Int. J. Electrochem. Sci., 3 **(2008)** 1044 - 1054

International Journal of ELECTROCHEMICAL SCIENCE
www.electrochemsci.org

Electrochemical Studies of Eriochrome Black T at Carbon Paste Electrode and Immobilized by SDS Surfactant: A Cyclic Voltammetric Study

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Received: 8 May 2008 / *Accepted:* 12 June 2008 / *Published:* 4 August 2008

Eriochrome Black T (EBT), one of the metallochromic indicators whose electrochemical behavior was studied at carbon paste electrode by cyclic voltammetry. The reduction of EBT was carried out in sulfuric acid as supporting electrolyte. Two reduction waves were observed for the reduction of –N=N- moiety in EBT between the potential ranges +100 mV to – 450 mV. The reduction mechanism was discussed on the basis of obtained voltammogram. The concentration effects of both EBT and sulfuric acid were studied. The adsorption behavior of sodium dodecyl sulfate (SDS) surfactant on a carbon paste electrode was investigated.

Keywords: Eriochrome black T, carbon paste electrode, cyclic voltammetry, surfactant, immobilization.

1. INTRODUCTION

Azo compounds are the largest class of organic dyes. These are the largest group of organic dyes for their widespread applications in many areas of dye-stuff industry, pharmacy and dosimetry due to the presence of azo (-N=N-) linkage [1–7]. Azo dyes have wide interest of application in complexometric titration [8] and in analytical chemistry [9]. The oxidation-reduction behaviour of these compounds plays an important role in biological system [10-11]. Various synthetic azo dyes have been shown to induce a variety of tumors in mice and rats and to exhibit inhibitory effects on the biosynthesis of RNA, DNA and proteins [12]. When orally administered, azo compounds are found to reduce, mainly in liver and intestine, to the corresponding amines [13].

Electrochemistry provides convenient methods for studying mechanisms and kinetics. It is well known that the reduction of aromatic azo compounds depends on the type and position of substituents on aromatic rings and often is accompanied by fast homogenous chemical reactions that yield corresponding amines [14, 15].

Few literatures are available based on the voltammetric study of metallochromic indicators. Metallochromic indicators are basically water-soluble used in complexometric titration. These are the ionochromic dye containing, C=C, C=N and N=N groups. These are containing arylazo groups, which can be reduced very easily. PAN [1-(2-pyridylazo)-2-napthol] has been used for the better selective and sensitive determination of Pb on PAN modified carbon electrode [16, 17]. PAN modified CPE used for trace cobalt (II) determination by differential pulse cathodic voltammetry [18]. Many electrochemical experiments have been done by electropolymerizing this EBT indicator and discussing their voltammetric behavior by modifying with electrodes. Hong Yao, et. al has detected the epinephrine selectively in the presence of ascorbic acid and uric acid by electrocatalytic oxidation and simultaneous determination of dopamine, ascorbic acid and uric acid by electropolymerizing the EBT on glassy carbon electrode [19, 20]. X. Lin et. al extend their knowledge for determination of noradrenalin in the presence of L-ascorbic and uric acids with poly (eriochrome black T)-modified electrode[21].

Surfactants are a kind of amphiphilic molecule with a polar head on one side and a long hydrophobic tail on the other. The applications of surfactants in electrochemistry and electro analytical chemistry have been widely reported [22]. Many of the studies of modified electrodes were undertake simply because electrochemists were curious about new species attached to electrode surface behave compared to these species in solution [23]. Some less soluble surfactants were employed in the immobilization of macro molecules or other functional materials, Wu et al [24] developed a stable multi-wall carbon nanotube (MWNT) modified electrode based on the immobilization of MWNT in the film of insoluble dihexadecyl phosphate (DHP) on a glassy carbon electrode. This electrode exhibited an electro catalytic activity towards biomolecules and has been used as a sensor for the determination of these species [25, 26].

In the present work, the electrochemical behaviour of EBT was studied at different concentrations of sulfuric acid media at carbon paste electrode using cyclic voltammetry. The reduction of EBT showed two reduction waves with irreversibility. From the obtained voltammogram the reduction mechanism was proposed and discussed.

2. EXPERIMENTAL PART

2.1. Reagents

Eriochrome Black T (EBT) was dissolved in dimethyl formamide (DMF) to prepare $25X10^{-3}$M stock solution. Sulfuric acid was used in different millimolar concentrations as supporting electrolyte. The SDS was dissolved in double distilled water to get $1X10^{-6}$M. Chemicals mentioned above were all purchased from Fluka and were analytical grade used without further purification.

2.2. Apparatus

The electrochemical experiments were carried out using a model-201 electroanalyser (EA-201 chemilink system). All the experiments were carried out in a conventional three electrochemical cell. The electrode system contained a working carbon paste electrode having home made cavity of 3mm diameter, a platinum wire as counter electrode and saturated calomel electrode as reference electrode.

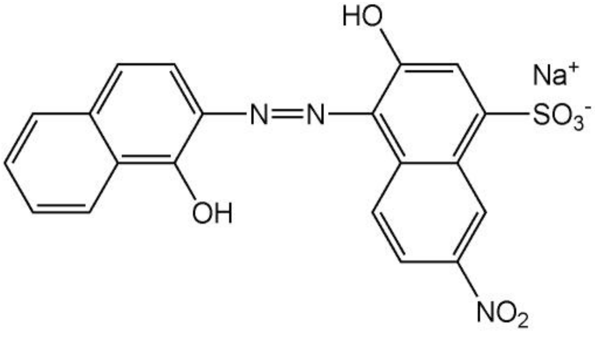
2.3. Preparation of carbon paste electrode

Carbon paste was prepared by grinding the 70% graphite powder and 30% silicon oil in an agate mortar by hand mixing for about 30 minute to get homogenous bare CPE. The paste was packed into the cavity of home made carbon paste electrode and smoothened on weighing paper. The surfactant immobilized carbon paste electrode was prepared by drying the known quantity of surfactant on the bare carbon paste electrode surface.

3. RESULTS AND DISCUSSION

3.1. Irreversible electrochemical character of EBT at CPE

EBT is a metallochromic indicator widely used in complexometric titration. It is an electroactive species with an azo group (-N=N-) in its molecular structure shown in (scheme 1). This azo group is easily reduced on carbon paste electrode by cyclic voltammetry. Cyclic voltammogram of $2X10^{-3}$M EBT was recorded in $80X10^{-3}$M sulfuric acid media as shown Fig. 1. The irreversibility was confirmed by the absence of anodic peak in voltammogram between the potential of +100 mV to – 450 mV. The voltammogram of EBT showed two reductive peaks were found at –68 mV/s (E_{Pc1}) and at – 275 mV/s (E_{Pc2}) potentials. The EBT reduced in the two-step one-electron reduction of the azo group, which is similar with the literature [27]. The reduction mechanism of EBT was illustrated as below (scheme 2). The multiple cycle was applied, which results in greatly decrease in reductive peak current with the increase of scanning cycle. This was the characteristic of the strong adsorption behavior of EBT on carbon paste electrode



Scheme 1. Structure of EBT.

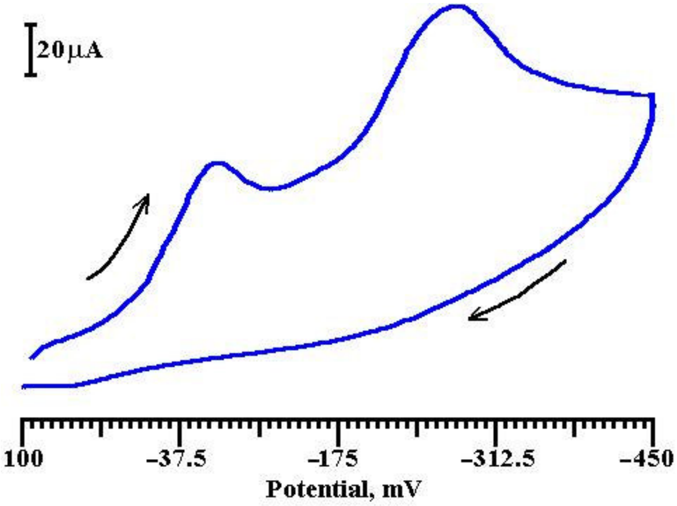
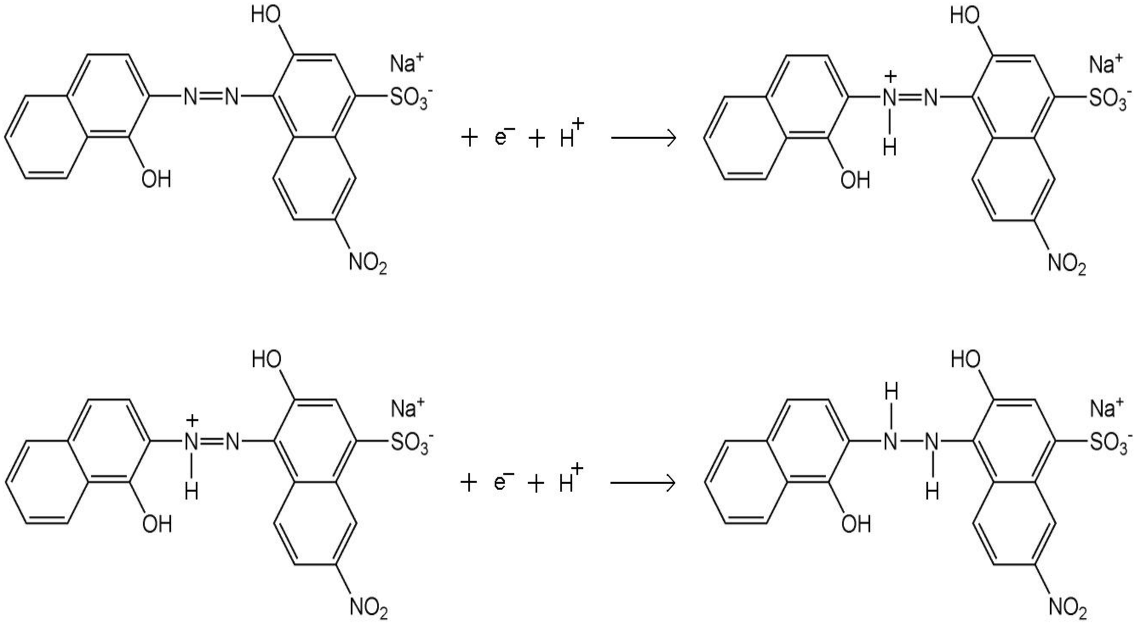


Figure 1. Cyclic voltammogram of $2X10^{-3}M$ EBT in $80X10^{-3}M$ sulfuric acid.



Scheme 2. Reduction mechanism of EBT

3.2. Effect of Scan Rate

Effect of scan rate was studied by placing $2X10^{-3}M$ stock solution and $80X10^{-3}M$ sulfuric acid media in an electrochemical cell. Cyclic voltammetric behavior of the EBT was studied by varying the sweep rate from $25mVs^{-1}$ to 150 mVs^{-1} (Fig. 2a). In Fig.2b the i_{pc1} and i_{pc2} was found to increase linearly with the square root of sweep rate ($\nu^{1/2}$) and the current function values ($i_p/\nu^{1/2}$) are found to be constant. These observations suggest that the process was diffusion controlled [28]. Peak potential E_{pc} was found to shift in the cathodic direction with increase in sweep rate indicating the irreversible nature of the electrode reaction [29-31].

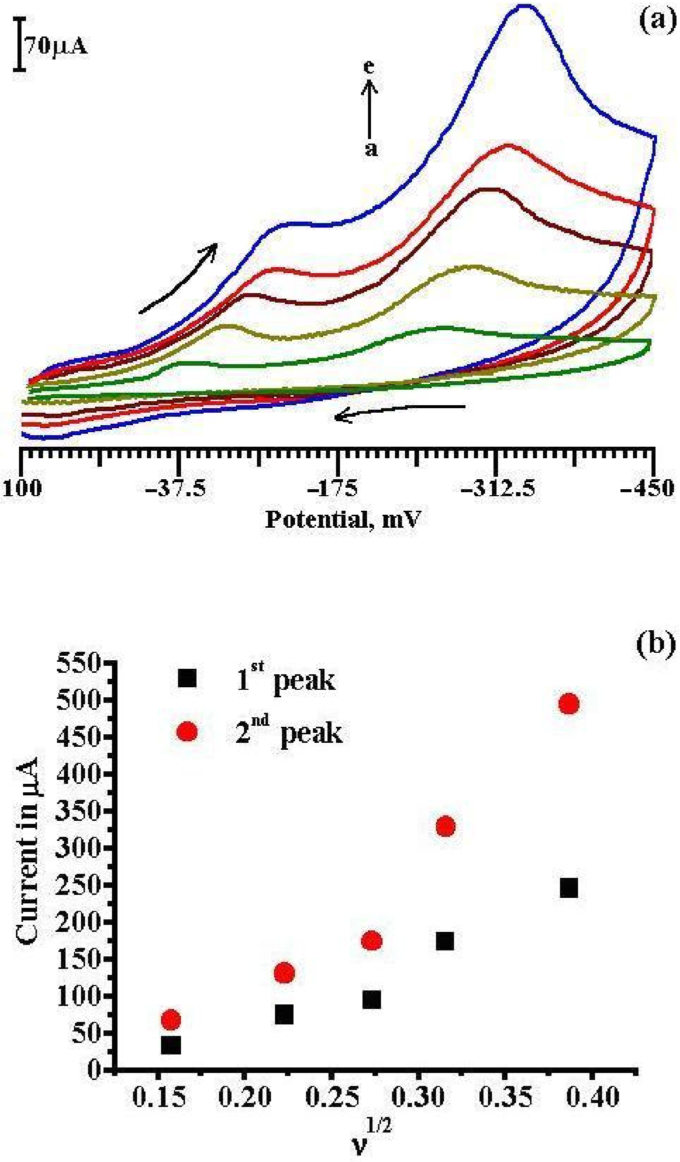


Figure 2. a) Cyclic voltammogram of different scan rate (a-e; 25mV/s, 50mV/s, 75mV/s, 100mV/s and 150mV/s). b) Graph of current vs. square root of scan rate.

The electrochemical parameters can be calculated for the reduction mechanism of EBT in sulfuric acidic media. Because of strong adsorption behavior and irreversible electrode reduction process of EBT, the following Laviron's equation [32-35] may be used to calculate the electrochemical parameter on the carbon paste electrode.

$$E_p = E^0 + RT/(\alpha nF)\ \{ln[(RT\ k_s)/(\alpha nF)] - ln\nu\}$$

Where, α – the charge transfer co-efficient, n – the number of electron transferred, k_s – the electron transfer rate constant, ν – the scan rate, E^0 – the formal potential and F – Faraday constant.

The graph of E_p vs. $\ln\nu$ is linear, then the αn value can be calculated from its slope and k_s from the intercept. The E^0 value can be deduced from the intercept of E_p vs. ν plot on the ordinate by extrapolating the line to $\nu = 0$. The electrochemical parameters of EBT were calculated for different concentration of sulfuric acid from the above equation based on this method (Table.1).

Table 1. The electrochemical parameters of EBT for different concentration of sulfuric acid

Concentration of Sulfuric Acid (10^{-3}M)	$E_{pc\,2}$ mV	I_{pc2} µA	E^0 mV	αn_a	k^0 cm s^{-1}
80	278	130.7	173	0.326	0.0123
120	272	135	166	0.361	0.0085
160	270	146	160	0.394	0.0069
200	160	173	152	0.454	0.0065

3.3. Effect of concentration of sulfuric acid

As the concentration of sulphuric acid increased from 80mM to 200mM (Fig.3a), the cathodic peak potentials of two peaks were positively shifted thereby showing the involvement of proton in the reduction process [30, 31]. The standard heterogeneous rate constant values are calculated and found to decrease with increase in concentration of sulphuric acid indicating that the reduction process becomes easier at higher concentration of sulphuric acid (Table 1). Multicycle voltammograms indicate that the EBT got adsorbed on the surface of the electrode during the reduction process. This conclusion is supported by linear nature of i_{Pc} versus $\nu^{1/2}$ plots [36]. The graph of current vs concentration of sulfuric acid was also plotted (Fig. 3b) showing linear increase in current.

3.4. Effect of concentration of Eriochrome Black T

As the concentration of EBT was varied from $2X10^{-3}$M to $7X10^{-3}$M and cyclic voltammograms were recorded (Fig. 4a). The cathodic peak currents i_{pc1} and i_{pc2} obtained were found to increase linearly with increase in concentration of the EBT (Fig. 4b). It was also observed that the cathodic peak potentials (E_{pc}) and half peak potentials ($E_{p/2}$) were shifted towards more negative values. This kind of shift in E_{pc1} and E_{pc2} in cathodic direction with concentration of the EBT has indicated that product of EBT molecules are adsorbed over the electrode surface [37]. Such effects on CV behavior have been predicted theoretically [38, 39] and also observed experimentally for other reactions [40, 41].

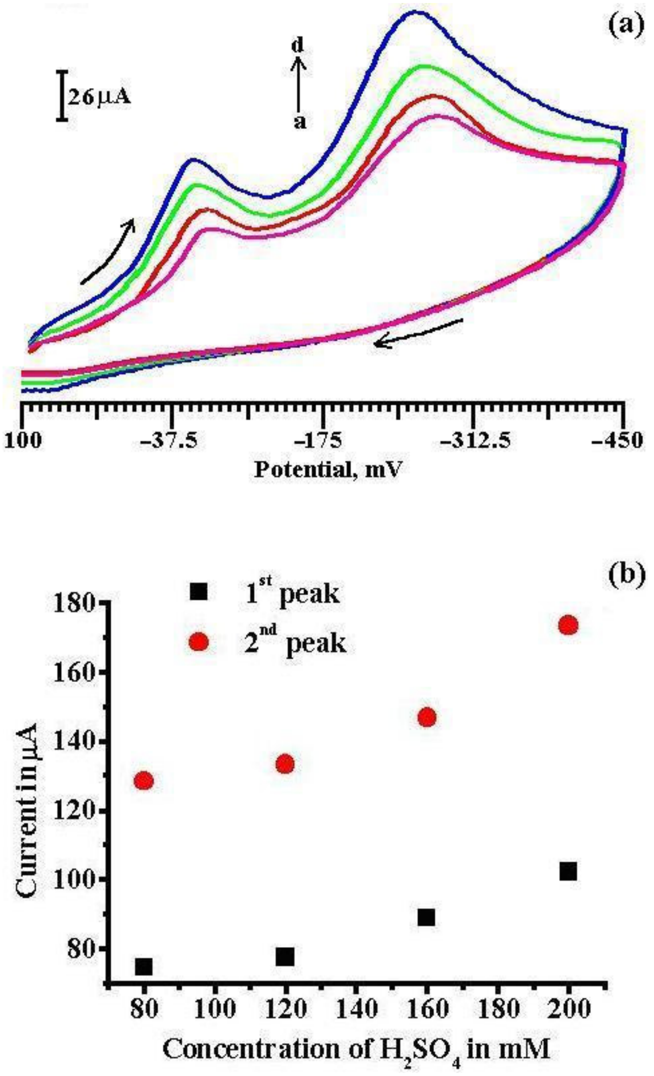


Figure 3. a) Cyclic voltammogram for the different concentration of sulfuric acid (a-d; $80X10^{-3}$M, $120X10^{-3}$M, $160X10^{-3}$M and $200X10^{-3}$M). b) Graph of current vs. sulfuric acid concentration

3.5. Effect of SDS surfactant

The electrochemical responses of EBT at carbon paste electrode were shown in Fig.5 with 80 mM sulphuric acid as supporting electrolyte with 50 mV/s scan rate owing to the complex properties and the roughness of the electrode surface, the cyclic voltammogram of EBT in the absence of SDS is low signal (Fig.5a). However, the voltammetric response is apparently improved in the presence of 2 μL SDS, reflected by the enlargement of cathodic peak currents (i_{pc}) (Fig.5b). The probable mechanism is the SDS surfactant molecule diffuses in to the carbon paste electrode along with the

EBT results increase in the signal. The dependence of the reduction peak current (i_{pc}) as well as peak current function ($i_p/ACv^{1/2}$) on the scan rate showed (v) were studied in the range 50-300 mV/s. A linear relation ship was observed between log i_p and log$v$, $i_p/v^{1/2}$ vs. log v and also peak potential (E_{pc}) vs logarithm of scan rate was linear with a correlation coefficient of 0.991 and this behavior was consistent with the EC nature of the reaction. [42 - 45]. The electrochemical response of EBT in the presence of SDS could be utilized to investigate the adsorptive behavior of SDS at a carbon paste electrode, which might be able to explain the enhancement effects of surfactants in some electro analytical systems.

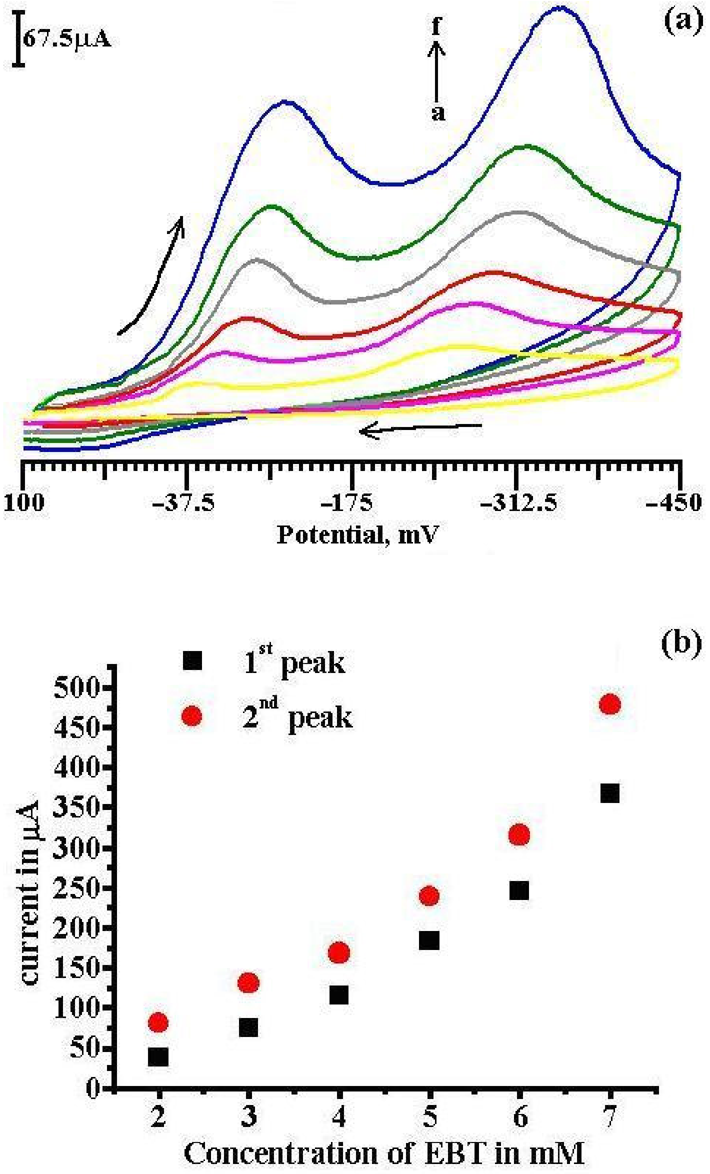


Figure 4. a) Cyclic voltammogram for the different concentration of EBT (a-f; 2 X10^{-3}M, 3 X10^{-3}M, 4 X10^{-3}M, 5 X10^{-3}M, 6 X10^{-3}M and 7 X10^{-3}M). b)Graph of current vs. EBT concentration

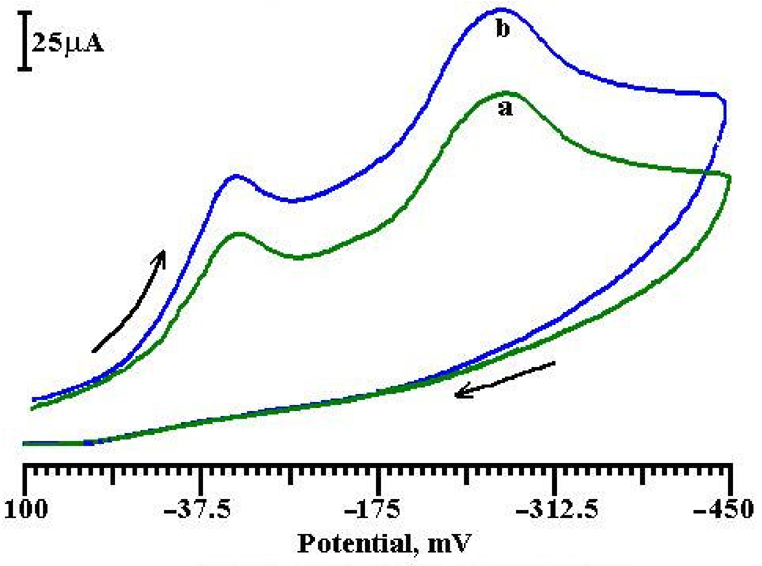


Figure 5. Cyclic voltammogram for the comparison of bare CPE and surfactant immobilized CPEs.

4. CONCLUSIONS

The electrochemical behaviour of Eriochrome Black T was studied at carbon paste electrode by cyclic voltammetry. The EBT showed irreversible two-step one electron –N=N- moiety reduction mechanism. The electrochemical process is diffusion controlled and reduction peak potentials decreases with increase in concentration of sulfuric acid. The increase in the concentration of the EBT showed enhancement in peak current with negative shifting of reduction peak potentials. The SDS immobilized carbon paste electrode improved the sensitivity of electrode and act as a good sensor up to 2 μL.

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