ANALYTICAL STUDIES ON ELECTROCHEMICAL ANODIC ETHOXYLATION OF SALICYLIC ACID

Dr. S. Antony Sakthi

PG & Research Department of Chemistry, St. Joseph's College, Trichy – 620 002.

Abstract

Electroorganic chemistry is a multidisciplinary science overlapping the vast fields of organic chemistry, biochemistry, physical chemistry and electrochemistry. The electrochemical oxidation of aromatic compounds on graphite and platinum electrode in alcoholic media has observed to yield ethers or acetals as a sequence of addition or substitution by alkoxy groups. This research work is having the major stress on electro analytical aspects of salicylic acid. These electro analytical studies include (i) cyclic voltammogram, (ii) working electrode variation studies (iii) pH variation studies (iv) scan rate variation studies and (v) multiple scan studies with an intention to explore whether the envisaged anodic process is possible or not. From the analytical studies, the oxidation potentials, favorable pH condition for the ethoxylation and also the formation of polymer on the working electrodes are predicted.

Key words: *Cyclic voltammetry, working electrode, ethoxylation, electro analytical studies.*

1. Introduction

This research work is having the major stress on electro analytical aspects of salicylic acid. Salicylic acid (SA) is a phenolic phyto hormone and is found in plants with roles in plant growth and development, photosynthesis, transpiration, ion uptake and transport. SA also induces specific changes in leaf anatomy and chloroplast structure. SA is involved in endogenous signaling, mediating in plant defense against pathogens.[3]

Among all other electrochemical processes, analogues to the corresponding chemical routs, anodic oxidations of aliphatics, aromatics, heterocyclic, etc., either directly from a major part of electro organic research.[4] Electrochemical hydroxylation, alkoxylation, acyloxylation, cyanation and halogenations are some of the important functionalization reaction exhaustively performed during the past three decades.[5-6]

In the normal procedure of manufacturing of certain pharmaceutical and industrial compounds, alkoxy compounds are found to be employed as source generator.[7] Henceforth, the electrochemical alkoxylation of aromatic compounds has evolved as a spontaneous choice for the current project.

The electro chemical oxidation of aromatic compounds on graphite or platinum electrode in alcoholic media has observed to yield ethers or acetals as a sequence of addition or substitution by alkoxy groups. The present study encompasses various aspects of the electro analytical studies on electrochemical ethoxylation of Salicylic acid.

In this present work, platinum and glassy carbon electrodes are taken as working electrodes. The electrode potentials of working electrodes are found out by taking Ag/AgCl electrode as reference. The ethoxylation of SA was carried out in ethyl alcohol medium. KOH, KCl, H_2SO_4 were used as supporting electrolytes in alkaline, weakly acidic and strongly acidic conditions respectively. The work is carried out to predict the anodic peak potentials at different pH media, to find out whether the reaction is diffusion or adsorption controlled and to ascertaining the formation of any polymer films on the surface of the working electrode.

2. Materials and method

2.1 Apparatus

Voltammogramms are recorded with potentiostat CH 10 (Sinsil international) interfaced to 663 VA stand (Metrohm) and SyncMaster B1930 computer. A three electrode configuration is used with platinum / glassy carbon electrode as the working electrode, a silver- silver chloride reference electrode and a platinum electrode wire as the auxiliary electrode. The working electrode was pretreated by polishing it with an alumina – water slurry followed by washing in an ultrasonic path.

2.2 Reagents and solutions

All reagents are of analytical reagent grade and ultra pure water is used throughout 0.001 M Salicylic acid, 1M H_2SO_4//KOH/ KCl, 0.5M Ethanol were prepared freshly. The pH of the different reaction mixtures measured with pen type pH meter. The solutions are stored in a light protected cool location.

2.3 Methodology

The three electrode system with platinum/glassy carbon electrode as the working electrode, platinum wire as the auxiliary electrode and Ag/AgCl electrode as the reference electrode is constructed in an undivided cell. In order to change the pH of the system 1M solutions of H_2SO_4/KOH/ KCl are taken. These solutions are also working as the sources of supporting electrolytes. Then the cylclic voltammogram is recorded with different scan rates, different working electrodes and different pH conditions. To arrive at an idea about the polymerization of SA on working electrode multiple scan cyclic voltammogram was also recorded.

3. Result and Discussion

3.1 STUDIES ON VARIATION OF SUBSTRATES AND pH

Cyclic voltammograms for salicylic acid (0.001M) with ethanol (0.1M) at platinum anode for 100 mVs^{-1}

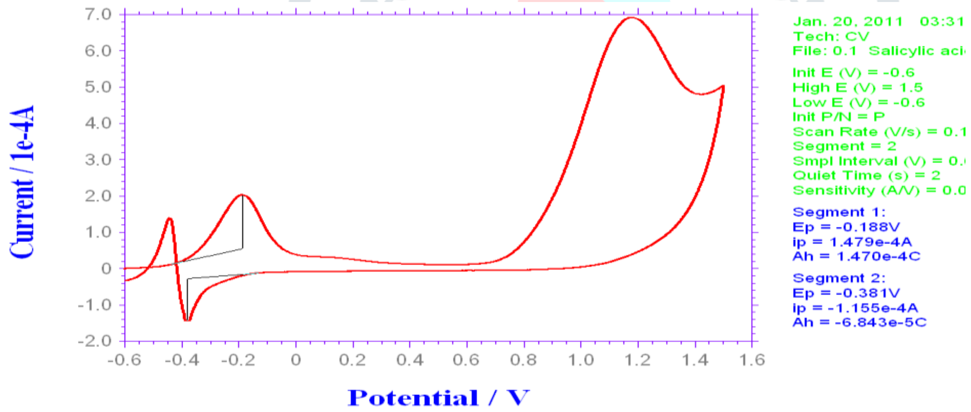


Figure 3.1.(a) Basic medium (KOH, 1M)

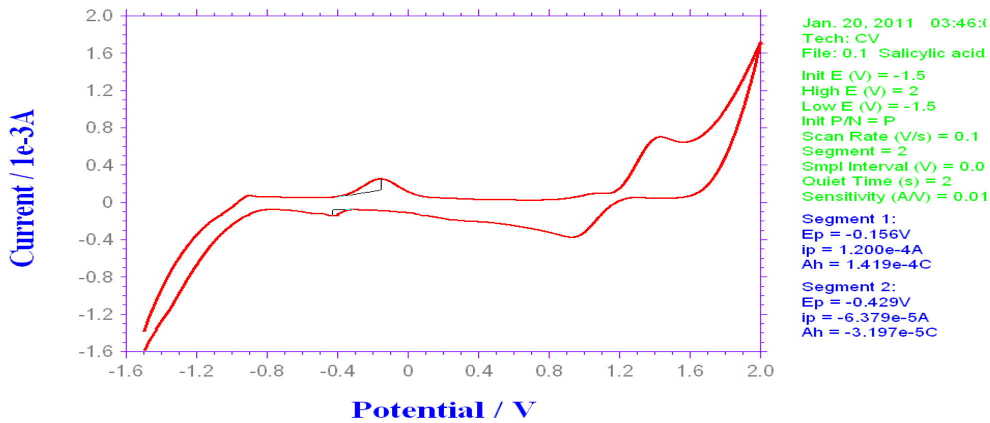


Figure 3.1.(b) Neutral medium (KCl,1M)

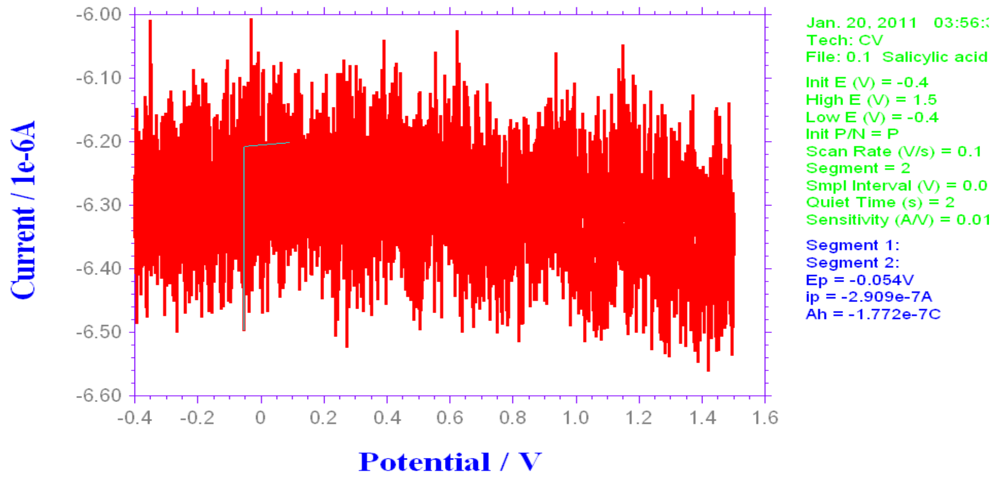


Figure 3.1.(c) Acidic medium (H_2SO_4, 1M)

The oxidation peaks were found at 1.1V in basic medium and at 1.3V in neutral medium but no peak in the acidic medium of the cyclic voltammograms obtained for the ethoxylation of salicylic acid.

3.2. Electrode Variation Studies

The following cyclic voltommograms obtained by using the working electrode as glassy carbon electrode.

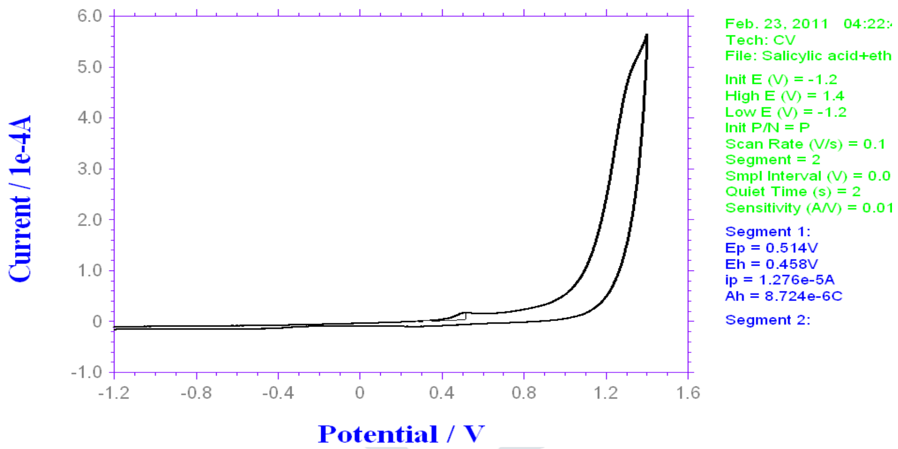


Figure 3.2. (a) Cyclic voltammogram for 10^{-3}M, salicylic acid at pH=12, in hydro-alcoholic solution at glassy carbon electrode

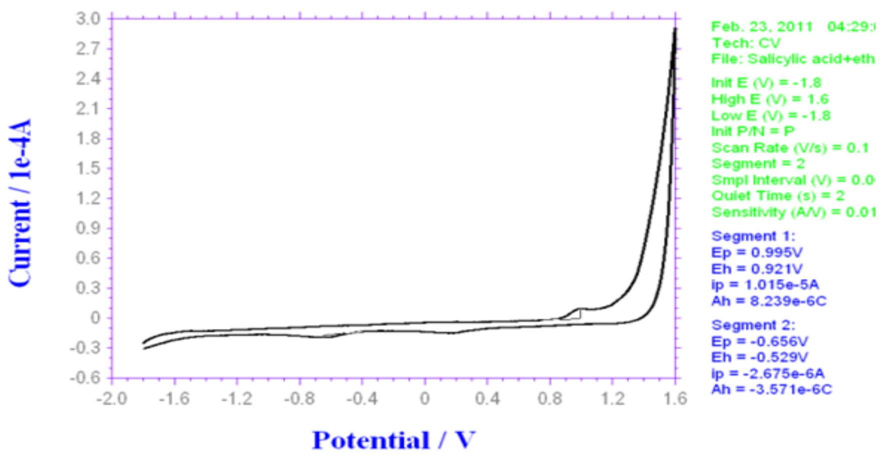


Figure 3.2.(b) Cyclic voltammogram for 10^{-3}M, salicylic acid at pH=7, in hydro-alcoholic solution at glassy carbon electrode

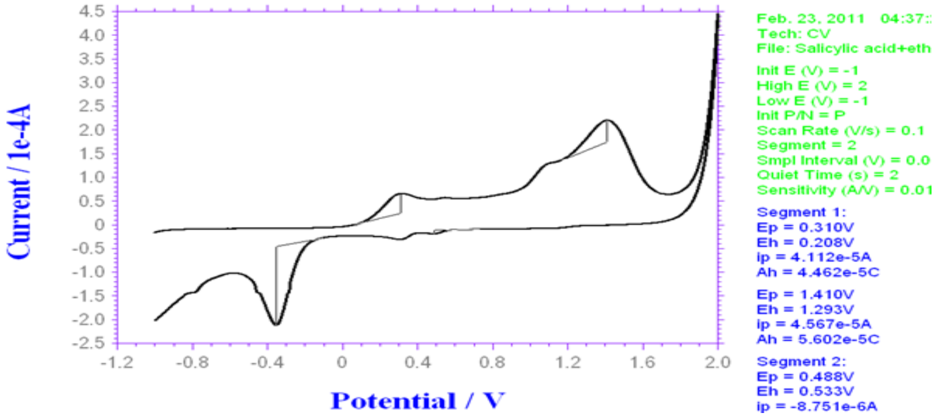
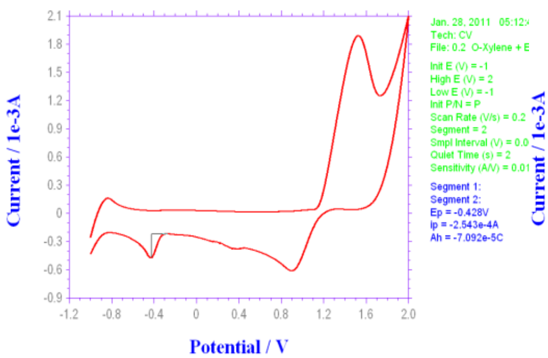


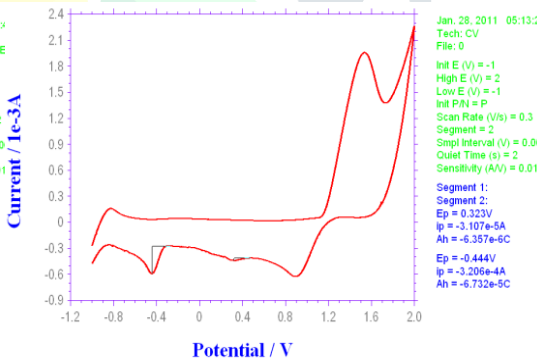
Figure 3.2 (c) Cyclic voltammogram for 10^{-3}M, salicylic acid at pH=2, in hydro-alcoholic solution at glassy carbon electrode

When the cyclic voltammograms were recorded with the working electrode glassy carbon, in general the oxidation potentials were found to be more positive for platinum and less positive for glassy carbon. This may be due to the changes in the thickness of electrical double layer formed around the electrodes.[8] In the glassy carbon electrode, the electrical double layer is very nearer to electrode surface. Therefore, a very small driving force in the form of electromotive force is sufficient to transfer the electrons from the system (aromatic moiety to the electrode by overcoming the barrier).

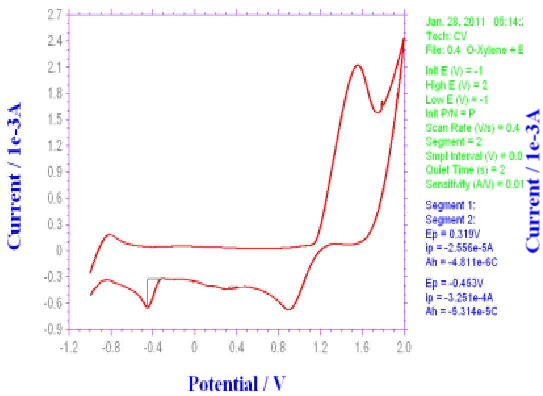
4.3 SCAN RATE VARIATION STUDIES



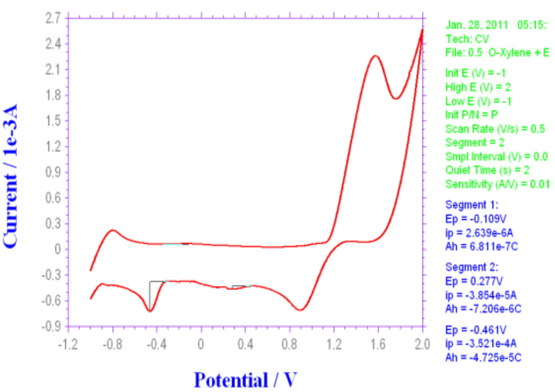
(a) 200 mV/s



(b) 300 mV/s



(c) 400 mV/s



(d) 500 mV/s

Parameter	Scan rate ν (mV/s)				
	100	200	300	400	500
ν ½	10	14.14	17.32	20	22.36
Ip (μA)	68	117	131	153	173
Ep (v)	1.17	1.24	1.27	1.31	1.73

Table: 3.3.Salicylic acid - Scan rate variation study

Figures 4.3. (a), (b), (c) & (d) Cyclic voltammograms recorded for salicylic acid in basic medium at different scan rates.

The cyclic voltammogram for salicylic acid in the entire three different pH medium showed that the anodic peak potentials are dependent on the scan rate. This study also revealed that increase in scan rate results in the increase of the anodic peak potential values. This behaviour is characteristic of reversible electron transfer pathway.[9]

3.4. MULTIPLE SCAN STUDIES

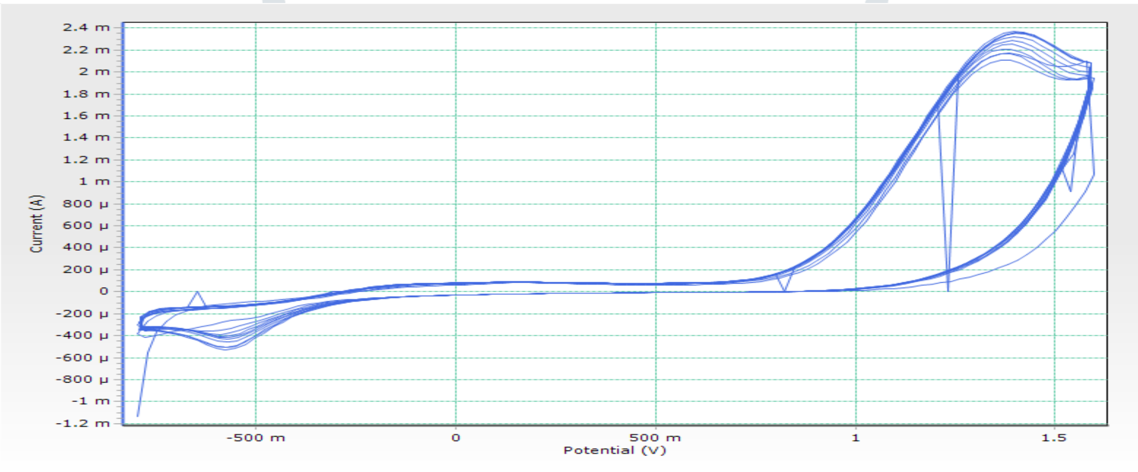


Figure 3.4. (a) Cyclic voltammogram for salicylic acid +ethanol +KOH mixture at pH=12

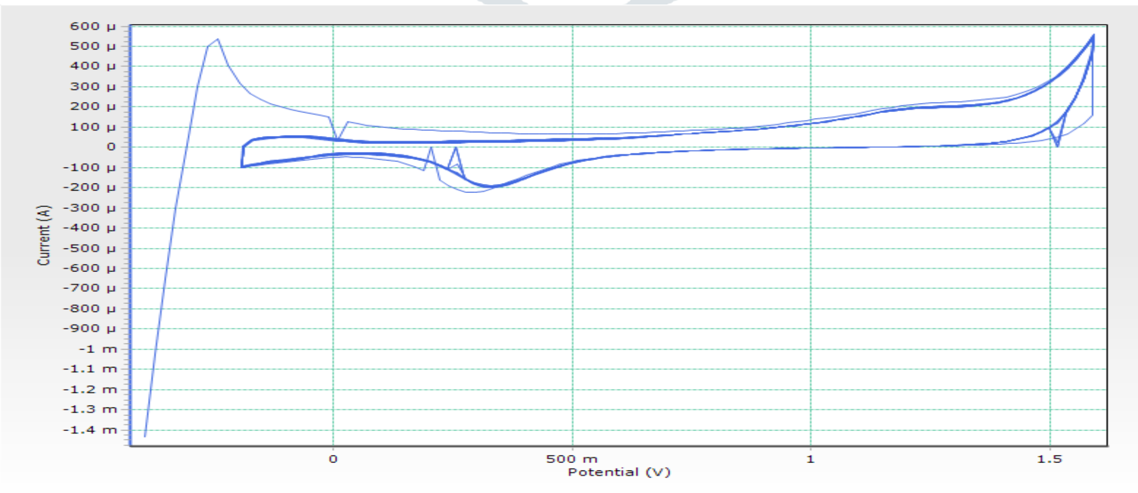


Figure 3.4. (b) Cyclic voltammogram for salicylic acid +ethanol + KCl mixture at pH=7

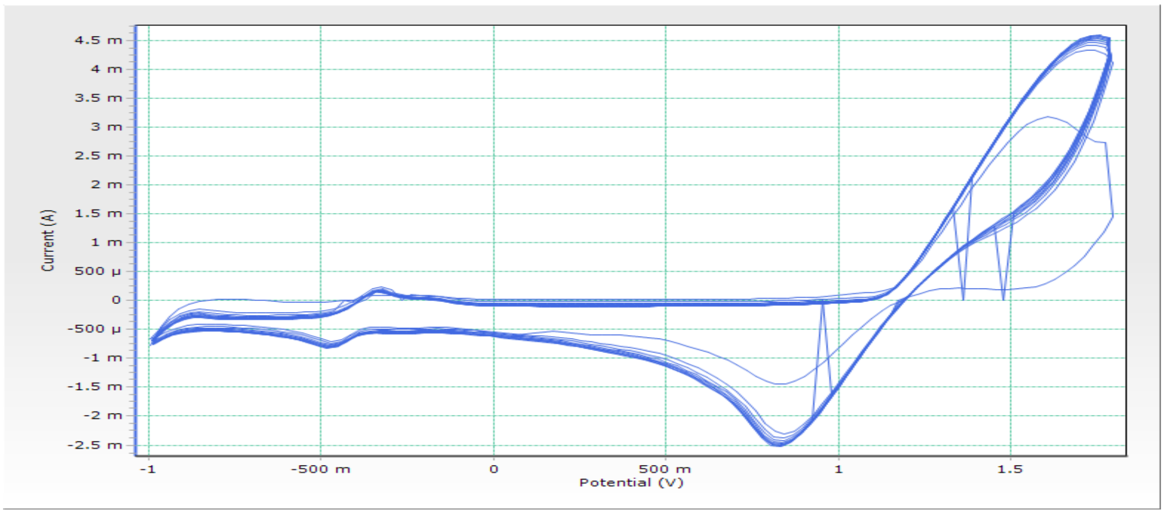


Figure 3.4. (c) Cyclic voltammogram for salicylic acid +ethanol + H_2SO_4 mixture at pH=2

The cyclic voltammograms of multiple scanning were recorded for the electrochemical ethoxylation of chosen substrates using platinum as the working electrode, a platinum wire as the auxiliary electrode and Ag/AgCl electrode as the reference electrode. In the multiple scan technique, the potential sweep at a specific scan rate namely 100 mV/s is repeatedly performed for 10 segments though the same solution without disturbing the assembly and the experimental set up. This technique finds its use in predicting the probability of formation of any polymer films on the surface of the working electrode.

For a system, which is capable of forming polymer coats, the potential sweep is responsible for the first segment by the way of initiating the polymerization. As the electrode gets coated with the polymer of conducting nature, the subsequent sweeps cannot show any peak current. In the present study of the cyclic voltammograms with such multiple scans for salicylic acid with ethanol solution of different pH media are studied.

From the cyclic voltammogram of multiple run studies of the substrates under investigation, it is very clear that the peak currents corresponding to the various peak potentials are very prominent and well realized.

This observation shows that the peak current fluctuations at the respective peak potential do appear at multiple scan rates. Therefore, it is concluded that there were no polymeric coatings seem to have formed in different pH medium.[10]

4. CONCLUSION

- The following conclusions are drawn from the electroanalytical studies on anodic ethoxylation of salicylic acid.
- The electroanalytical studies carried out with Pt & Glassy carbon as the working electrode. The possible anodic potentials for the electro chemical ethoxylation of salicylic acid are found out.
- It is also observed that the working potentials vary with Pt and Glassy carbon. The oxidation potentials were found to be more positive for platinum and less positive for glassy carbon.
- The scan rate variation studies, reveals that ethoxylation of salicylic acid is diffusion controlled and not adsorption controlled.
- From the multiple scan rate studies, it is concluded that anodic ethoxylation of salicylic acid has shown no polymer coating formation during the oxidation.

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