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# Electro Chemical Comparative Studies Of Ortho, Meta and Para Nitro Phenols

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*Abstract*

*Nitro phenol exists in three isomeric forms namely ortho, meta and para nitro phenols. Their susceptibility for electrochemical oxidation was studies by cyclic voltammetric method and polarization studies. Plenty of chemical studies are available in the literature. But a very little work has been done on the electrochemistry of nitro phenols. In the present study electrochemical approach was made to compare ortho, meta and para nitro phenols. The cyclic voltammograms were recorded using platinum working electrode. Polarisation studies were also done using platinum working electrode to find out the decomposition potential of the nitrophenols. From these studies it is found that ortho and para nitro phenols are susceptible for electro oxidation but meta nitrophenol is not susceptible for the same.*

*Key words: Cyclic voltammetry, Anodic oxidation, Electro oxidation, nitrophenols, Platinum electrode, Electro analysis, Electrode process*

## Introduction:

Nitrophenols are commercially important chemicals. Ortho nitrophenol is used as an acid base indicator and corrosion inhibitor for aluminium – copper alloy. Meta nitrophenol finds its application in the synthesis of diazotized m-nitroaniline. Para nitrophenol is very much used in the manufacture of the common antipyretic paracetamol, fungicides and some insecticides. The chemical differences between ortho, meta and para nitrophenols are already available. Now a day's electrochemistry finds its importance in the chemistry field.[1] But a very little work has been done on the electrochemical comparative analysis of nitrophenols.[2]

Cyclic voltammetry technique is the simplest and the most accurate method to find the electrochemical changes that a compound undergoes. In this technique the current flowing through the system is plotted against potential difference applied across the electrodes. It consists of measuring the current resulting from an applied potential wave form.[3] The applied potential is cycled within a given potential range at a constant rate and the current is measured as a function of the potential. The rate at which the potential difference between the electrodes changes is called scan rate. The scan rate is expressed in mV/s. The scan rate can be varied from a few micro volts per second to several volts per second. 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 as working electrodes, Ag/AgCl electrode as reference electrode and platinum electrode as counter electrode. The cyclic voltammograms of nitrophenols were carried out in a solution containing $1X10^{-3}M$ nitrophenols, 0.5M ethanol and 1M KCl solution. The KCl solution was used as supporting electrolyte to make the reaction mixture electrical conductive. For assertion of polymer formation on the electrode surfaces, multiple scans study was also done. Polarisation studies were done with higher concentrations of the substrate with three electrode system containing platinum working electrode, platinum counter electrode and saturated calomel electrode (SCE) as reference electrode. The potential between the working and counter electrodes was controlled using an IC regulated constant power supply and the current flowing through the working electrode was noted. The graphical representation of the voltage current was used to find out the decomposition potential of the nitrophenols.

## 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, 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. For polarization studies platinum working electrode, saturated calomel electrode (SCE) as reference electrode and a platinum foil of dimension 1cm X 2cm as counter electrode were used. An IC regulated adjustable constant power supply unit (BESTO make) and digital voltmeters and ammeters were used.

### Reagents and solution

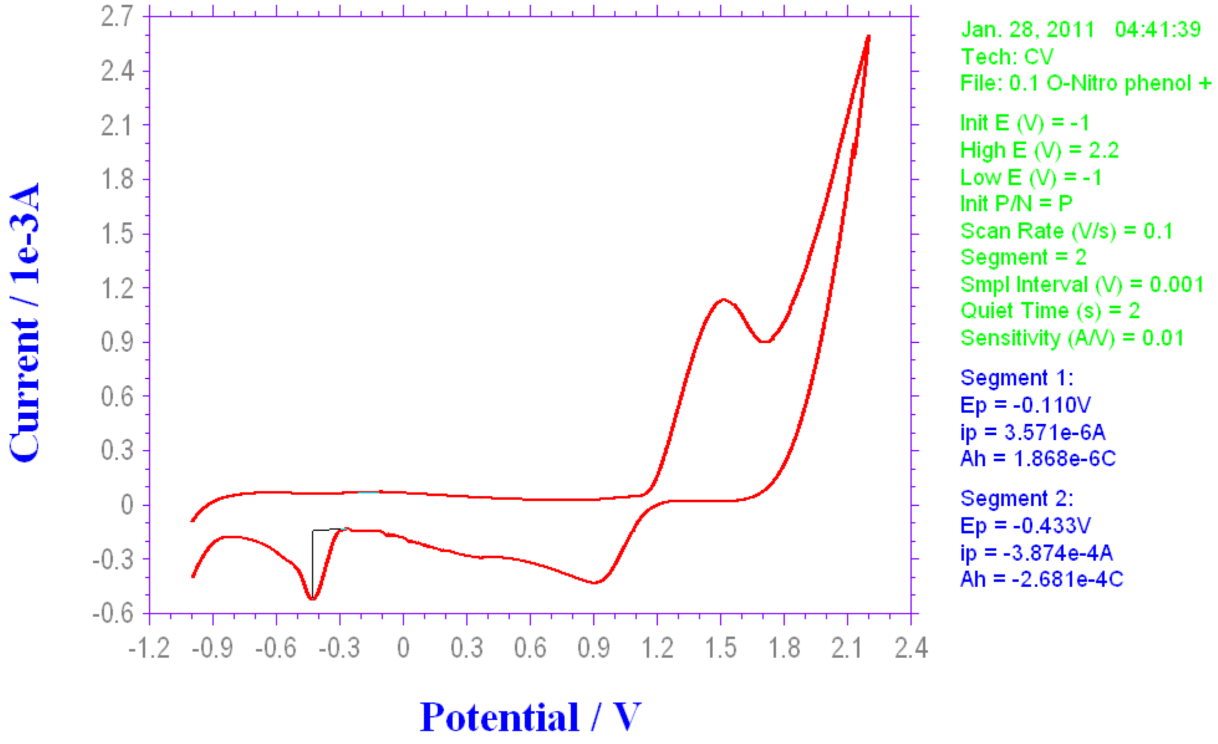
All the chemicals used were of analytical reagent grade. Double distilled water was used to prepare solutions. 0.001M nitrophenols, 0.5M ethanol and 1M KCl solutions were prepared freshly.

## Methodology

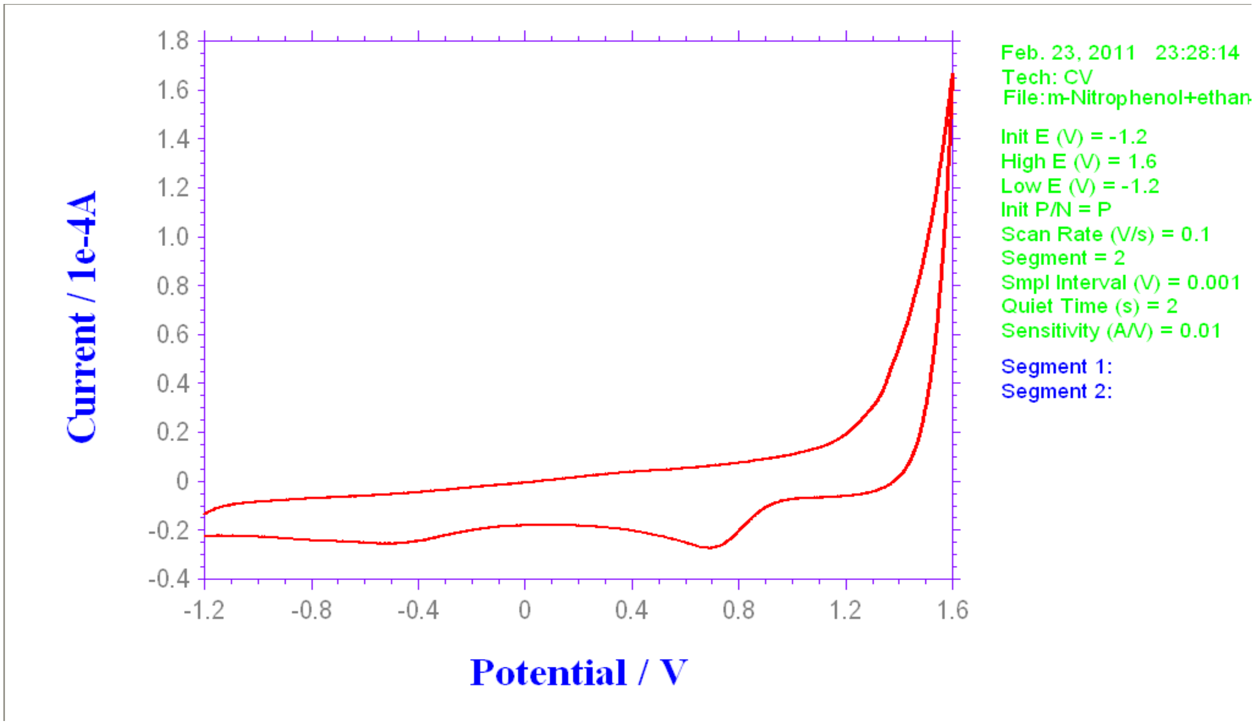
The three electrode system was constructed with platinum, platinum counter electrode and Ag/AgCl reference electrode in a beaker type undivided cell. To make the solution conductive 1M solution of KCl was added as supporting electrolyte. Then the cyclic voltammograms were recorded for ortho, meta and para nitrophenols in neutral medium on platinum working electrode. Multiple scan studies were also done. Polarisation studies were done using an adjustable constant power supply, the potential difference between the working electrode and reference electrode (SCE) was adjusted and the current flowing through the working electrode was monitored. Current – voltage graph was obtained from the data.

## Results and discussion

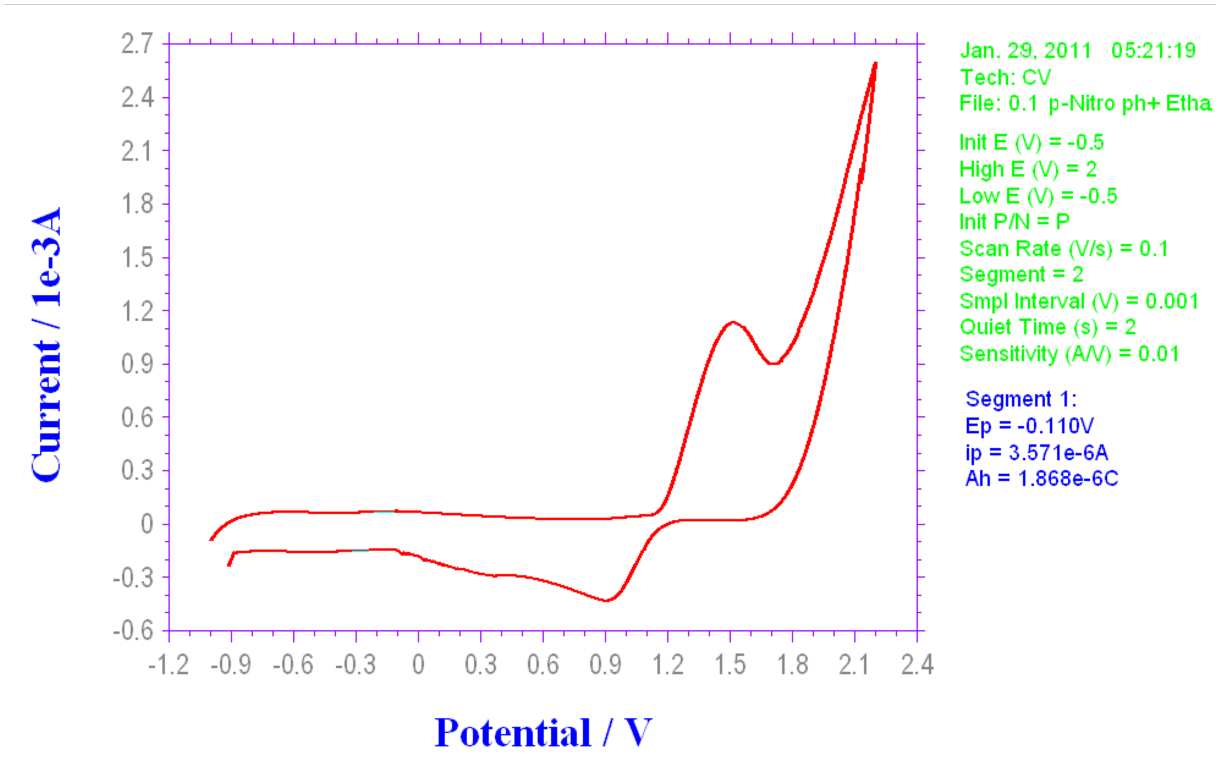
### Cyclic voltammogram of ortho nitrophenol on platinum electrodes:



**Cyclic voltammogram of meta nitrophenol on platinum electrodes:**



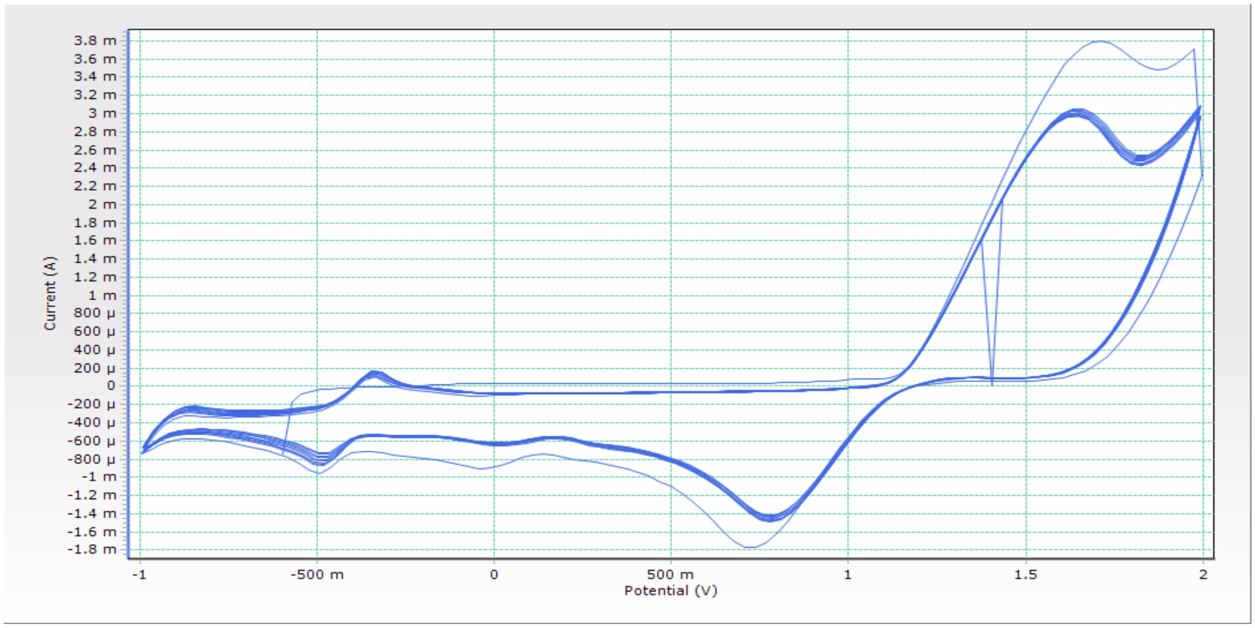
**Cyclic voltammogram of para nitrophenol on platinum electrodes:**



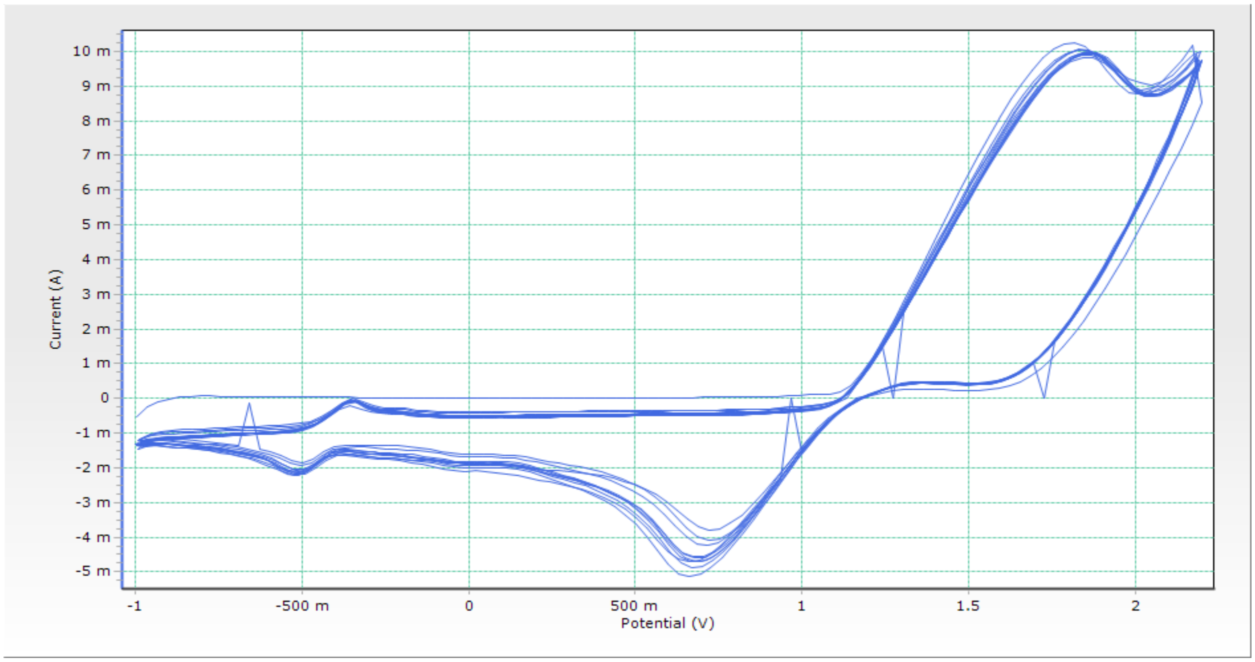
According to the earlier studies done by D.R. Henton[4], the oxidation of substituted aromatic compounds is a two electron process. Hence normally two distinct peaks were expected to be present in the cyclic voltammogram. If an electron donating group is present in the aromatic ring then the separation 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  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. Ortho, meta and para nitrophenols contain both electron withdrawing and electron donating groups. $NO_2$ group is an electron withdrawing group where as OH group is an electron donating group. The single peak obtained in the cyclic voltammogram indicated the dominant effect of $NO_2$ group. Even at slow scan rate one single peak was observed with increased current flow which indicated the effect of electron withdrawal from the aromatic ring. 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] From the cyclic voltammogram the oxidation potential for ortho and para nitrophenols was found to be 1.5V, but meta nitrophenol did not show any oxidation peak. The same trend was also observed in the polarization study. As significant oxidation peak was not found in the cyclic voltammogram of meta nitrophenol, multiple scan studies were restricted to ortho and para nitrophenols.

## Multiple scan studies

### Ortho nitrophenol



### Para nitrophenol



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]

**Polarisation studies:**

Polarisation studies were done at neutral medium on platinum working electrode. The current – potential values obtained for ortho, meta and para nitrophenols are given below.

**Table: 1 Current – Voltage study of nitrophenols in neutral medium on platinum electrode.**

| Potential Vs SCE In Volt | Current (mA) | | |
|---|---|---|---|
| | Ortho Nitrophenol | Meta nitrophenol | Para nitrophenol |
| 0.1 | -0.1 | 0.1 | -0.1 |
| 0.2 | 0 | 0.2 | 0 |
| 0.3 | 0.2 | 0.8 | 0.2 |
| 0.4 | 0.5 | 1 | 0.5 |
| 0.5 | 0.7 | 1.2 | 0.7 |
| 0.6 | 0.9 | 1.4 | 0.9 |
| 0.7 | 1.2 | 1.6 | 1.2 |
| 0.8 | 1.3 | 2 | 1.3 |
| 0.9 | 1.5 | 2.4 | 1.5 |
| 1 | 1.7 | 2.7 | 1.7 |
| 1.1 | 1.8 | 3.4 | 1.8 |
| 1.2 | 2 | 3.8 | 2 |

| | | | |
|---|---|---|---|
| 1.3 | 2.3 | 4 | 2.3 |
| 1.4 | 3.5 | 4.4 | 3.4 |
| 1.5 | 6.4 | 4.7 | 6.4 |
| 1.6 | 9.5 | 5 | 9.5 |
| 1.7 | 11.5 | 5.4 | 11.5 |
| 1.8 | 14.9 | 5.8 | 14.9 |
| 1.9 | 17.3 | 6.5 | 17.3 |
| 2 | 22.3 | 7 | 22.3 |
| 2.1 | 25.6 | 7.6 | 25.5 |
| 2.2 | 28.3 | 9.2 | 28.3 |
| 2.3 | 32.2 | 9.4 | 32.2 |
| 2.4 | 34.6 | 10.6 | 34.6 |
| 2.5 | 37.6 | 12.3 | 37.6 |
| 2.6 | 39.4 | 12.8 | 39.4 |
| 2.7 | 45.2 | 13.6 | 45.2 |

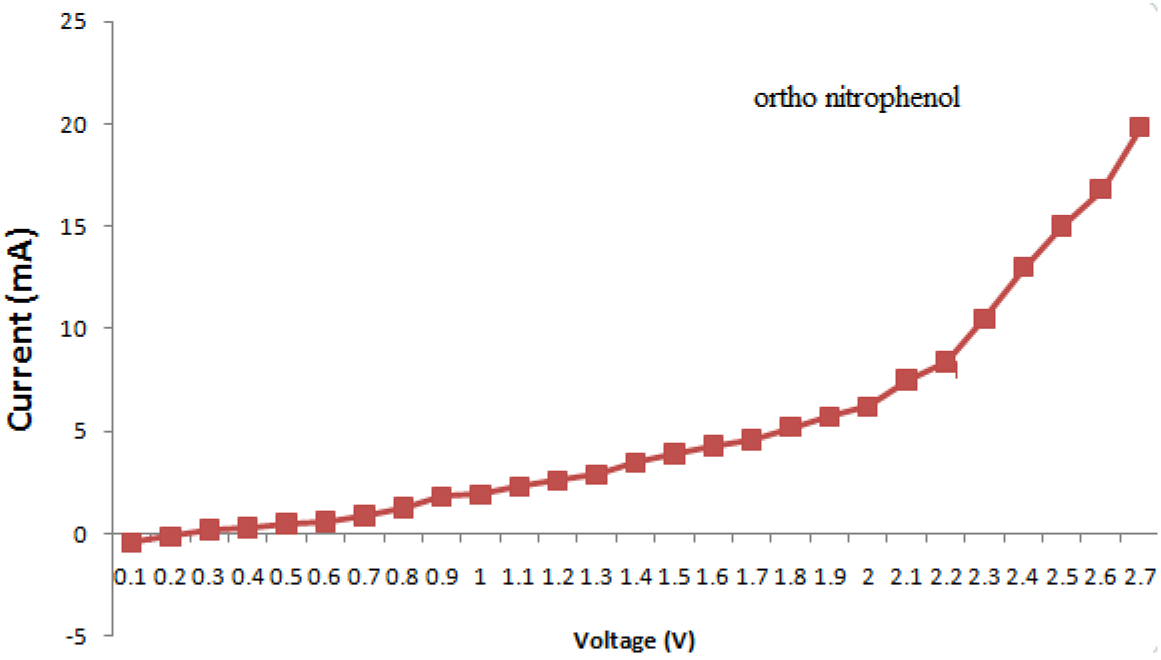


Fig 1. Polarisation study of ortho nitrophenol on platinum working electrode in neutral medium

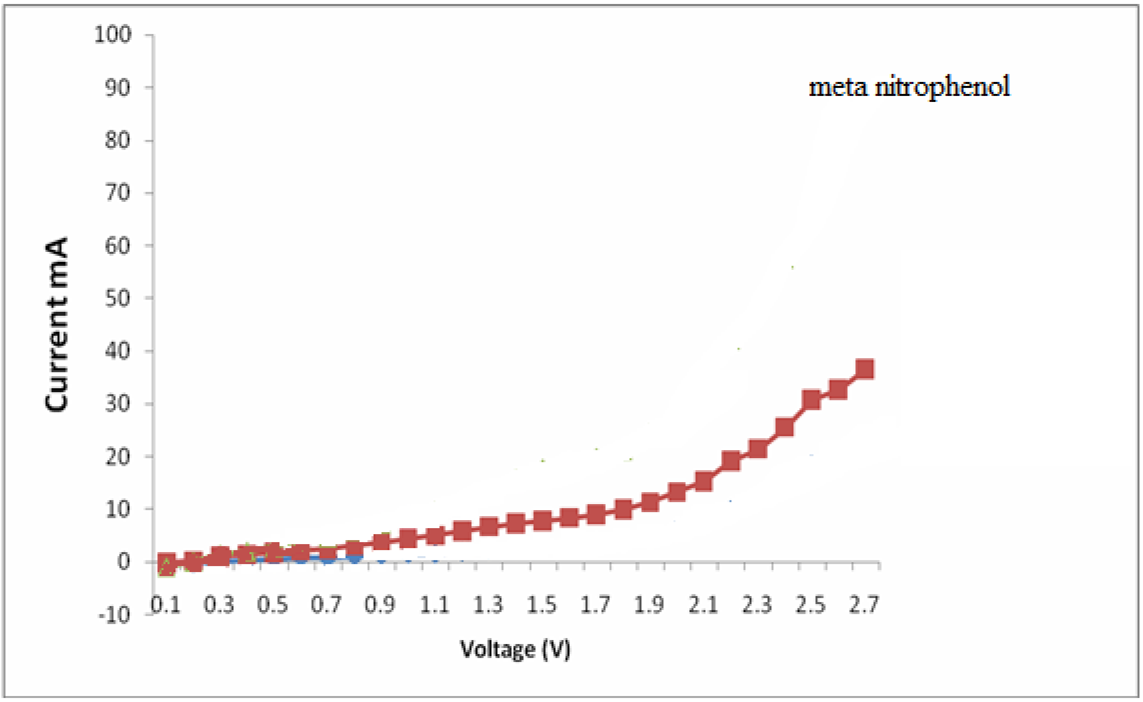


Fig 2. Polarisation study of meta nitrophenol on platinum working electrode in neutral medium

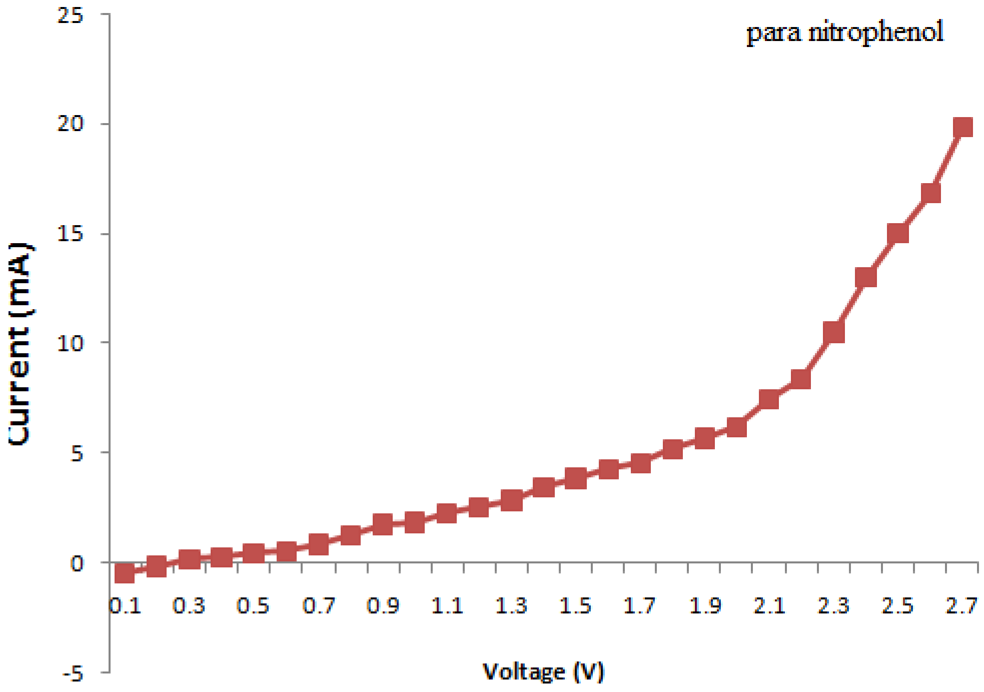
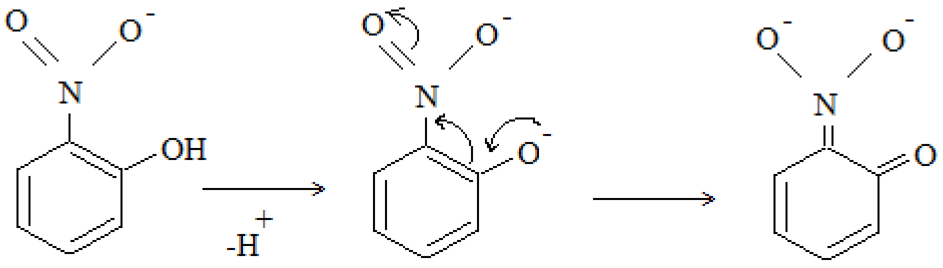


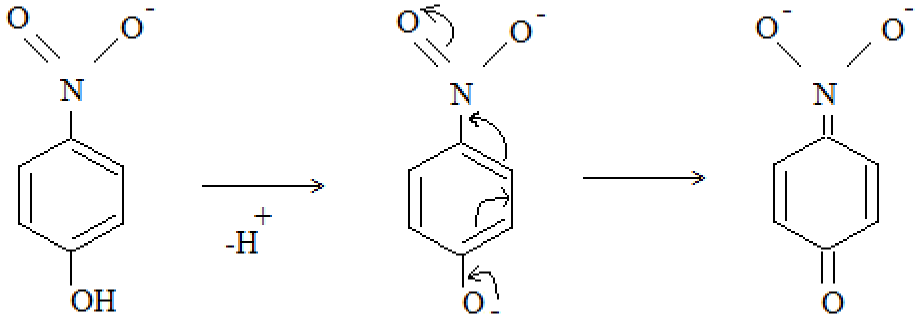
Fig 3. Polarisation study of para nitrophenol on platinum working electrode in neutral medium

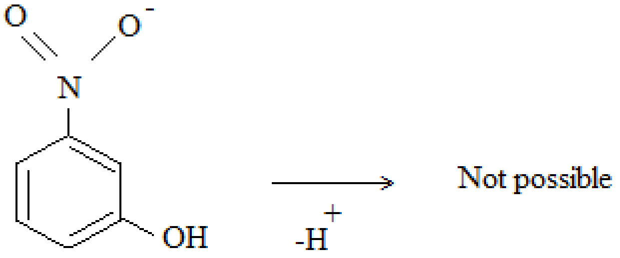
The working potentials or decomposition potentials were calculated using the graphical representations of polarization studies. The following are the working or decomposition potentials of ortho, meta and para nitrophenols calculated with respect to SCE.

| | |
|---|---|
| Ortho nitrophenol | 1.4 V |
| Meta nitrophenol | 1.8 V |
| Para nitrophenol | 1.4 V |

The observation was in accordance with the oxidation potentials obtained from cyclic voltammograms. Ortho and para nitrophenols showed oxidation peak in cyclic voltammogram and lower decomposition potential. Meta nitrophenol did not show oxidation peak and also had comparatively higher decomposition potential. These electrochemical observations were supported by the conventional chemistry of nitrophenols. Susceptibility of ortho and para nitrophenols for oxidation and resistance of meta nitrophenol for oxidation are due to quinol formation as given below.







## Conclusion:

In the present work the cyclic voltammograms of nitrophenols acid were recorded using platinum working electrode in neutral medium. Polarisation studies of nitrophenols were also done using platinum working electrode. From the results obtained the electrochemical properties of ortho, meta and para nitrophenols were compared. The following are the conclusions arrived at from the observations

- Ortho nitrophenol and para nitrophenol are susceptible for oxidation
- Meta nitrophenol is not susceptible for oxidation
- The oxidation potentials obtained from cyclic votammograms and the decomposition potentials obtained from polarization studies indicated that the electrochemical behavior of ortho and para nitrophenols are identical.
- Meta nitrophenol showed higher oxidation potential in cyclic voltammetric study and higher decomposition potential in polarization study. This is due to the

impossibility of quinol formation from meta nitrophenol.

## References:

1. Ellis, Frank (2002). *Paracetamol: a curriculum resource*. Cambridge: Royal Society of Chemistry.
2. S. Baumer and H.J. Schafer, *Journal of App. Electrochemistry*, 2..5, 35, 1283-1292
3. R. Greef, R. Peat, L.M. Peter, D. Pletcher, J. Robinson, *Instrumental Methods in Electrochemistry*, Ellis Horwood Limited, Southampton, 1990, Chapter 6.
4. Norman L. Weinberg, Anodic oxidation of organic compounds. IV Mechanism of electrochemical methoxylation of benzyl alcohol, *J.Org. Chem*., **1968,** 33 (12): pp 4326 – 4329,
5. D.R. Henton, B.L. Chenard and J.S. Swenton, *J.Chem. soc, Chem. Commun*, **1979,** 326
6. E. Ahlberg and V.D. Parker, *Acta Chem. Scand*. B **1980,** 34,71,
7. B. Scharbert and B. Speiser, *J. Chemomet*, **1988,** 3, 61-80.
8. C.H. Evans, *Chem. Rev*. **1990,** 90, 739-751,
9. C. Amatore and J.M. Saveant. *J. Electro anal. Chem*. **1997,** 85, 27-46,
10. Reeve, Erikson and Aluotto, *Can. J. Chem*., **1979,** 57, 2747.
11. S.W. Feldberg and L. Jeftic, *J. Phys.Chem* **1972,** 76, 2439.
12. Shui Ya Kishika and Akifuni Yawada, *Electrochimca Acta*, **2005,** 51, 464.
13. D.S. Yuan, S.Z. Tan, J.H. Zeng, F.P Hu, X.Wang and P.K. Shen, *Carbon***2008**, 46, 531.