMCPE without giving any peaks. However in the presence of 1×10^{-4} M DA a well defined strongly enhanced redox peaks were observed (solid line). The results of the enhancement of the peak current showed the excellent catalytic ability of CTABMCPE.

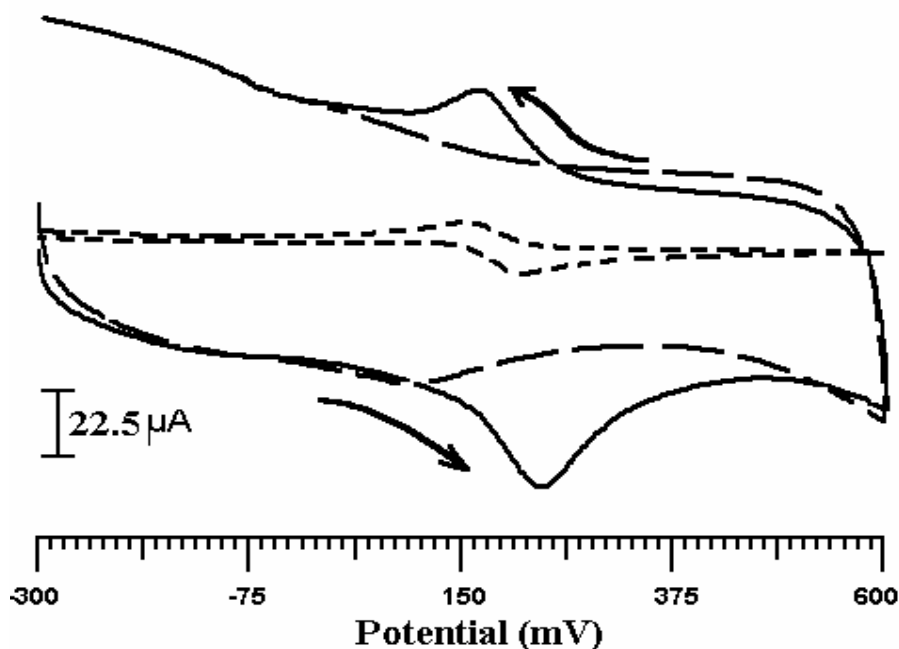
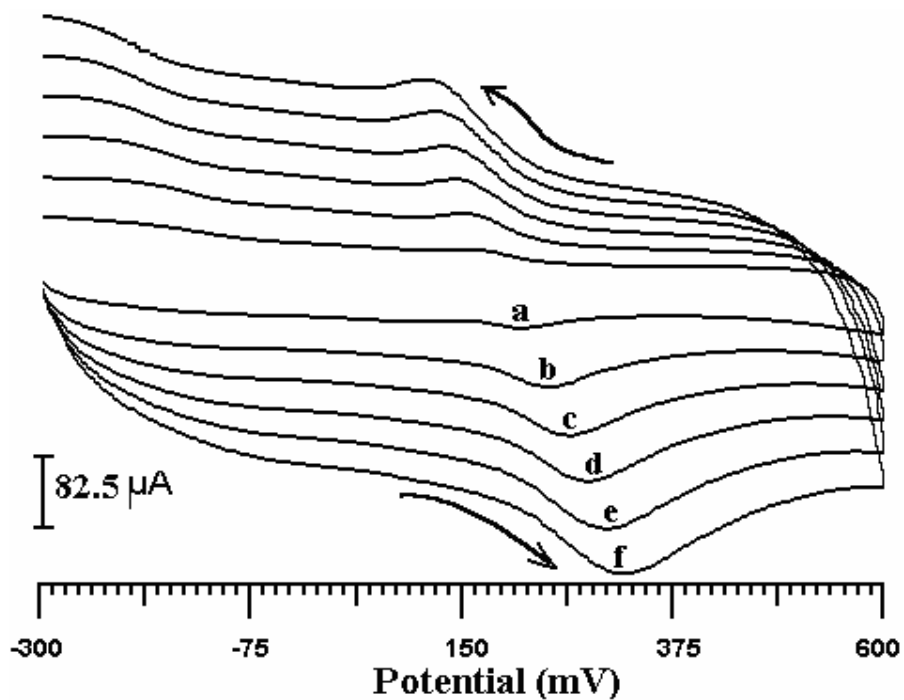


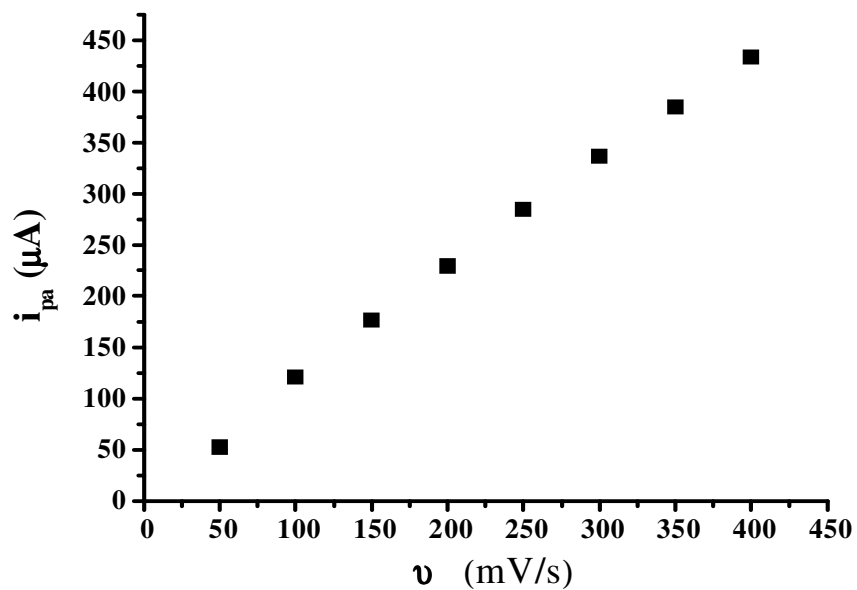
Figure 2. Cyclic voltammograms of 1×10^{-4} M DA obtained at the bare CPE (dotted line) and in the absence (dashed line) or in the presence (solid line) of 1×10^{-4} M DA at CTABMCPE scan rate 50 mV/s in 0.2M PBS (pH. 7.4).

3.3. Effect of scan rate

Fig.3a shows the cyclic voltammograms of 1×10^{-4} M DA on CTABMCPE at different scan rates. The increase of scan rate the redox peak current also increased gradually. The relationship of the anodic peak current with scan rate was constructed and the results are shown in the Figure 3b in the range from 50-300 mV/s, the anodic peak current were proportional to the scan rate with correlation coefficient 0.9986, which indicates the electrode process was adsorption controlled.



(a)



(b)

Figure 3. (a) Cyclic voltammograms of $1 \times 10^{-4} M$ DA on the CTABMCPE at different scan rates (a-f; 50-300mV/s) and (b) Graph of the anodic peak current versus scan rate.

3.4 Effect of concentration of DA

The electrocatalytic oxidation of DA was carried out by varying the concentration of DA at CTABMCPE. By increasing the concentration of DA, the electrochemical anodic and cathodic peak current goes on increasing with shifting E_{pa} towards positive and E_{pc} with negligible shifting of 1.0×10^{-4} to 3.0×10^{-4} DA concentration. The plot of i_{pa} vs concentration (Fig.4) showed increase in the electrochemical peak current, the graph obtained linearly increased in peak current with increase in the DA concentration and i_{pa} proportional to concentration of DA.

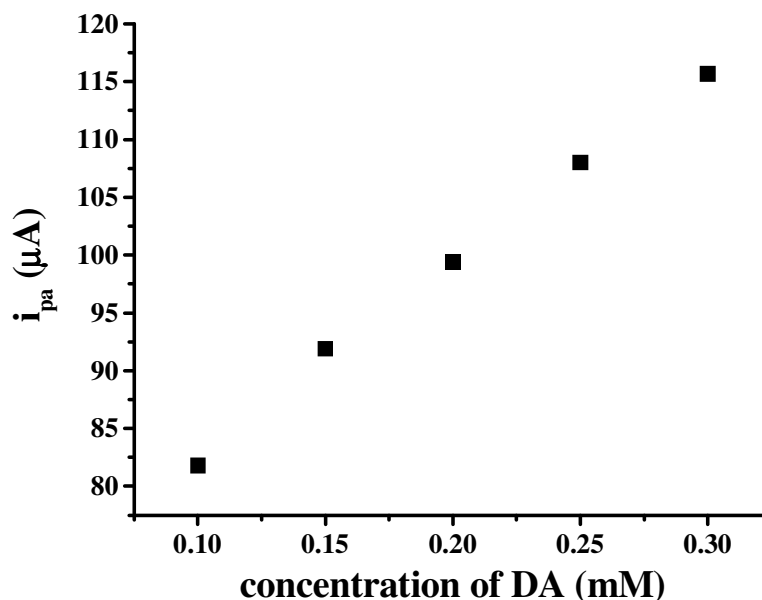


Figure 4. Graph of anodic peak current of DA verses concentration.

3.5. Electrochemical oxidation of AA at the CTABMCPE

Fig.5 shows the cyclic voltammogram of 1×10^{-3} M AA at the bare CPE (dashed line) and CTABMCPE (solid line). At the bare CPE the oxidation peak occur at around 192mV. Oxidation of AA at bare electrode is generally believed to be totally irreversible and requires high over potential due to fouling of the electrode by the adsorption of oxidized product of AA. However at the CTABMCPE, the oxidation peak potential of AA was obtained at around -62mV which is shifted more towards negative potential as compared to that of bare CPE, indicating that the CTABMCPE film on the electrode surface favors the oxidation process of AA. This film prevents the fouling of the electrode surface, hence faster electron transfer kinetics of AA at the CTABMCPE. Since the oxidation peak of AA is shifted to less positive potential it would not interfere with the measurement of DA.

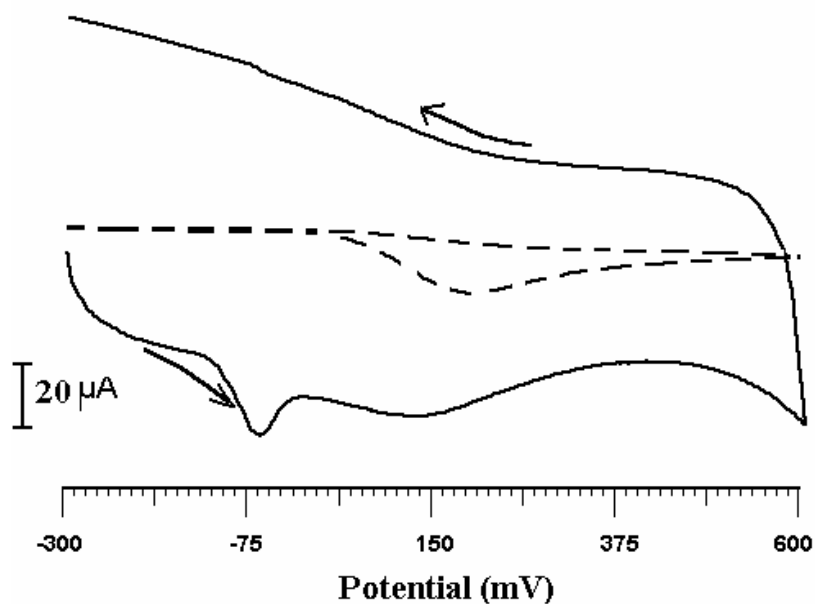


Figure 5. Cyclic voltammograms obtained for the oxidation of 1×10^{-3} AA at CTABMCPE (solid line) and bare CPE (dashed line) at scan rate 50mV/s, 0.2M PBS (pH. 7.4).

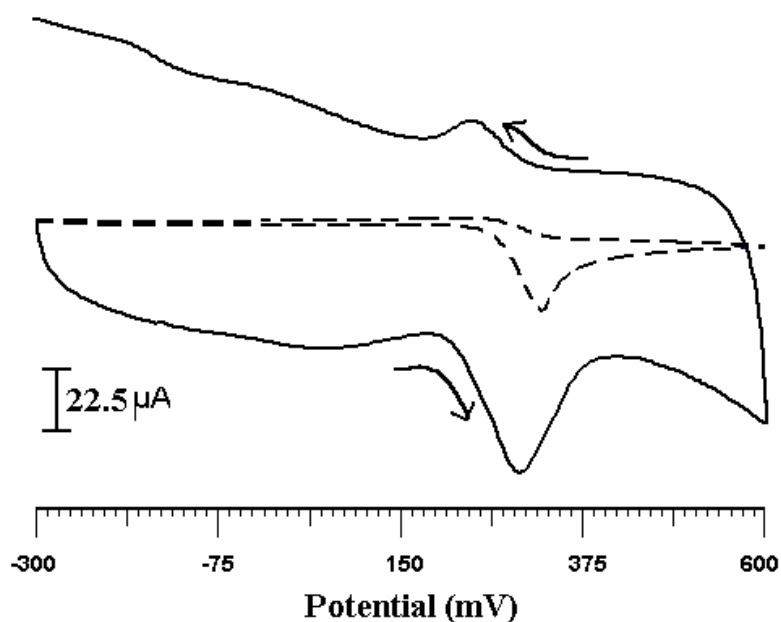


Figure 6. Cyclic voltammograms obtained for the oxidation of 1×10^{-3} UA at CTABMCPE (solid line) and bare CPE (dashed line) at scan rate 50mV/s, 0.2M PBS (pH. 7.4).

3.6. Electrochemical oxidation of UA at CTABMCPE

Fig.6 shows the cyclic voltammogram of $0.5 \times 10^{-3} \text{M}$ UA at a bare CPE (dashed line) and CTABMCPE (solid line) in presence of phosphate buffer of pH 7.4. At the bare electrode, the electrocatalytic oxidation of UA occurs at approximately 324mV and the voltammetric peak is rather broad, suggesting slow electron transfer kinetics, presumably due to the fouling of the electrode surface by the oxidation product. However at CTABMCPE the UA showed well defined redox peak with the oxidation peak potential at 296mV, which was negatively shifted by 28mV and reduction peak potential was at 234mV.

3.7. Simultaneous detection of dopamine uric acid and ascorbic acid at CTABMCPE

AA and UA are present along with DA in mammalian brain. The concentration of AA and UA is much higher than that of DA. Since the oxidation potential of AA and UA are nearly same as that of DA, at bare electrode which result in an overlapped voltammetric response. However the CTABMCPE has ability to separate the oxidation peak potentials of AA, DA and UA.

Fig .7 showed the cyclic voltgrams for solution containing mixture of both $1 \times 10^{-3} \text{M}$ AA and $1 \times 10^{-4} \text{M}$ DA and $0.5 \times 10^{-3} \text{M}$ UA in phosphate buffer solution of pH 7.4. The bare CPE (dashed line) showed only one broad and less sensible single anodic peak. The CTABMCPE was able to separate the oxidation peaks of AA, DA and UA by showing three anodic peaks and cathodic peaks (solid line) with strong enhancement. The peak to peak separation of DA-AA was 231mV and DA-UA was 103mV. These separations were large enough to identify DA, UA and AA peaks individually. Hence CTABMCPE can act as a good sensor for determination of important neurotransmitter.

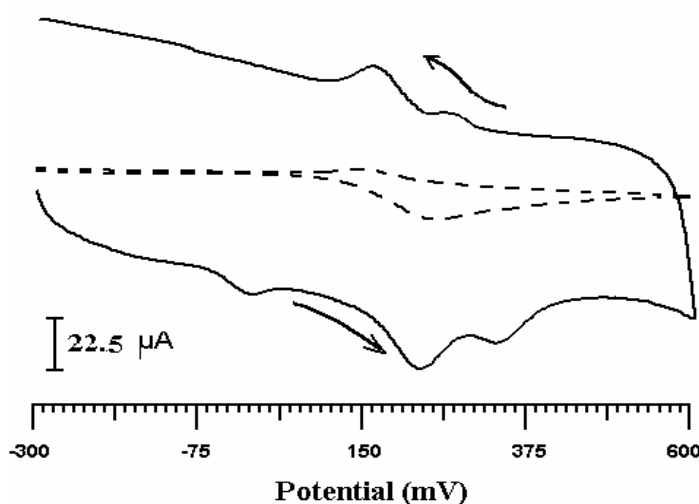


Figure 7. Cyclic voltammograms obtained at bare CPE (dashed line) and CTABMCPE (solid line) containing mixture of both $1 \times 10^{-3} \text{M}$ AA and $1 \times 10^{-4} \text{M}$ DA and $0.5 \times 10^{-3} \text{M}$ UA in 0.2M phosphate buffer solution of pH 7.4.

4. CONCLUSIONS

In this work CTAB, a cationic surfactant as a modifier to study the electrochemical response of an interesting neurotransmitter DA, CTABMCPE strongly enhanced both anodic and cathodic peak current of DA. The increase in the concentration of DA result in greater the enhancement of electrochemical oxidation at certain stage. Electrochemical process was found to be adsorption controlled and the results also indicated that the problem of the overlapped voltammetric responses of DA with AA and UA, due to their co-existence in real biological matrixes can be effectively overcome by use of CTABMCPE the modified electrode has a good selectivity, sensitivity and reproducibility. With its low cost and ease of preparation CTABMCPE will have good application for further sensor development.

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