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Cyclic Voltammetric Investigations of Alizarin at Carbon Paste Electrode using Surfactants

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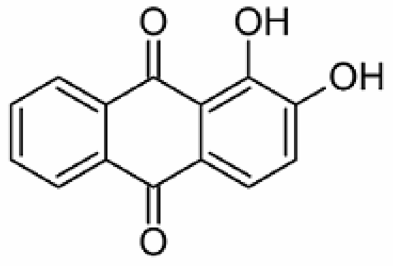
Electrochemical behavior of alizarin was investigated at carbon paste electrode in 0.2 M acetate buffer solution at pH 3.5 by using cyclic voltammetric technique (CV). Alizarin showed one oxidation peak and two reduction peak between potential range 0 to 1000 mV at scan rate of 50mV/s. The effect of scan rate and concentration was found to be diffusion-controlled electrode process. The electrocatalytic effect of alizarin was dependent on pH. Surfactants effect study showed that the TX-100, a non ionic surfactant has highest electrocatalytic activity towards alizarin.

Keywords: Alizarin, electrocatalytic effect, carbon paste electrode, cyclic voltammetry, TX-100.

1. INTRODUCTION

Alizarin is an orange-red compound having molecular formula $C_{14}H_8O_4$. The compound is a derivative of anthraquinone, with hydroxyl groups substituted at the 1 and 2 positions (Scheme. 1). It is an important dyestuff producing red or violet lakes with metal hydroxide. Alizarin occurs naturally as the glucoside in madder plant (Rubia tinctorum). It comes under mordant vegetable dye, as the name suggests that these dyes require a mordant. This improves the fastness of the dye on the fibre such as water, light and perspiration fastness. The choice of mordant is very important as different mordants can change the final colour significantly. Alizarin is a histochemical stain that highlights calcium. It is used by dermatopathologists to detect dermal calcium in disorders such as pseudoxanthoma elasticum and calcinosis cutis. Alizarin red is used in a biochemical assay to determine, quantitatively by colorimetry, the presence of calcific deposition by cells of an osteogenic lineage. As such it is an early stage marker (days 10-16 of *in vitro* culture) of matrix mineralisation, a crucial step towards the formation of calcified extracellular matrix associated with true bone. In clinical practice it is also used to stain synovial fluid to assess for basic calcium phosphate crystals.



Scheme 1. Structure of Alizarin.

Some metals such as zirconium (IV) has been determined by complexing with alizarin red (ARS) [1-4]. The corrosion inhibition of mild steel using alizarin yellow GG in the presence of iodide ions was studied by E.E. Ebenso group [5]. H.E. Zittel group has studied the zirconium alizarin red S complex by using voltammetry and spectrophotometry methods [6]. Alizarin is used as a mediator on glassy carbon electrode to investigate the electrochemical behaviors of hydrazine [7]. Some of the proteins like lysozyme are determined complexed with alizarin red s using linear sweep voltammetric studies [8]. Alizarin red s was used to modify graphite electrode to determine the ultra trace copper adsorptive stripping voltammetry [9]. The adsorption of alizarin on silica surface was discussed by O.A. Zaporozhets group [10].

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 electroanalytical chemistry have been widely reported [11-15]. 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 [16]. Some less soluble surfactants were employed in the immobilization of macro molecules or other functional materials. Wu et al [17] 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 [18, 19]. The cetyl trimethyl ammonium bromide, a cationic surfactant was immobilized on carbon paste electrode for simultaneous determination of dopamine with ascorbic acid and uric acid by our group [20].

In the present work, the electrochemical behavior of alizarin was studied in 0.2M acetate buffer at pH 3.5 at carbon paste electrode using cyclic voltammetry. The cyclic voltammogram of alizarin showed one oxidation peak for two hydroxyl groups and two reduction peaks for four keto groups. From the obtained voltammogram the redox mechanism was proposed and discussed.

2. EXPERIMENTAL PART

2.1. Reagents

Alizarin (AZ) was dissolved in dimethyl formamide (DMF) to prepare $10X10^{-3}$M stock solution. Acetate buffer was used as supporting electrolyte. The TX-100 surfactant was dissolved in double distilled water to get $1X10^{-5}$M. Chemicals mentioned above were all purchased from Himedia and were analytical grade used without further purification. The water used in all measurements was double distilled water. Graphite powder of 50mm particle size was purchased from Loba Chemie and silicon oil from Himedia were used to prepare carbon paste electrode.

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 to the surface of the bare carbon paste electrode surface.

3. RESULTS AND DISCUSSION

3.1. Electrochemical behavior of Alizarin at CPE

AZ is an anthraquinone derivative, with hydroxyl groups substituted at the 1 and 2 positions. These hydroxyl groups easily oxidized on carbon paste electrode by cyclic voltammetry. Cyclic voltammograms of AZ were recorded in both dimethyl formamide (DMF) (solid line) and dimethyl sulfoxide (DMSO) (dashed line) for comparing the solvent effect (Fig.1a). The result showed, AZ in DMF media has high current signal compared to AZ in DMSO. Cyclic voltammogram of $1X10^{-3}$M AZ was recorded in DMF with acetate buffer solution at pH 3.5 as shown in Fig. 1b. The obtained voltammogram showed one oxidation peak and two reduction peaks at scan rate of 50 mV/s. The oxidation peak potential was occurred at 739mV. The reduction peak (1) potential and peak (2) potential were occurred at 619mV and 184mV respectively. The redox mechanism of AZ was explained in the scheme. 2. The AZ (I) undergo oxidation of two hydroxyl groups by giving anthracene-1,2,9,10-tetrone compound (II) in forward scan in equation (1). While in reverse scan the compound (II) undergo reduction by giving two cathodic peaks [(III) and (IV)] for reduction of four keto groups by step wise [Equation (2)]. The reduced compound (III) was same as AZ and this could be an intermediate compound. The final reduced compound (IV) was 9,10-dihydroanthracene-1,2,9,10-tetrol.

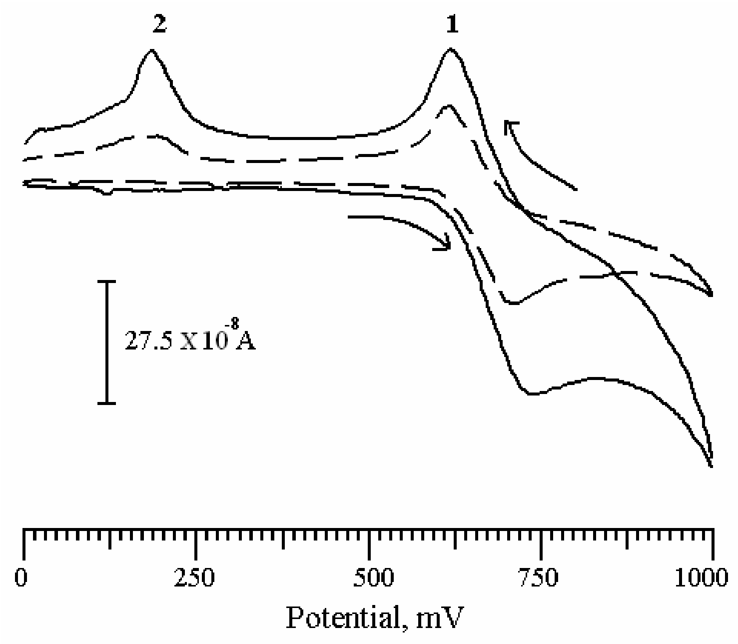


Figure 1a. Cyclic voltammograms of 1X10^{-3}M AZ at carbon paste electrode in DMF (solid line) and in DMSO (dashed line) with 0.2M acetate buffer solution (pH 3.5) at scan rate 50mV/s.

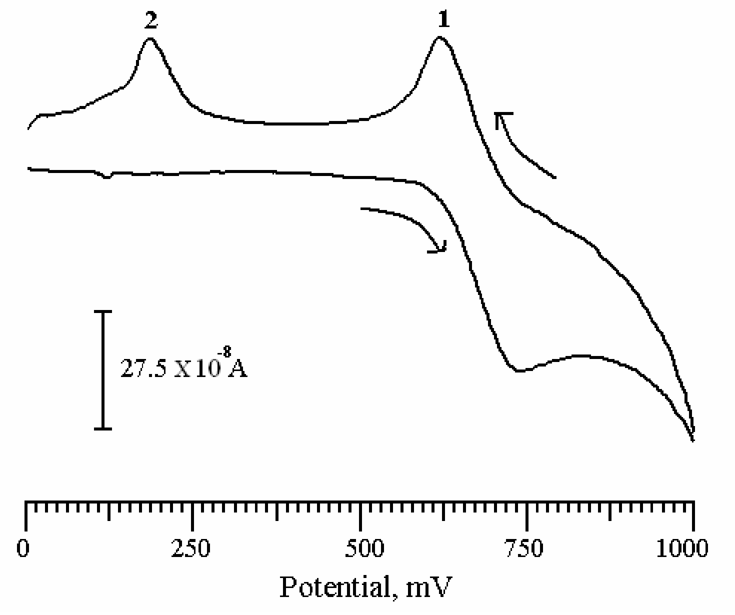
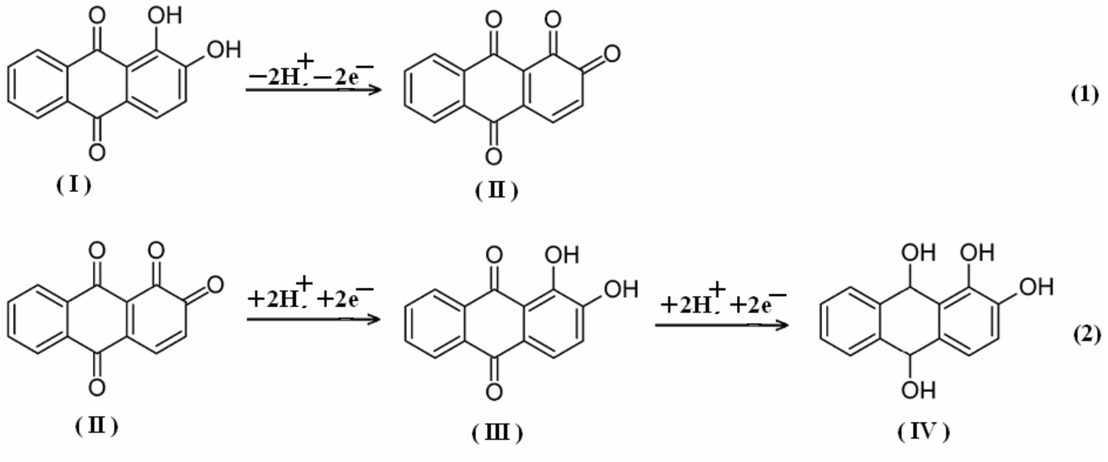


Figure 1b. Cyclic voltammogram of 1X10^{-3}M AZ at carbon paste electrode in DMF with 0.2M acetate buffer solution (pH 3.5) at scan rate 50mV/s.



Scheme 2. Redox mechanism of Alizarin.

3.2. *Effect of Scan Rate*

Effect of scan rate was studied by placing 1X10^{-3}M stock solution and acetate buffer at pH 3.5 in an electrochemical cell. Cyclic voltammetric behavior of the AZ was studied by varying the sweep rate from 50mVs^{-1} to 110mVs^{-1} . In Fig.2 both anodic and cathodic peak currents were proportional with the square root of sweep rate ($\nu^{1/2}$) with correlation coefficient 0.9974. The plot shows anodic peak current is linear with $\nu^{1/2.}$ .These observations suggest that the process was diffusion-controlled.

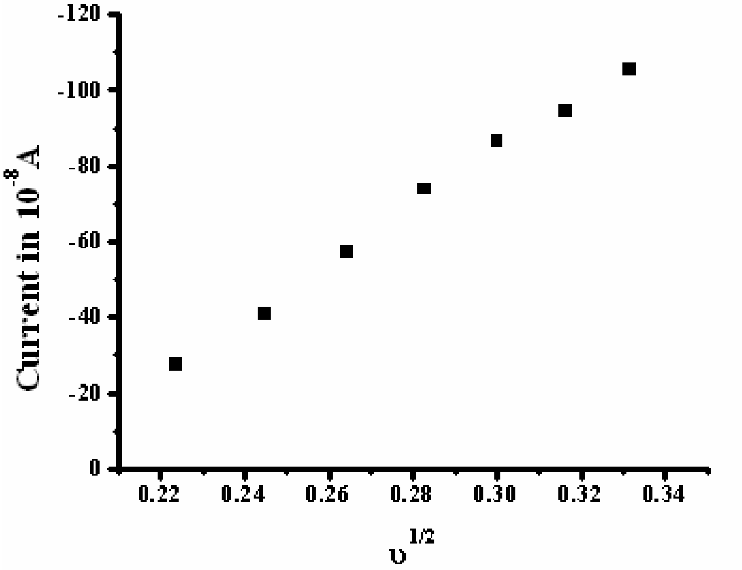


Figure 2. Graph of Ipa vs. square root of scan rate

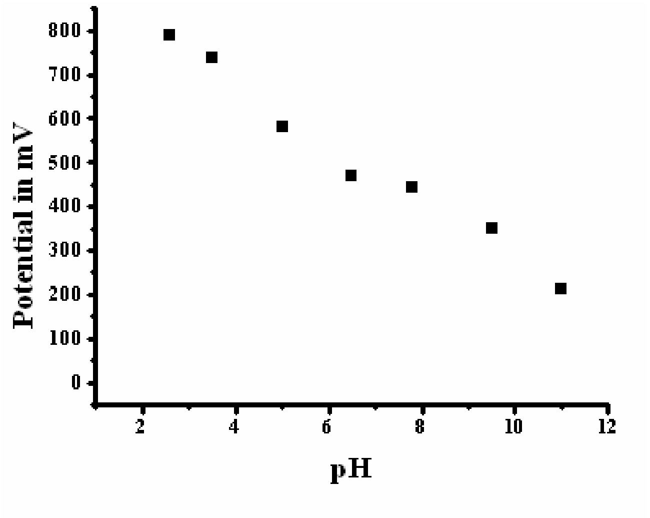


Figure 3. Graph of Epa vs. different pH

3.3 Effect of pH

The pH effect was studied by varying the pH range from 2.6 to 11.0 using 0.2M acetate buffer solution as a supporting electrolyte at a sweep rate of 50mV/s. This study results that the redox peak potentials of AZ was depended on pH. The two cathodic peaks and one anodic peak were shifted towards negative direction from the pH range 2.6 to 11.0. The reduction peaks (1) and (2) were appeared strongly between at pH 2.6 to 5.0, diminished at pH 6.5 and disappeared from 7.8 to 11.0 pH. This is due to the above neutral pH, the oxidized AZ compound suffer difficult to reduce again. The graph of Epa vs pH showed the linear relation between Epa and pH as shown in Fig.3. The slope was obtained from the graph was 65.9, which was confirms the involvement of both proton and electron ratio was 1:1.The well defined redox peaks were obtained at pH 3.5 and hence this pH taken as optimum for complete investigation.

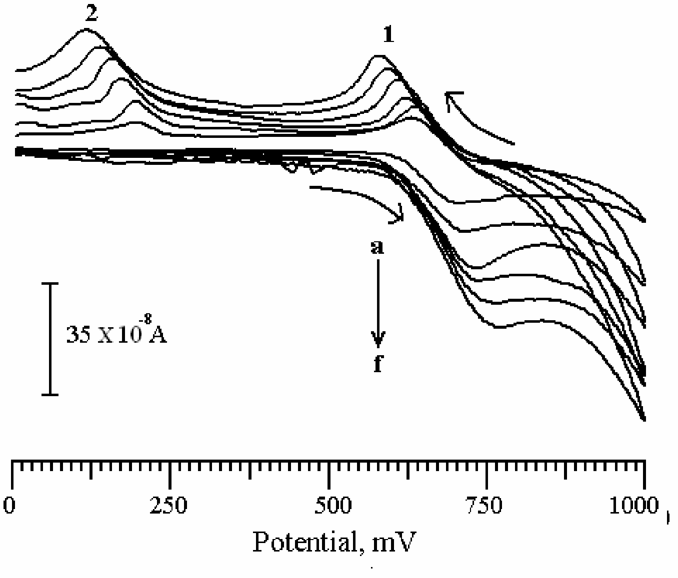


Figure 4a. Cyclic voltammogram of AZ at different concentration (a-f; 0.5X10^{-3}M, 1X10^{-3}M, 1.5X10^{-3}M, 2X10^{-3}M, 2.5X10^{-3}M and 3X10^{-3}M).

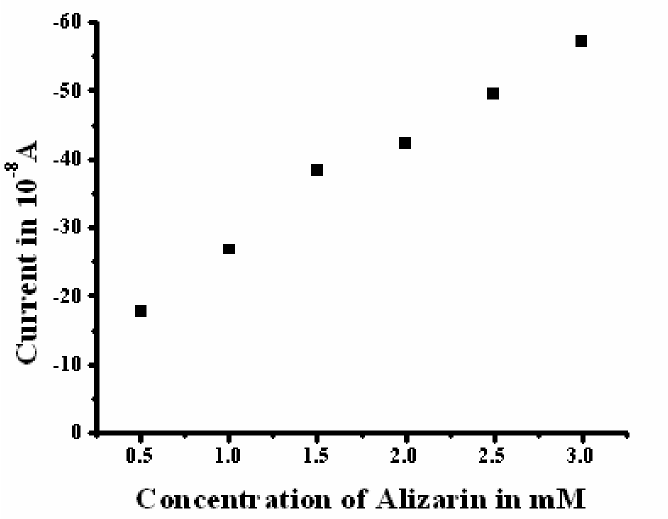


Figure 4b. Graph of Ipa vs. different concentration of AZ

3.4. Effect of concentration of Alizarin

The concentration of AZ was varied from 0.5X10^{-3}M to 3.0X10^{-3}M and corresponding cyclic voltammograms were recorded (Fig. 4a). The one anodic peak currents and two cathodic peaks obtained were found to increase with increase in concentration of the AZ. The graph the Ipa vs concentration was plotted and result showed the linear dependence of anodic peak current with the concentration of AZ (Fig. 4b).

3.5. Effect of TX-100 surfactant

Surfactants are having a polar head on one side and a long hydrophobic tail on the other. In this work, the three types of surfactants viz [sodium dodecyl sulphate (SDS) (anionic), cetyl trimethyl ammonium bromide (CTAB) (cationic) and Triton x-100 (non ionic)] were used as both mobilized and immobilized method to check the electrocatalytic effect of AZ. Among theses the Triton X-100 (TX-100) was showed excellent electrocatalytic activity in both methods for investigation of AZ (Fig.5a). The trace amount of TX-100 i.e. 20µL was immobilized on the carbon paste electrode was enhanced both anodic and cathodic peak current signals (Fig.5b). The TX-100 could increase the polarity on the surface of carbon paste electrode, which results in the enhancement of current signals. The concentration of TX-100 was varied from 5µL to 20µL for immobilization. The graph of Ipa vs concentration of TX-100 was shown in Fig. 5c is the range from 5µL to 20µL. The TX-100 in mobilization method also enhanced the current signals of AZ. This result was compared with SDS and CTAB surfactant (Fig.6a). The current signals of both anodic and cathodic peaks of AZ were improved in the presence of 7µL of TX-100 when compared with bare carbon paste electrode (Fig. 6b). The concentration of TX-100 was varied from 1µL to 7µL. The graph of Ipa vs concentration showed the current signal was increased linearly with increase in concentration of surfactant (Fig.6c).

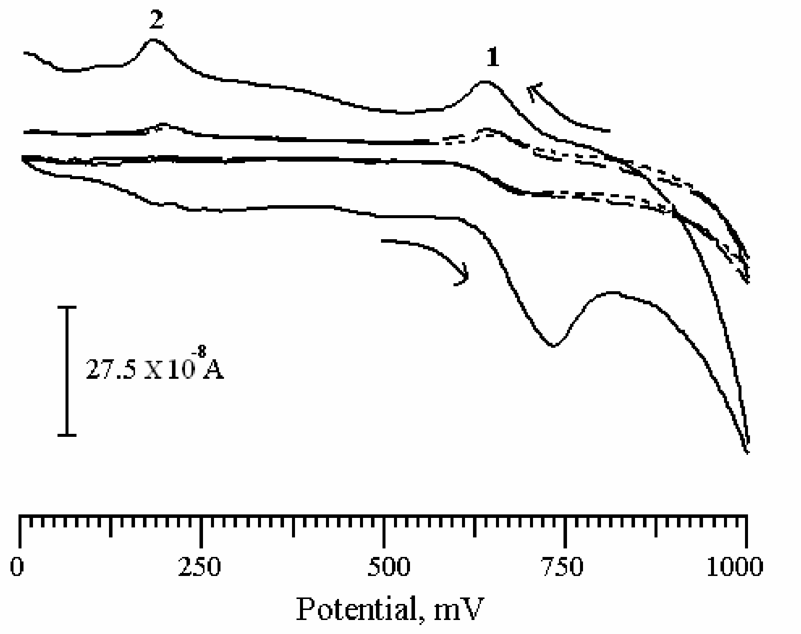


Figure 5a. Cyclic voltammogram of 1X10^{-3}M AZ at a) 10µL SDS (dotted line) b) 10µL CTAB (dashed line) c) 10µL TX-100 (solid line) immobilized carbon paste electrode in 0.2M acetate buffer solution (pH 3.5) at scan rate 50mV/s.

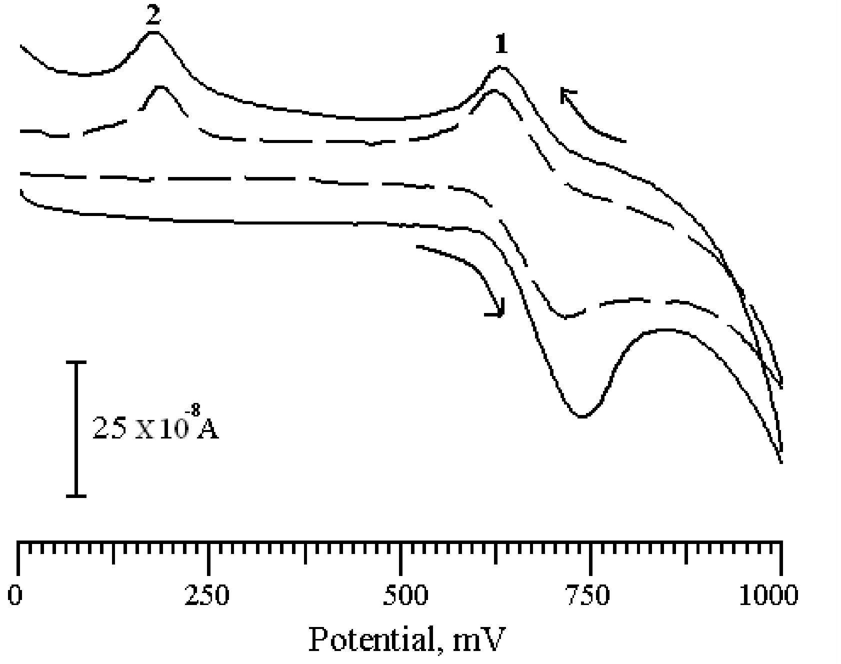


Figure 5b. Cyclic voltammogram of 1X10^{-3}M AZ at a) bare (dashed line) b) TX-100 immoblised carbon paste electrode (solid line) in DMF with 0.2M acetate buffer solution (pH 3.5) at scan rate 50mV/s.

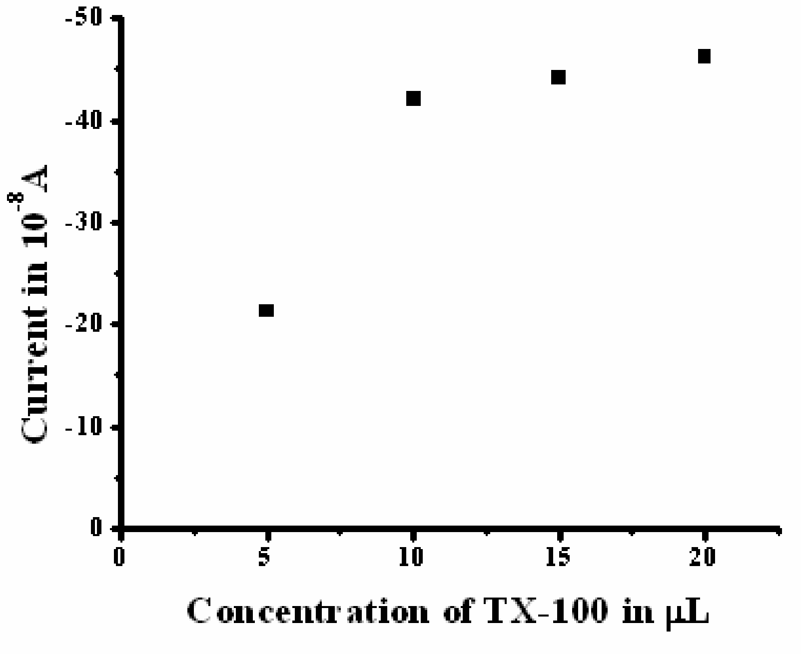


Figure 5c. Graph of Ipa vs. different concentration of TX-100 on to the surface of carbon paste electrode.

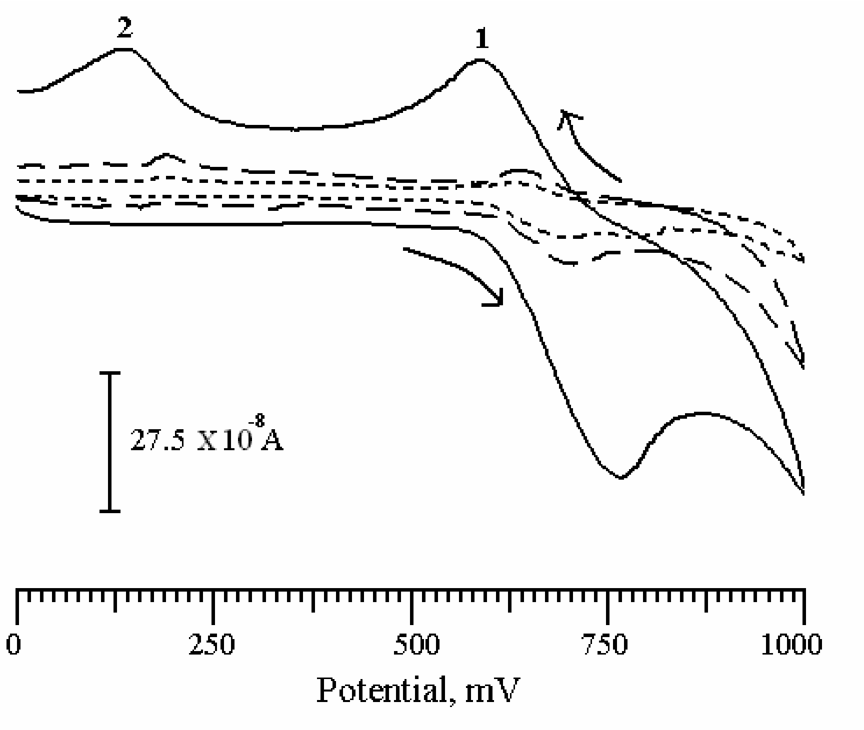


Figure 6a. Cyclic voltammogram of $1X10^{-3}$M AZ a) 1µL SDS (dotted line) b) 1µL CTAB (dashed line) c) 1µL TX-100 (solid line) mobilized at carbon paste electrode in 0.2M acetate buffer solution (pH 3.5) at scan rate 50mV/s.

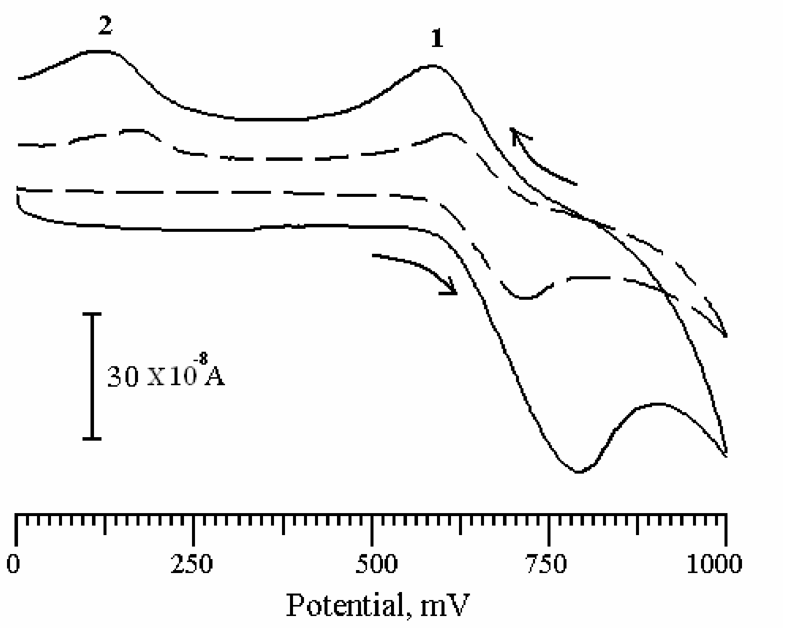


Figure 6b. Cyclic voltammogram of 1X10^{-3}M AZ at a) absence (dashed line) b) presence (solid line) of TX-100 at carbon paste electrode in DMF with 0.2M acetate buffer solution (pH 3.5) at scan rate 50mV/s.

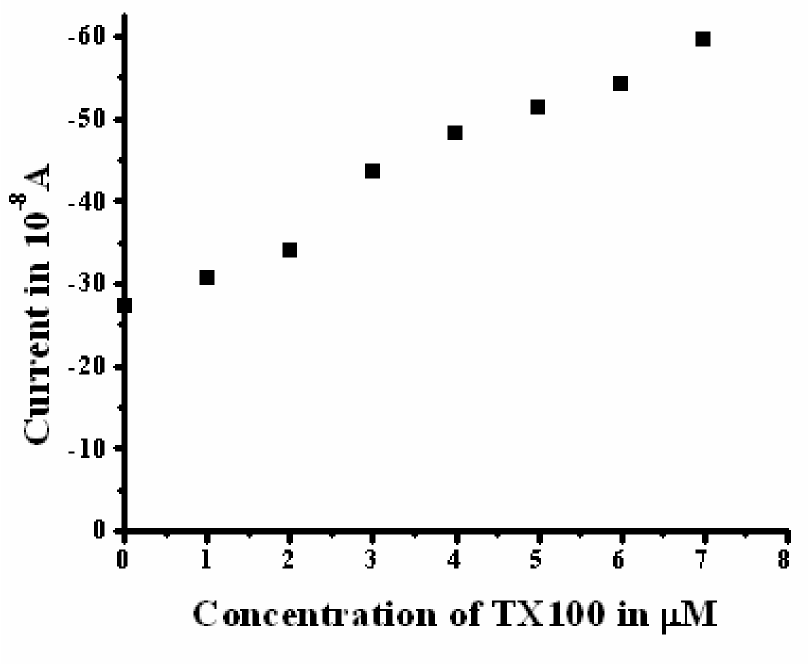


Figure 6c. Graph of Ipa vs. different concentration of TX-100 into the solution.

4. CONCLUSIONS

Alizarin is a derivative of anthraquinone showed one anodic peak and two cathodic peaks at carbon paste electrode by using cyclic voltammetric technique. The electrode process was found to be diffusion controlled. The concentration and pH effect was linear. The TX-100 surfactant was showed good electrocatalytic property towards the investigation of alizarin. Hence TX-100 acting as good sensor and can be applicable for further electrochemical investigation of different compounds.

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