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## Voltammetric Behaviour of m-nitrophenol at Platinum and Stainless Steel Electrodes at Different pH

**Sangita Gupta[*], Kripa Sharma[a], Manish Gupta[b] , PS Verma**

Department of Chemistry, University of Rajasthan, Jaipur (Rajasthan)-302004 INDIA
[a]Koutilya Institute of Technology and Engineering, Jaipur, Rajasthan, India.
[b]Dy. Director, RCEE, Shiksha Sankul, J.L.N.Marg, Jaipur, Rajasthan, India.

## ABSTRACT

Voltammetric curves of m-nitrophenol in aqueous-methanol medium for different pH using B.R. Buffer for various concentrations (0.05mM, 0.1mM, 0.15mM, 0.2mM) and scan rates at Pt electrode were obtained. The prominent three reduction peaks corresponding to $4e^-$ change of m-nitrophenol was characterized at 0.2mM concentration in basic medium at scan rate 90mV/sec. The reversibility and the mechanism of the reaction was also studied by the Cyclic Voltammetry. Constant current electrolysis of 0.02mM m-nitrophenol in basic medium give m-Hydroxy phenyl hydroxyl amine(m-HPHA) at stainless steel (type 316) cathode and counter electrode of same size and material at constant current 1.9 Ampere respectively, as a major product which were confirmed by spectral and chemical analysis.

**Keywords:** Electrochemical reduction, m-nitrophenol, Cyclic Voltammetry, Constant Current electrolysis, SS cathode

***Corresponding author**
Email: sangita.uor@gmail.com

## INTRODUCTION

Numerous investigations have been made on the reduction of the aromatic nitro compounds [1-3]. The nitro group is one of the best electrophores as regards to both ease of reduction and versatility of derived products. By the electroreduction [1] of nitrophenol isomer using stationary and rotating Cu electrodes and $Ti(SO_4)_2$ as additional agent, aminophenols were obtained in good yield. Depending on the electrolysis conditions, a great variety of products can be obtained by electroreduction of nitrophenols. Stainless Steel electrode has been used widely in our laboratory for the electrochemical reduction of some aromatic compounds [4-13].

The present work deals with the Voltammographic studies of m-nitrophenol carried out in acidic, neutral and basic medium by Cyclic Voltammetry and electrochemical reduction of m-nitrophenol at Stainless Steel electrode by Constant Current Electrolysis, products depending upon the conditions of the reduction. Under the basic condition m-nitrophenol is reduced to the corresponding hydroxylamine derivatives (m-HPHA), which is further reduce to m-aminophenol.

### Experimental

Solutions were prepared from A.R. methanol and double distilled water. Reagents such as Acetic acid, phosphoric acid, boric acid, sodium hydroxide, oxalic acid, sodium acetate, potassium chloride and sodium chloride used were of A.R. grade. m-nitrophenol was crystallized from methanol and the pale yellow, odorless crystals (m.p. $97^0$C) were used. The purity was checked by single spot TLC. I.R. Spectra of m-nitrophenol and the product obtained, were recorded and studied to confirm the structure.

Cyclic Voltammetric studies were carried out using a three electrode cell assembly having Pt as the working electrode, Ag/Agcl as reference electrode and Pt wire as the counter electrode. Voltammograms of m-nitrophenol are recorded in 1:1 (V/V) water: methanol at 0.05mM, 0.1mM, 0.15mM and 0.2mM concentrations. B.R. Buffer was used to maintain desired pH viz. 3.9, 7.0, 9.1, 11.1.

An ELICO MODEL CL-95 Potentiostat cum Galvanostate coupled with a sweep generator were used for carrying out Controlled Current Electrolysis. Stainless Steel (SS316) electrode was used as cathode and counter electrode. The solution was stirred by a Remi 2LH hot plate stirrer throughout the electrolysis. H-cell was used as electrolysis cell to carry out Constant Current Electrolysis. F.T.-I.R. spectra of m-nitrophenol and the product was obtained and compared for analysis, identification and characterization.

The preparative electrolysis of 100 ml of 0.02M m-nitrophenol were carried out at Constant Current 1.9 Ampere in basic medium (pH=10) for 6 hours. The thermometer was kept dipped under the surface of the catholyte. Stirring was done at the maximum speed of the magnetic stirrer. The potential was recorded at the start of the electrolysis and then after 15 minutes. The temperature was also recorded simultaneously at regular intervals. The electrolysis was terminated when the potential becomes constant with change in time.

### Work-Up

After the electrolysis the catholyte was distilled under reduced pressure so that the volume of the catholyte was reduced to one third of it's original volume. No precipitate was obtained due to absence of azoxy and azo derivatives. The catholyte was then saturated with sodium chloride and cooled to less than $5^0$C and extracted with three lots of 15ml each of benzene light petroleum. On evaporation solid m-HPHA was obtained in 90% yield. The purity of the compound was checked by single spot TLC. The Product was confirmed by chemical and spectral analysis.

## RESULT AND DISCUSSION

### *Cyclic Voltammetry*

Cyclic Voltammograms were recorded with an applied potential 0.0V Intial potential, 0.5V and final potential as -1.3V at different pH, concentrations and scan rates. Table 1 summarized the Voltammetric data for m-nitrophenol in acidic, basic as well as neutral medium at 0.1mM Concentration and 90mV/Sec Scan Rate.

### Effect of the pH

pH was varied in the range of 3.9 to 11.1 using B.R. Buffer at the Scan Rate of 90mV/s as shown in Fig. 1 to 3. Electrochemical reduction of m-nitrophenol is easier in basic medium because of these reasons.

(i) In acidic medium (pH = 3.9) at concentration 0.1mM, no peak was obtained.
(ii) In neutral medium (pH = 7.0) at concentration 0.1mM one cathodic wave (IInd) is appeared which is irreversible.
(iii) In basic medium (pH = 9.1) at concentration 0.1mM three cathodic waves are appeared, all wave are irreversible.

Hence, there are no peaks in acidic, less defined peaks in neutral medium but prominent peaks were obtained in basic medium.

(iv) Stainless Steel can be easily used as cathode in basic medium for constant current electrolysis due to its corrosive tendency in acidic media.
(v) For constant current electrolysis the reduced product m-HPHA was obtained in reasonably good yield (90%) in basic medium.

The cathodic peak potential ($Ep_c$) shifted towards more negative potential and then constant at pH 7 to 11 at 0.1mM and scan rate 90mV/s as shown in Fig. 4. This behaviour shows that the reaction is adsorption control. Table 2 summarized the voltammetric data for m-nitropheniol at different pH.

### Effect of Concentration

Three reduction waves are obtained for basic medium (pH = 9.1) as shown in Figs. 5,2,6 and 7 at different concentrations. When the concentration is increased from 0.05 to 0.15mM, the peak current (Ip) also increases (for second peak). As the concentration increased further from 0.15 to 0.2 mM, Ip remains constant. This show that the reaction is adsorption control, as shown in Fig. 8. Table 3 summarized the voltammetric data for m-nitropheniol in basic medium (pH = 9.1) at different concentrations at 90mV/S Scan rate.

### Effect of scan rates

The Scan rate varies from 50 to 90mV/s. The peak current was gradually shifted towards higher values as shown in Fig 5.

### *Constant Current Electrolysis*

The result of the preparative electrolysis at constant current of 1.9 Ampere using S.S. electrode led to the isolation of m-Hydroxy phenyl hydroxyl amine (m-HPHA). This is the 4-electron change process in basic conditions. Purity is checked by single spot TLC. The product is confirmed by the chemical and spectral analysis.

### Chemical analysis

(1) The product reduced Tollen's reagent confirming that it was m-HPHA.
(2) The product gives a precipitate with $FeCl_3$, which confirms the presence of m-HPHA.
(3) The product did not respond to the dye test indicating the absence of primary amino group and thus there was no formation of m-aminophenol.

### Spectral analysis

The peak due to the nitro group which were originally present in the starting material (m-nitrophenol) were no longer found in the products indicating that the reaction being completed.

The Hydroxyl amine derivative was confirmed by a broad band in the region 3600-3000cm$^{-1}$ and the primary amine salt had sharp peaks in the region 3000-2800 cm$^{-1}$.

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**Table1: Current-potential measurements in cyclic voltammetry**

X-axis = 0.1V/cm Applied E = 0.0V +E = 0.5V -E = -1.5V

| pH | Fig. no. | Cathodic wave | | | Remark |
|---|---|---|---|---|---|
| | | Wave no.. | Potential (V) | Current (μ A) | |
| 7.0 | 1(a) | I | Not appeared | | There are no anodic waves observed. All the Cathodic wave observed are irreversible |
| | | II | -0.43 | 12.5 | |
| 9.1 | 2 (a) | I | -0.25 | 2.3 | |
| | | II | -0.64 | 14.5 | |
| | | III | -0.96 | 20.2 | |
| 11.1 | 3 (a) | I | -0.25 | 2.5 | |
| | | II | -0.64 | 14.5 | |

**Table 2 : Relation between pH and Peak potential for peak II**

| **pH** | **$Ep_c$ (V)** |
|---|---|
| 7 | -0.43 |
| 9 | -0.64 |
| 11 | -0.64 |

**Table 3 : Current measurement with Concentration for peak II**

| **Concentration (mM)** | **$I_P$ (μA)** |
|---|---|
| 0.05 | 9.4 |
| 0.1 | 14.5 |
| 0.15 | 16.6 |
| 0.2 | 16.6 |

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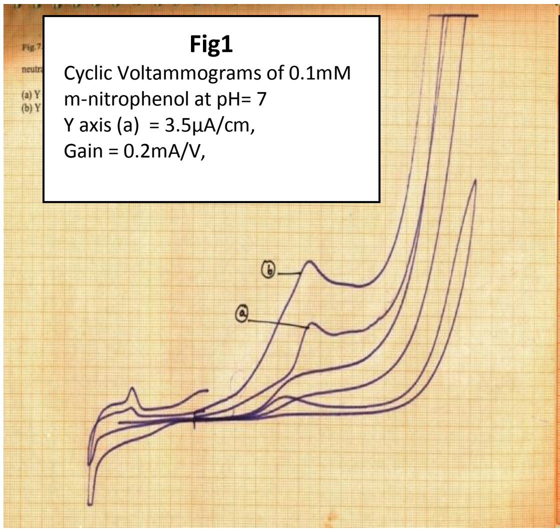


**Fig1**
Cyclic Voltammograms of 0.1mM m-nitrophenol at pH= 7
Y axis (a) = 3.5µA/cm,
Gain = 0.2mA/V,

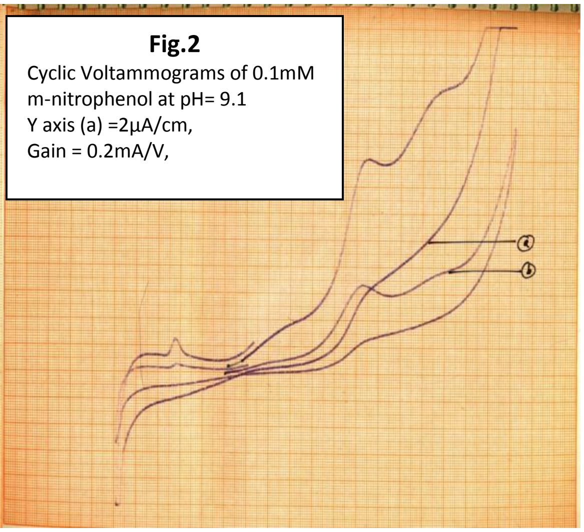


**Fig.2**
Cyclic Voltammograms of 0.1mM m-nitrophenol at pH= 9.1
Y axis (a) =2µA/cm,
Gain = 0.2mA/V,

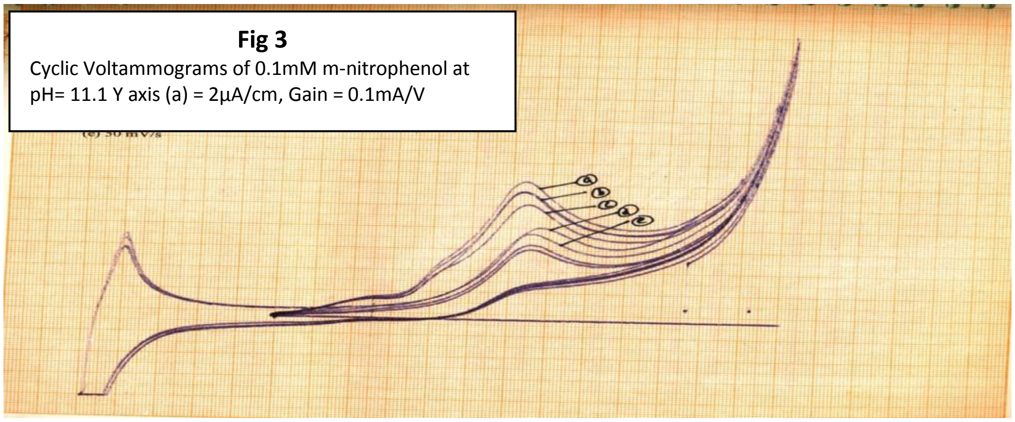
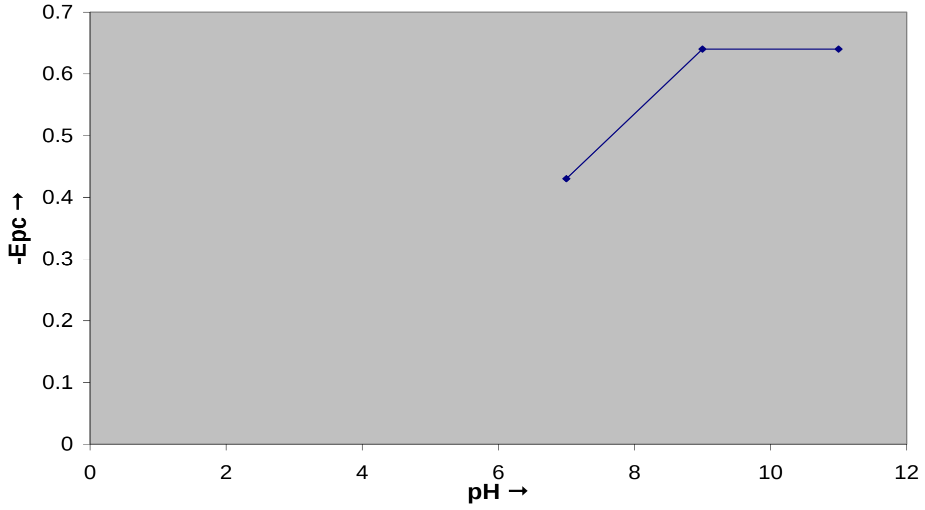


**Fig 3**
Cyclic Voltammograms of 0.1mM m-nitrophenol at pH= 11.1 Y axis (a) = 2µA/cm, Gain = 0.1mA/V

**Fig.4 Graph between pH and Epc**



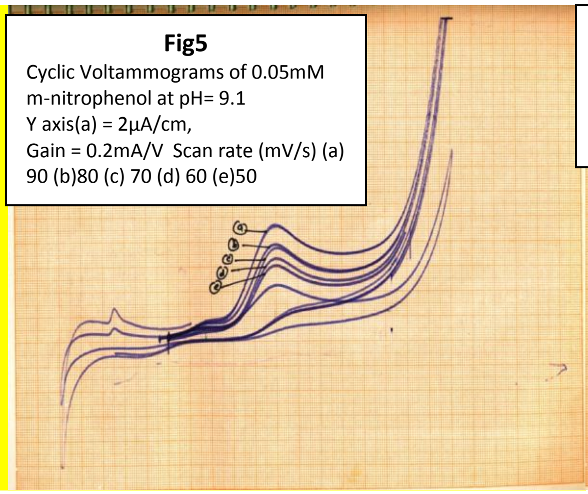


**Fig5**

Cyclic Voltammograms of 0.05mM m-nitrophenol at pH= 9.1
Y axis(a) = 2µA/cm,
Gain = 0.2mA/V Scan rate (mV/s) (a) 90 (b)80 (c) 70 (d) 60 (e)50

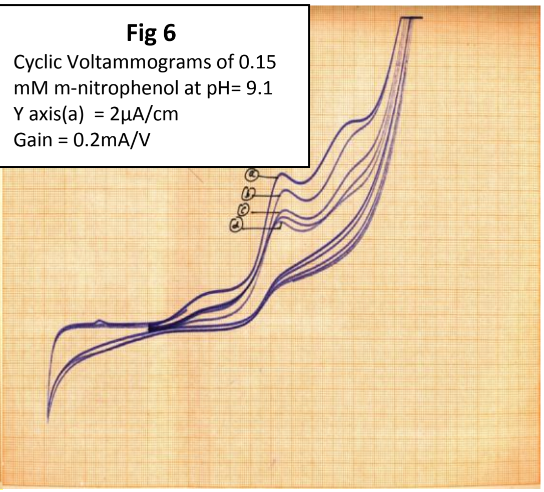


**Fig 6**

Cyclic Voltammograms of 0.15 mM m-nitrophenol at pH= 9.1
Y axis(a) = 2µA/cm
Gain = 0.2mA/V

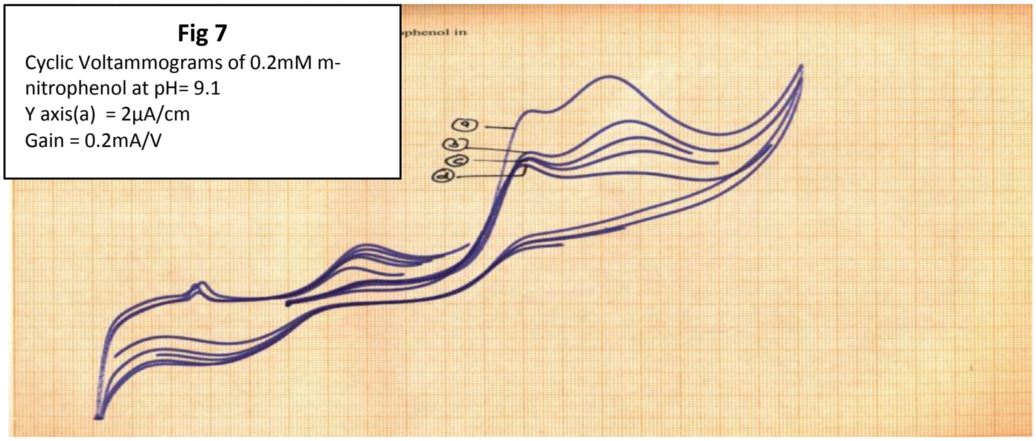
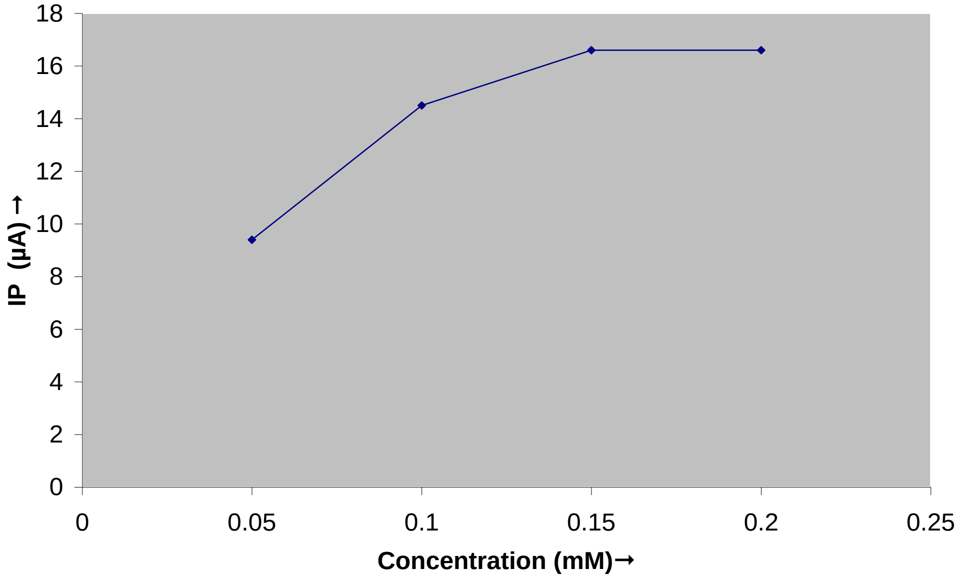


**Fig 7**

Cyclic Voltammograms of 0.2mM m-nitrophenol at pH= 9.1
Y axis(a) = 2µA/cm
Gain = 0.2mA/V

**Fig.8 Graph between Concentation and Ip**



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