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Cyclic Voltammetric Studies of Sulphanilic Acid on Platinum Electrode

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Abstract:
Sulphanilic acid (4-amino benzene sulphonic acid) is a commercially very important aromatic compound. The literature revealed that the chemical and physical properties of sulphanilic acid had been explored much. In the present study cyclic voltammetric studies of sulphanilic acid is concentrated. The working electrodes used were platinum and glassy carbon. To visualize the influence of pH on the anodic oxidation of sulphanilic acid cyclic voltammograms were recorded in acidic, neutral and alkaline conditions. Scan rate variation studies and multiple scan studies were also done. From these studies it found that sulphanilic acid is susceptible for anodic oxidation and the process is diffusion controlled on platinum electrode and is not forming any polymer on the electrode surface.
Key words: Cyclic voltammetry, Anodic oxidation, Sulphanilic acid, Platinum electrode, Electro analysis, Electrode process

INTRODUCTION

Sulphanilic acid is an aromatic compound of industrial importance. It finds its usage in the synthesis of diazo compounds and sulpha drugs.[1] It is also used in the qualitative analysis of nitrite and nitrate. The literature on sulphanilic acid is very much scattered and is found to have exhaustive study on the physical and chemical properties of sulphanilic acid, but a very little work has been done on the electrochemical analysis of sulphanilic acid. The electrochemical conversion of organic compounds is appearing to be an attractive alternative to chemical oxidation or reduction which needs reagents and byproduct elimination.[2] Cyclic voltammetry is a technique which is frequently used to study the electrochemical behavior of compounds. It consists of measuring the current resulting from an applied potential wave form.[3] The potential is cycled within a given potential range at a constant rate and the current is measured as a function of the potential. The scan rate can be varied. The potential at which oxidation or reduction of the substrate takes place, arising of a current is observed which is due to the depletion of the species in the vicinity of the electrode surface. Actually the current starts rising as the potential enters the area where oxidation or reduction occurs. In the present work cyclic voltammograms were recorded using platinum and glassy carbon electrodes as working electrodes, Ag/AgCl electrode as reference electrode and platinum electrode as counter electrode. The cyclic voltammograms of sulphanilic acid was carried out in a solution containing $1X10^{-3}M$ sulphanilic acid, 0.5M ethanol and 1M $H_2SO_4/KCl/KOH$. H_2SO_4, KCl and KOH were used as supporting electrolytes and also used to change the pH of the medium. In the present work anodic peak potential was found out in different pH conditions and on different working electrodes. The scan rate was varied to find out whether the oxidation of the substrate taken is diffusion controlled or adsorption controlled. For assertion of polymer formation on the electrode surfaces, multiple scans study was also done.

MATERIALS AND METHODS

Apparatus

Voltammograms were recorded using VersaSTAT 3 (Princeton Applied Research, USA) interfaced with a computer. Three electrodes system containing a working electrode of platinum or glassy carbon, a reference electrode of Ag/AgCl electrode and a counter electrode of platinum foil of dimension 1cm X 2 cm was used. The working electrodes and the counter electrode were pretreated by polishing them with alumina-water slurry followed by washing in an ultrasonic bath.

Reagents and solution

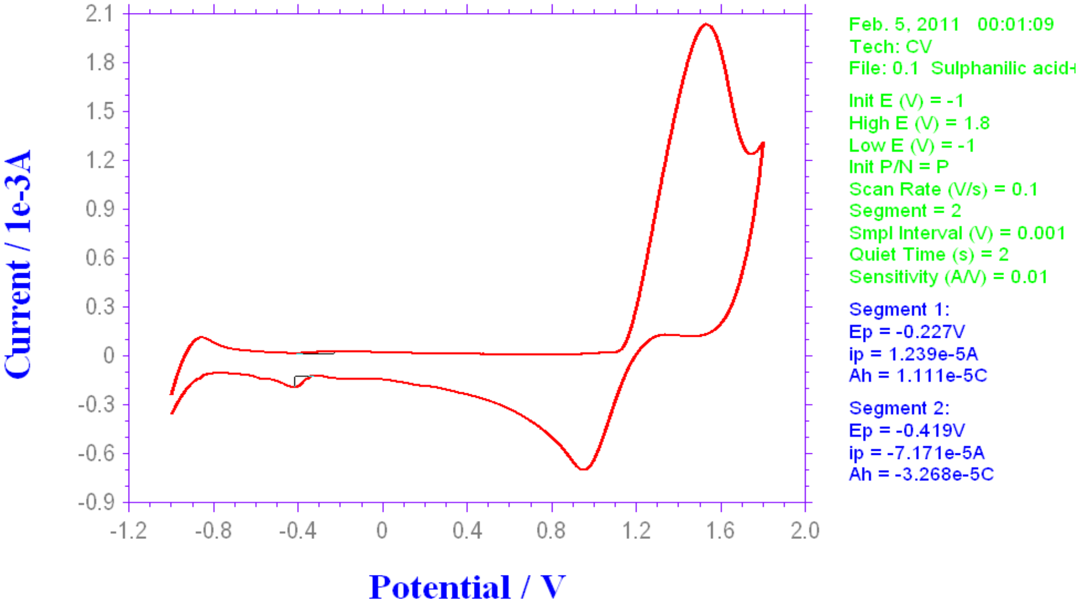
All the chemicals used were of analytical reagent grade. Double distilled water was used to prepare solutions. 0.001M sulphanilic acid, 0.5M ethanol and 1M $H_2SO_4/KCl/KOH$ were prepared freshly. A pen type pH meter was used to find the pH of the reaction mixture. The solutions were stored in a light tight and cool location.

Methodology

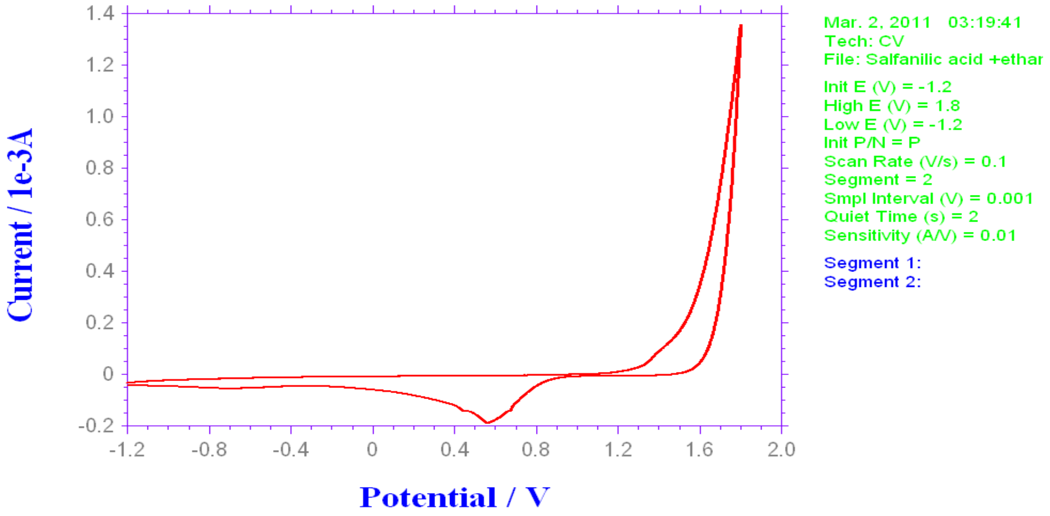
The three electrode system was constructed with platinum/glassy carbon working electrode, platinum counter electrode and Ag/AgCl reference electrode in a beaker type undivided cell. To change the pH of the reaction mixture 1M solution of H_2SO_4/KCl/KOH was added. These solutions also worked as sources of supporting electrolytes. Then the cyclic voltammograms were recorded at different working electrodes, with different pH conditions and with different scan rates.

RESULTS AND DISCUSSION

Cyclic voltammogram on platinum electrodes:

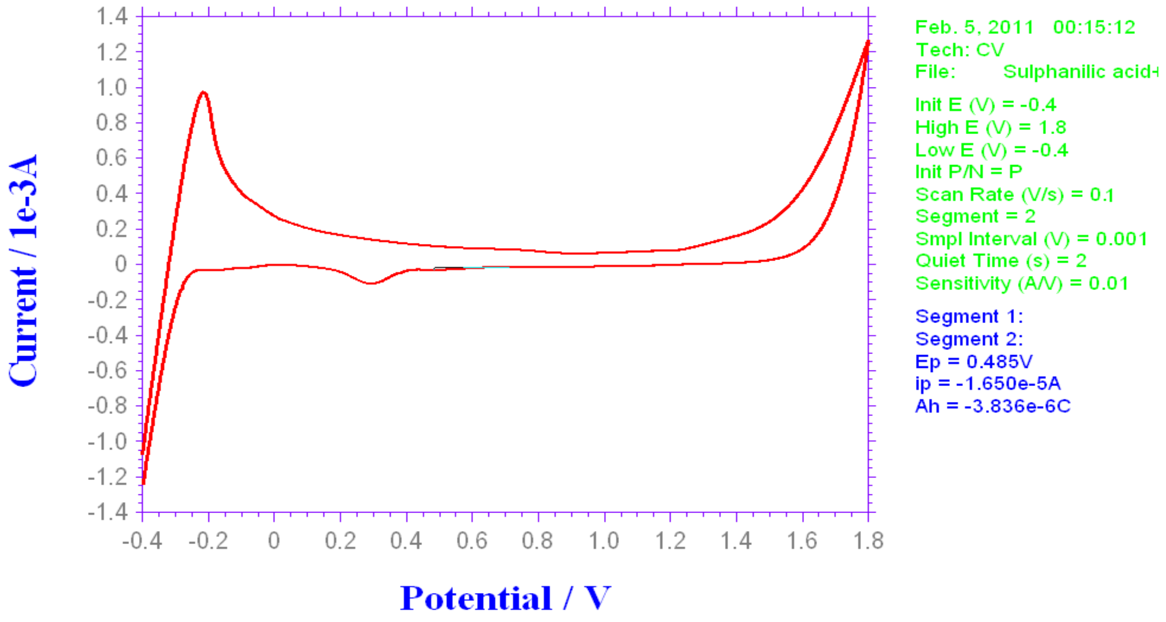


Cyclic voltammogram on glassy carbon electrodes:

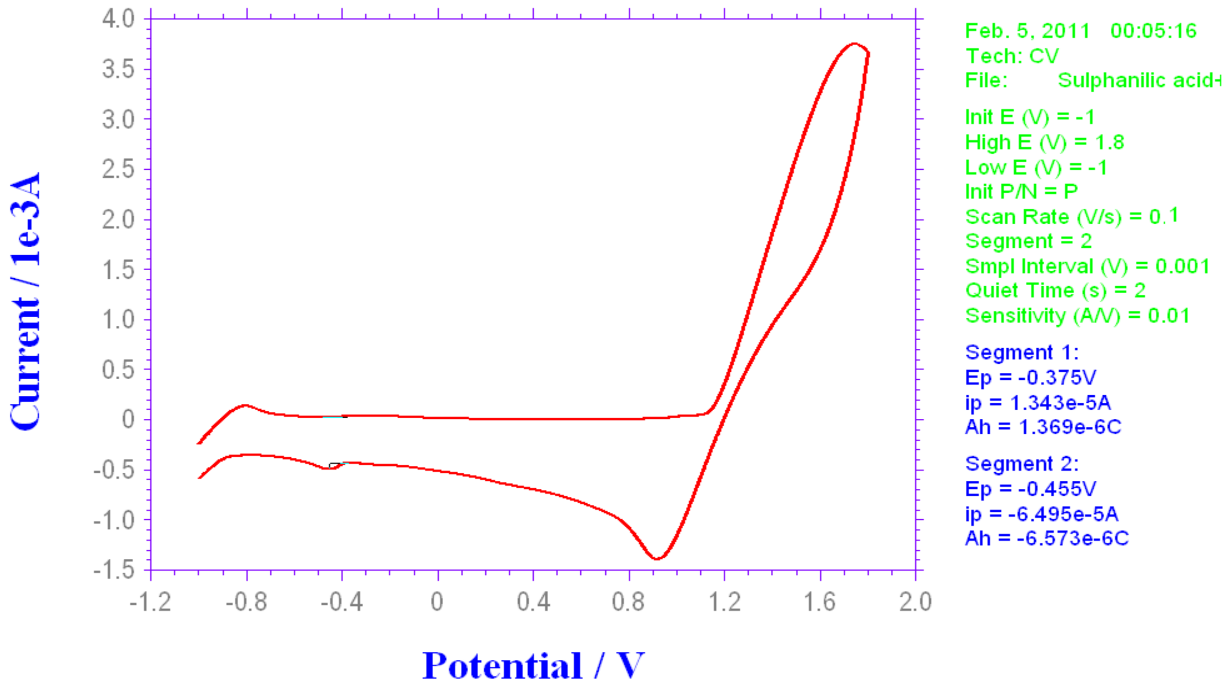


According to the earlier studies done by D.R. Henton[4], the oxidation of substituted aromatic compounds is a two electron process. Hence normally two distinct peaks were expected to be present in the cyclic voltammogram. If an electron donating group is present in the aromatic ring then the separation between the two peaks will be more and if an electron withdrawing group is present in the ring, it will destabilize the aromatic system and reduce the π electron density, consequently making the removal of electron difficult. Then the oxidation potential increases to higher positive value. Hence in systems containing electron withdrawing groups, the potential peak corresponding to the first electron oxidation is normally shifted to the second electron oxidation potential. In the case of sulphanilic acid, electron donating $-NH_2$ group and electron withdrawing $-SO_3H$ groups are present. Even at slow scan rate one single peak was observed with increased current flow which indicated that the predominance of electron withdrawing effect. The height of the peak is a qualitative indication of extend of current flow. On the basis of electrokinetic principle, the peak height and the rate of the reaction are in direct correlation.[5,6] Hence increased height is the indication of difficulty in the formation of intermediate and the low reaction rate.[7,8,9] Significant peaks were not observed on glassy carbon electrode. This may be due to the adsorption of the reactant molecules on the electrode surface. Hence the further studies like pH variation study, scan rate variation study and multiple scan study were done with platinum working electrode.

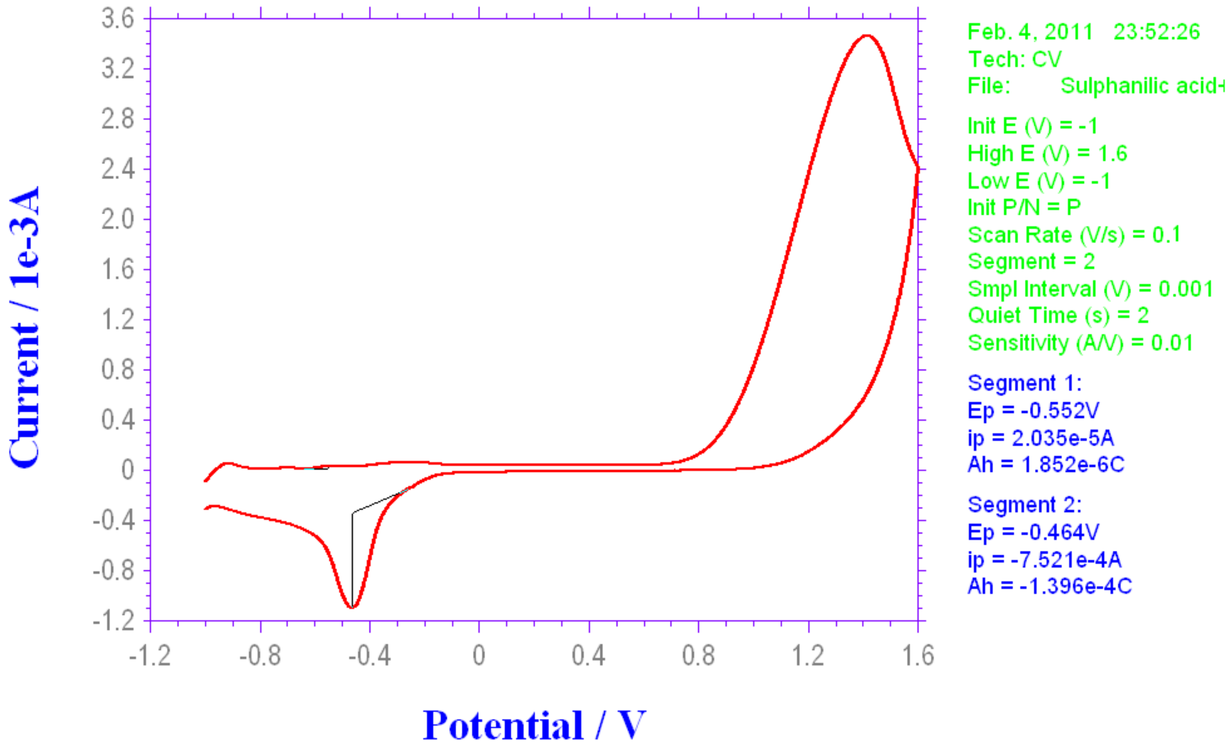
pH variation studies; **Acidic condition**



Neutral condition



Alkaline condition

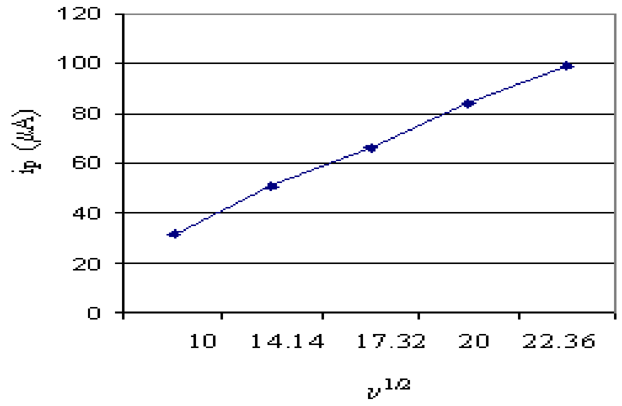


Feb. 4, 2011 23:52:26
Tech: CV
File: Sulphanilic acid
Init E (V) = -1
High E (V) = 1.6
Low E (V) = -1
Init P/N = P
Scan Rate (V/s) = 0.1
Segment = 2
Smpl Interval (V) = 0.001
Quiet Time (s) = 2
Sensitivity (A/V) = 0.01
Segment 1:
Ep = -0.552V
ip = 2.035e-5A
Ah = 1.852e-6C
Segment 2:
Ep = -0.464V
ip = -7.521e-4A
Ah = -1.396e-4C

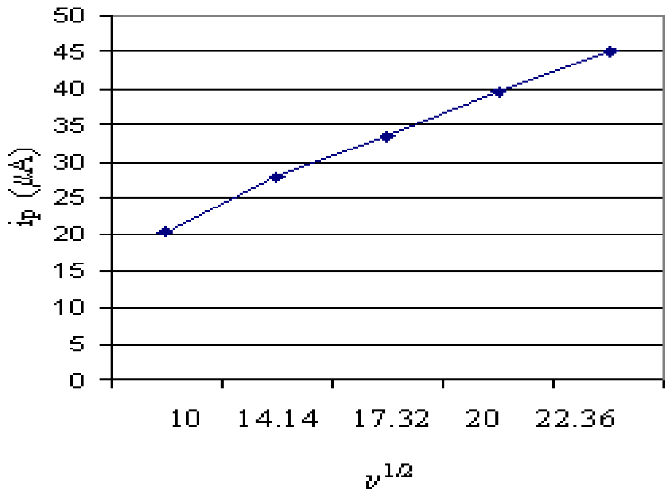
In neutral and alkaline condition the peak potentials were almost similar. The oxidation and reduction peaks obtained in the acidic condition were not as significant as they are found in the neutral and alkaline conditions. This is due to the difficulty in the formation of ethoxide ion and also due to the protonation of the medium to a greater extend. In the ethoxylation process, production ethoxide ion from ethanol was expected to happen. Production of ethoxide ion is evident by the work done by Reeve, Erikson and Alutto.[10] According to them ethoxide ion formation is favoured in neutral and alkaline conditions but such ion formation is not found in acidic condition.

Scan rate variation studies

Neutral condition



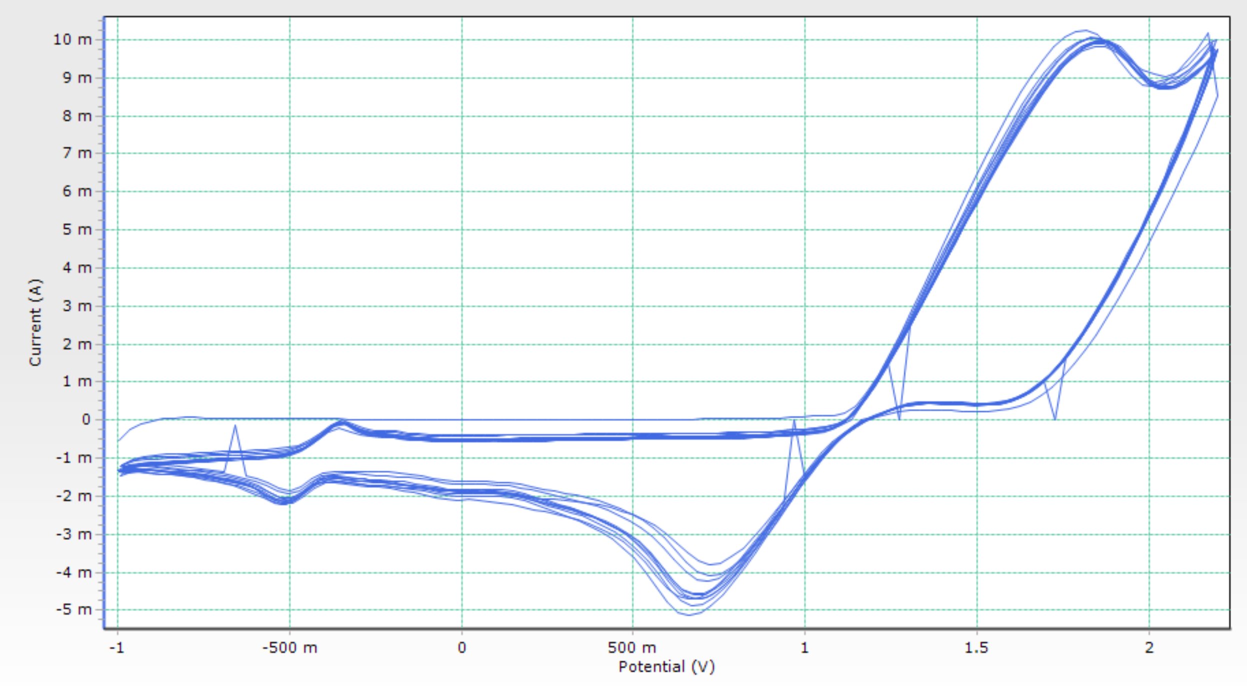
Alkaline condtion



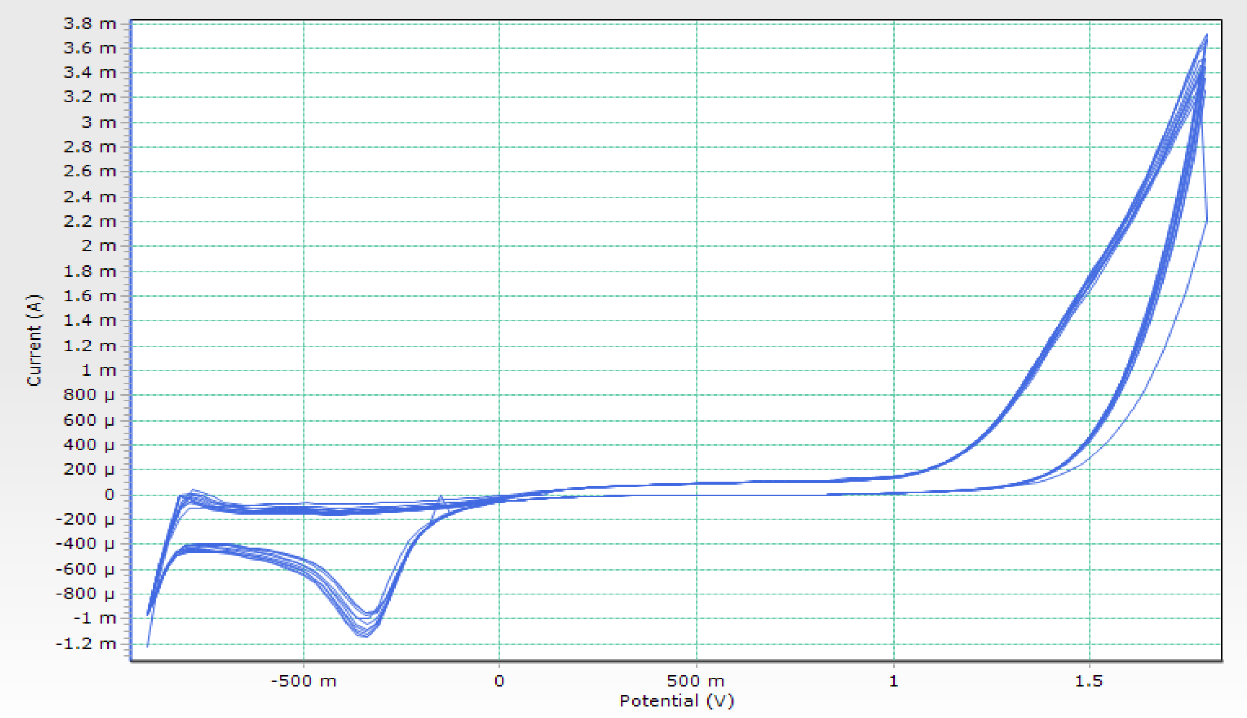
As significant peaks were missing in the cyclic voltammograms recorded in acidic condition, scan rate variation studies were done in neutral and alkaline media. In both cases a linear relationship is observed between log (i_{pa}) and log □ (where i_{pa} is anodic peak current and □ is scan rate). Furthermore the plot between the peak current and the square root of scan rate produces a straight line which does not pass through origin which suggests the irreversible character of the electron transfer[11] and the direct proportional relation between anodic peak current and the square root of scan rate indicates that the electron transfer process is diffusion controlled.[12]

Multiple scan studies

Neutral condition



Alkaline condition



In the multiple scan studies, the potential sweep at a scan rate of 100mV/s was repeated for ten times, through the same reaction mixture without disturbing the assembly of the experimental setup. This was done to ascertain the probability of formation of polymers on the electrode surface. If polymerization was possible, anodic peak current would be present in the first scan, at this potential polymerization would take place and a film would be formed on the electrode, and the peak would be missing in the subsequent scans. In the present study anodic peak was observed in all scans, but there was a small lowering of the anodic peak current, with the number of successive scans, this was due to the adsorption tendency of the ethoxylated product but not due to polymer formation. [13]

CONCLUSION

In the present work the cyclic voltammograms of sulphanilic acid were recorded by changing the conditions like pH, working electrodes, scan rate and multiple scan. The following are the conclusions arrived at from the observations

- Sulphanilic acid is susceptible for oxidation
- Anodic oxidation of sulphanilic acid is not taking place on glassy carbon electrode
- Oxidation process is effective in neutral and alkaline condtions.
- The process is diffusion controlled on platinum electrode
- The oxidation process is irreversible.

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