

## Voltammetric Behaviour of *m*-Nitroaniline in Aqueous Methanol Medium at Various Electrodes

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Voltammetric curves of *m*-nitroaniline in aqueous-methanol medium for acidic, basic and neutral ranges using B.R. Buffer for various concentrations (0.05, 0.1, 0.15, 0.2 mM) and scan rates were obtained. Constant current electrolysis of 0.02 mM *m*-nitroaniline in basic medium gives *m*-azoxyaniline (3,3'-diamino-azoxybenzene), respectively as a major product which were confirmed by TLC and IR spectra.

**Key Words:** Electrochemical reduction, *m*-Nitroaniline, Cyclic voltammetry, Constant current electrolysis, SS cathode.

### INTRODUCTION

Numerous investigations have been made on the reduction of the aromatic nitro compounds and number of different products have been obtained under various conditions. Stainless steel electrode have been used successfully in our laboratory for the electrochemical reduction of some nitro compounds<sup>1-10</sup>.

The present work deals with the electrochemical reduction of *m*-nitroaniline at stainless steel electrode, products depending upon the conditions of the reduction. Voltammographic studies of *m*-nitroaniline were carried out in acidic, neutral and basic medium.

### EXPERIMENTAL

Solutions were prepared from AR methanol and double distilled water. Reagents such as NaOH, CH<sub>3</sub>COONa, CH<sub>3</sub>COOH, H<sub>3</sub>PO<sub>4</sub> and boric acid were of AR grade. *m*-Nitroaniline, recrystallized from methanol and purity was checked by single spot TLC. IR spectra of *m*-nitroaniline 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 glassy carbon as the working electrode Ag/AgCl as reference electrode and Pt wire as the counter electrode.

Voltammograms of *m*-nitroaniline are recorded in 1:1 (v/v) water:methanol at 0.05 mM, 0.1 mM, 0.2 mM concentrations. BR Buffer was used to maintain desired pH viz., 3.1, 7.0, 9.1, 11.1.

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An ELICO MODEL CL-95 Potentiostat cum galvanostat coupled with a sweep generator and x-y recorder were used to carrying out controlled current electrolysis. Stainless steel (SS316) electrode was used as cathode. The solution was stirred by a Remi 2LH hot plate stirrer throughout the electrolysis. FT-IR spectra of *m*-nitroaniline and the product was obtained and compared for analysis, identification and characterization.

The preparative electrolysis of 200 mL of 0.02M *m*-nitroaniline was carried out at constant current 2 Ampere in basic medium (pH = 10) for 5.25 h. After the electrolysis the volume of the catholyte was reduced to almost one third of the original volume by distilling at reduced pressure. A bulky precipitate was obtained. It was cooled under ice and filtered in a pre weighed sintered crucible. The precipitate was washed with ether, filtered through pump, dried and weighed. Product was recrystallized from ethanol. The purity was checked by singal spot TLC and m.p. of yellow colour product was 150 °C indicating that it was 3,3'-diaminoazoxybenzene (*m*-azoxyaniline).

## RESULTS AND DISCUSSION

Cyclic voltammograms were recorded with an applied pot. 0.3 V Intial pot., 0.5 V and final pot. -1.5 V at different, pH, concentrations and scan rates. Table-1 summarized the voltammetric data for *m*-nitroaniline in acidic, basic as well as neutral medium.

TABLE-1  
CURRENT-POTENTIAL MEASUREMENTS IN CYCLIC VOLTAMMETRY  
X-axis = 0.1 V/cm, Scan rate = 90 mV/S, Applied E = 0.3 V,  
+E = 0.5 V, -E = -1.5 V, Concentration = 0.1 mM

pH	Fig. No.	Cathodic wave			Anodic wave			Remark
		Wave No.	Potential (V)	Current (A)	Wave No.	Potential (V)	Current (A)	
3.1	1(b)	I	Not appeared		I	Not appeared		Cathodic wave is irreversible
		II	-0.49	47.5	II	Not appeared		
6.9	2(a)	I	-0.04	7.5	I	Not appeared		I cathodic wave is irreversible but II is reversible
		II	-0.61	59.0	II	0.35	19	
9.1	3(d)	I	-0.12	6.75	I	-0.47	2	II cathodic wave is reversible but I is irreversible
		II	-0.59	23.75	II	Not appeared		
		III	-.99			Not appeared		

**Effect of the pH:** Electrochemical reduction of *m*-nitroaniline is easier in alkaline medium because of these reasons. (1) In acidic medium (pH = 3.1) at concentration 0.1 mM, one cathodic wave (IInd) is appeared which is irreversible as shown in Fig. 1. (2) In neutral medium (pH = 7.0) at concentration 0.1 mM two cathodic waves are appeared but both are irreversible as shown in Fig. 2. (3) In basic medium (pH = 9.1) at concentration 0.1 mM three cathodic waves are

appeared, in which IInd wave is reversible as shown in Fig. 3. Hence, in acidic and neutral medium less defined peaks are obtained but in basic medium prominent peaks are appeared. (4) Stainless steel can be easily used as cathode in basic medium for constant current electrolysis due to its corrosive tendency in acidic media. (5) For constant current electrolysis the reduced product *m*-azoxyaniline was obtained in reasonably good yield (90 %).

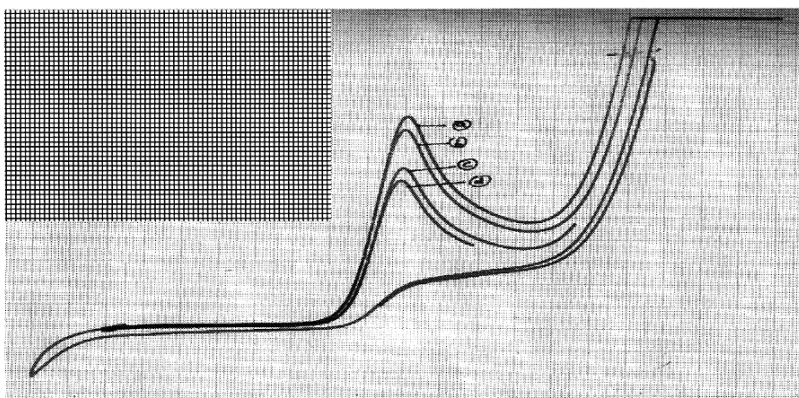


Fig. 1. Cyclic voltammograms of 0.1 mM *m*-nitroaniline at pH = 3.1, Y axis = 50 mV/cm, Gain = 0.1 mA/V, Scan rate = (a) 100 mV/s (b) 90 mV/s (c) 80 mV/s (d) 70 mV/s

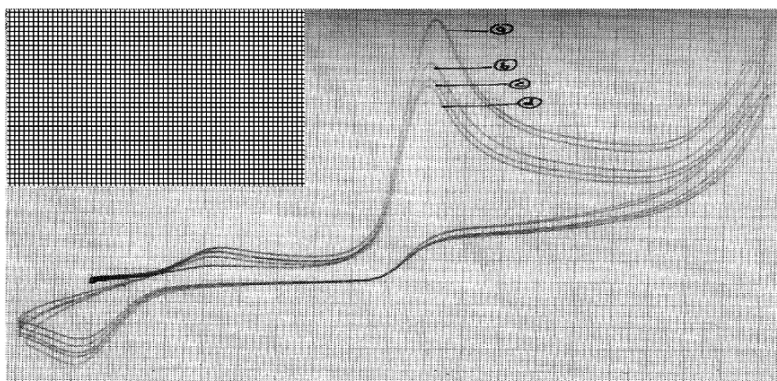


Fig. 2. Cyclic voltammograms of 0.1 mM *m*-nitroaniline at pH = 7.0, Y axis = 50 mV/cm, Gain = 0.1 mA/V, Scan rate = (a) 90 mV/s (b) 80 mV/s (c) 70 mV/s (d) 60 mV/s

**Effect of concentration:** In alkaline medium (pH = 11.1), at lower concentration (0.05 mM) three reduction waves are obtained, first and second are reversible. When we increase the concentration (0.1, 0.15, 0.2 mM) the prominent peaks are not appeared as shown in Fig. 4 and 5. Table-2 summarized the voltammetric data for *m*-nitroaniline in basic medium (pH = 11.1) at different concentrations.

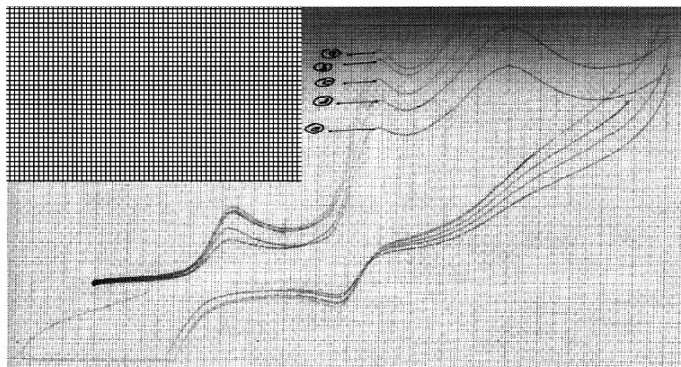


Fig. 3. Cyclic voltammograms of 0.1 mM *m*-nitroaniline at pH= 9.1, Y axis = 25 mV/cm, Gain = 0.1 mA/V, Scan rate = (a) 105 mV/s (b)100 mV/s (c) 95 mV/s (d) 90 mV/s (e) 80 mV/s

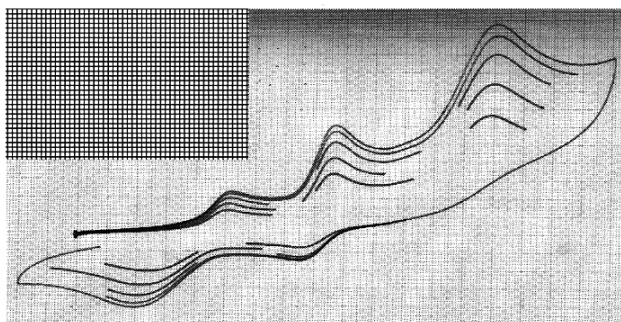


Fig. 4. Cyclic voltammograms of 0.05 mM *m*-nitroaniline at pH = 11.1, Y axis = 50 mV/cm, Gain = 0.05 mA/V, Scan rate = (a) 100 mV/s (b) 90 mV/s (c) 80 mV/s (d) 70 mV/s

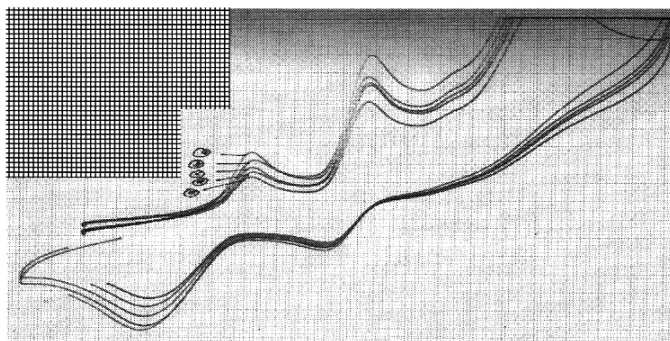


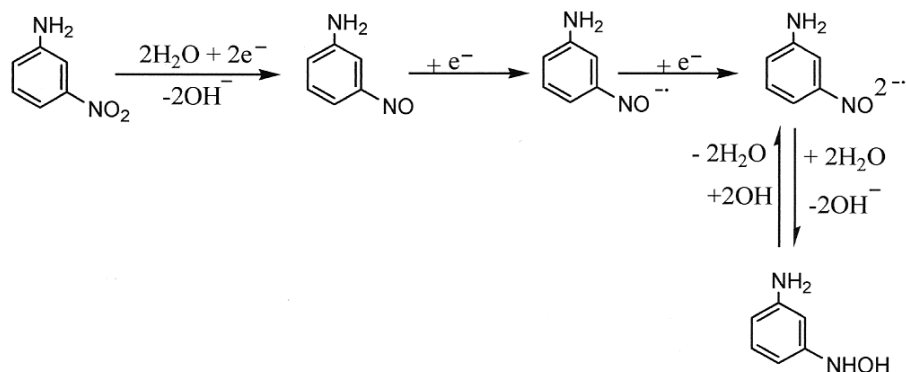
Fig. 5. Cyclic voltammograms of 0.1 mM *m*-nitroaniline at pH = 11.1, Y axis = 25 mV/cm, Gain = 0.1 mA/V, Scan rate = (a) 100 mV/s (b) 90 mV/s (c) 80 mV/s (d) 70 mV/s (e) 60 mV/s

TABLE-2  
CURRENT-POTENTIAL MEASUREMENTS IN CYCLIC VOLTAMMETRY  
X-axis = 0.1 V/cm, Scan rate = 90 mV/S, Applied E = 0.3 V,  
+E = 0.5V, -E = -1.5V, pH = 11.1

pH	Fig. No.	Cathodic wave			Anodic wave			Remark
		Wave No.	Potential (V)	Current (A)	Wave No.	Potential (V)	Current (A)	
0.05	4(b)	I	-0.22	6.5	I	-0.46	3.25	Ist and IInd Cathodic waves are reversible but IIIrd is not reversible
		II	-0.57	15.5	II	0.1	10	
		III	-1.11	30	III	Not appeared	Not appeared	
0.1	5(b)	I	-0.22	10.5	I	-0.44	3.25	I and II both waves are reversible
		II	-0.58	25	II	0.13	14	

**Effect of scan rates:** As the sweep rate was gradually increased to 70, 80, 90, 100 mV/s peak gradually shifted towards higher values as shown in Fig. 1.

**Chemical reaction:**



The result of the preparative electrolysis at constant current of 2 ampere using S.S. electrode led to the isolation of yellow precipitate compound *m*-azoxyaniline m.p. (150 °C). The compound 3,3'-diaminoazoxybenzene (*m*-azoxyaniline) re-crystallized from ethanol. Purity is checked by single spot TLC.

**Infrared spectra:** The following absorption bands were observed in the IR spectrum of the yellow compound *m*-azoxyaniline. 3080(s)  $\text{cm}^{-1}$  shows C-H stretching, 1650-1440 (b.s.)  $\text{cm}^{-1}$  shows aromatic ring and band at 1510-1498(s)  $\text{cm}^{-1}$  is assigned to azoxy group

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**REFERENCES**

1. A. Tondon, P.S. Verma, S.K. Mukharjee and K.N. Tondon, *Trans. SAEST*, **26**, 141 (1991).
2. V.S. Gurjar, P.S. Verma, S.K. Mukharjee and K.N. Tondon, *Trans. SAEST*, **28**, 145 (1993).
3. N. Singhal, I.K. Sharma and P.S. Verma, *Trans. SAEST*, **32**, 77 (1997).
4. R. Malik, I.K. Sharma and P.S. Verma, *Bull. Electrochem.*, **15**, 529 (1999).
5. S.R. Yadav, R. Yadav., A. Sharma, I.K. Sharma and P.S. Verma, *Bull. Electrochem.*, **18**, 87 (2002).
6. S.R. Yadav, P. Goyal, A. Sharma, I.K. Sharma and P.S. Verma, *J. Indian Chem. Soc.*, **79**, 695 (2002).
7. M. Vijay, A. Sharma, I.K. Sharma and P.S. Verma, *J. Electrochem. Soc. (India)*, **55**, 70 (2006).
8. M. Vijay, B. Sahay, M. Gupta, I.K. Sharma and P.S. Verma, *Asian J. Exp. Sci.*, **21**, 377 (2007).
9. M. Vijay, G. Wadhvani, V. Chippa, N. Jain, I.K. Sharma and P.S. Verma, *Asian J. Exp. Sci.*, **21**, 389 (2007).
10. M. Vijay, N. Kharia, S. Varshney and P.S. Verma, *J. Indian Chem. Soc.*, **46A**, 778 (2007).

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