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ELECTROCHEMICAL STUDIES OF NITRO BENZOIC ACIDS AT DIFFERENT pH ON GLASSY CARBON AND STAINLESS STEEL (SS-316) ELECTRODE

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ABSTRACT

Reduction behaviors of *o, m* and *p* nitro benzoic acids have been investigated electrochemically on glassy carbon and stainless steel (SS-316) electrodes. The aqueous methanolic solution (1:1) of *o,m* and *p* nitro benzoic acids (1mM each) was used to observe the effects of scan rates at pH 5.0,7.0 and 9.0. At various scan rates, peak potential (*Ep*) shifted towards the cathodic side which indicates that these reductions are irreversible and diffusion-controlled processes. The linear nature of I_{pc} vs.√V plots and constant values of I_{pc} vs.√V indicates nitrobenzoic acids reduction is a diffusion-controlled process.

In acidic and alkaline medium electrolysis at a constant current of *o,m* and *p* nitro benzoic acids give *o,m* and *p* aminobenzoic acids and 2,2',3,3'and 4,4'-dicarboxyazobenzene respectively. The resulting products were analyzed by spectroscopic techniques (IR, NMR).

Keywords: Reduction, Constant Current Electrolysis, Glassy Carbon Electrode and Stainless-steel Electrode (SS-316)

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INTRODUCTION

Nitro compounds's electrolytic reduction played a vital role in the development of electrochemistry of the organic compounds[1]. The study of stepwise reduction of nitrobenzene led Haber[2] to the idea that the deciding factor in the determination of the product was the potential of the working electrode. Thus he also became the first one to apply this principle to organic electrolysis. The electrochemical reduction of nitrobenzene has been extensively studied, perhaps for two reasons: (i) because of the complexity of the reduction, and (ii) because of its importance in organic synthesis [3-10]. The following compounds have been obtained from the reduction of nitrobenzene: aniline, *p*-aminophenol, hydroxylamine, azoxybenzene, azobenzene and hydroazobenzene. By careful choice of potential nitrobenzene an inexpensive compound, whose reduction can lead to a variety of, expensive products. For example, *p*-aminophenol is used, as a monomer, in a number of polymerization reactions.

The reductions of nitro and *m*-dinitrobenzenes in neutral and basic media have been extensively studied, using cost-effective stainless steel electrode (SS-316 type) [11-16]. In the present work, an attempt has been made to wider this area of knowledge by studying the electrochemical behavior of those aromatic compounds in which other groups are also present on the benzene ring in addition to the nitro functional group i.e –COOH group is also present on the ring along with nitro group i.e. *o*-,*m*- and *p*-nitrobenzoic acid. Reduction behaviors of *o*, *m* and *p* nitro benzoic acids have been investigated electrochemically on glassy carbon and stainless steel (SS-316) electrodes. Potential scan rate, solution's pH which are operational factor that affects the results were evaluated and were optimized.

EXPERIMENTAL

Materials and Instrumentations

o-, *m*- and *p*-nitro benzoic acid, KCl, etc. used were of AR grade and their purity was further checked by single spot TLC. All the solutions used in experiments were prepared in doubly distilled water. Potassium Chloride (1M) was used as a supporting electrolyte. the pH of the solution at 5.0,7.0 and 9.0 was maintained using Britton-Robinson (BR) buffer.

All electrochemical measurements were carried out with the basic electrochemical system ECDA-001

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(Conserve Enterprises, Mumbai, India) potentiostat. A conventional three-electrode system was used for all electrochemical measurements, in which an Ag/ AgCl /3M KCl was used as a reference electrode, a glassy carbon electrode used as a working electrode and a platinum wire used as the counter electrode. For constant current electrolysis, Galvanostat was used that assembled by CDPE (Center for Development of Physics Education), University of Rajasthan, Jaipur. The constant current electrolysis carried out in a two-compartment H-shaped glass cell provided with a fritted glass disc (G-4) was used as an electrolysis vessel. Stainless steel (SS-316) rectangular plates (size 4 cm × 4 cm) were used as cathode and anode electrodes [17-29]. Approximately two-thirds area of the electrode was immersed in the electrolytic solution. A magnetic stirrer (Remi model) was used to stir the electrolytic solution. Elico digital pH meter was used for pH measurements. FT-IR spectra were recorded on TENSOR 27, Bruker, USA. NMR data were obtained from ECS 400MHz (JEOL), USA.

General Procedure

For Voltametric Studies

KCl [1 ml (1.0 M) aqueous solution] and BR buffer (5.0 ml of the desired pH) were taken in the electrochemical cell and this mixture was added to double-distilled water the volume of the mixture was set up to 10 ml. After purging this solution, by bubbling nitrogen for 10 minutes to remove the dissolved oxygen, it was used to record the cyclic voltammogram of the blank solution. Appropriate volume of the chosen nitrobenzoic acid solution (0.1 M solution) was added to the blank solution to get the experimental solution of nitrobenzoic acid of desired concentration (1mM). This was again deoxygenated and used for recording the voltammograms. Most of the cyclic voltammograms were recorded within the range of 1400 to -1000 mV. The effect of potential scan rate and pH was studied on reduction potential and the nature of the electrochemical reduction process.

Constant Current Electrolysis

The preparative electrolysis of nitrobenzoic acids (200mL 0.1M) was carried out at constant current (1amp.) in acidic media (pH=5.0) containing (1M CH_3COONa+1M CH_3COOH) and alkaline media (pH=9.0) containing (1M CH_3COONa+0.5 M NaOH) in 1:1CH_3OH:H_2O media. The constant current (1amp.) was passed through the electrolyte with the help of galvanostat for 10-12 hours. Once the electrolysis was over, distillation was done to remove methanol. Ether was used to extract catholyte wherein ether was removed by a simple evaporation method, the leftover product was recrystallized using alcohol. In the acidic medium products (*o,m* and *p*-aminobenzoic acids) and alkaline medium products (2,2', 3,3'and 4,4'-dicarboxyazobenzene) were identified based on spectroscopic techniques (IR, NMR). Tables-1, 2, 3, 4, 5 and 6 summarize all the characteristic data for the electrochemically obtained products.

Table-1: Characterization Table for Reduction of *o*-nitrobenzoic Acid in Acidic Medium

Name of Substrate	IR (cm^{-1})	NMR (δ)	Product Identified	Yield (%)
o-nitro benzoic acid	3800-3205 (O-H), 3275-3155 d (N-H), 3100-3050(aromatic =C-H), 3060 (C-H) 1737 (C=O), 1675 b (N-H),1293 (C-N),1216 (C-O),980-920 b (O-H) 800-730 *(o*-substitution)	8.9 (1H),4.5 (2H) 7.7 (1H),6.9 (1H) 6.6 (1H),5.9 (1H)	*o*-amino benzoic acid	88.7

Table 2: Characterization Table for Reduction of *o*-nitrobenzoic Acid in Alkaline Medium

Name of Substrate	IR (cm^{-1})	NMR (δ)	Product Identified	Yield (%)
o-nitro benzoic acid	3812-3250(O-H), 3100-3050 (aromatic=C-H), 3060(C-H), 1510-1420(N=N),1280(C-N), 1725 (C=O), 1220 (C-O), 980-920 b (O-H) 800-730 *(o*-substitution)	6.0-8.4 (8H) 9.0-11.0 (2H)	2,2'-dicarboxy azobenzene	89.6

Table-3: Characterization Table for Reduction of *m*-nitrobenzoic Acid in Acidic Medium

Name of Substrate	IR (cm^{-1})	NMR (δ)	Product Identified	Yield (%)
m-nitro benzoic acid	3840-3210 (O-H), 3290,3185 d (N-H), 3100-3050(aromatic =C-H), 3069 (C-H), 1730(C=O), 1669-1590 b (N-H),1285-1215 (C-N),1285-1215(-C-O), 970-900 b (O-H),790-690 & 858-790(*m*-substitution)	9.2-10.5 (1H), 3.8 (1H),7.2 (1H), 6.6 (1H),5.2 1H), 4.9 1H)	*m*-amino benzoic acid	89.4

Table 4: Characterization Table for Reduction of *m*-nitrobenzoic Acid in Alkaline Medium

Name of Substrate	IR (cm^{-1})	NMR (δ)	Product Identified	Yield (%)
m-nitro benzoic acid	3800-3200(O-H), 3100-3050 (aromatic =C-H), 3060 (C-H), 1730 (C=O), 1500-1400 (N=N), 1280-1200(C-O),965-915 b(O-H),790-695&850-790 (*m*-substitution)	6.2-8.3 (8H) 9.2-10.8 (2H)	3,3'-dicarboxy azobenzene	91.3

RESULTS AND DISCUSSION

Effect of Scan Rate

Typical cyclic voltammograms of *o*-, *m*- and *p*-nitrobenzoic acids at different scan rates are given in Figs.-1 to 3, Figs.- 4 to 6 and Figs.-7 to 9 respectively. The shape of cyclic voltammograms indicates the irreversible nature of reduction.

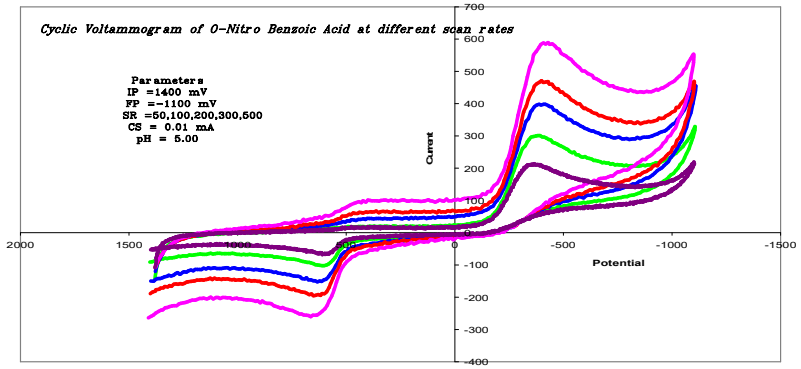


Fig.-1: Cyclic Voltammograms of *o*-nitrobenzoic acid at pH 5 with Different Scan Rates

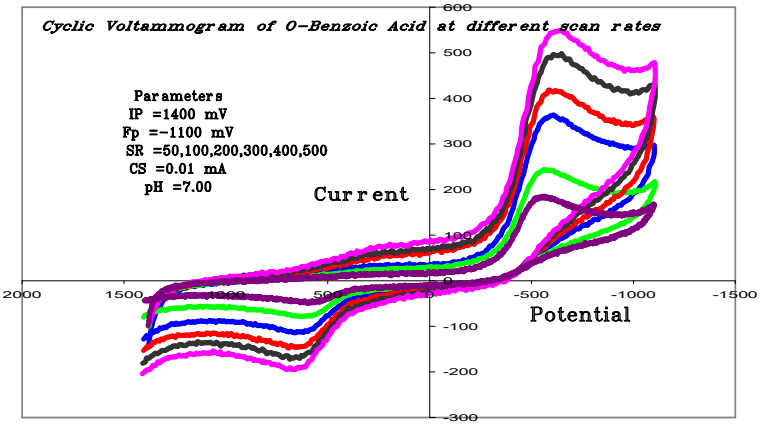


Fig.-2: Cyclic Voltammograms of *o*-nitrobenzoic acid at pH 7 with Different Scan Rates

Table-5: Characterization Table for Reduction of *p*-nitrobenzoic Acid in Acidic Medium

Name of Substrate	IR (cm^{-1})	NMR (δ)	Product Identified	Yield (%)
p-nitro-benzoic acid	3850-3290 (O-H), 3290-3170 d (N-H), 3100-3050 (aromatic =C-H),3060 (C-H), 1720 (C=O), 1690-1670 b (N-H), 1365-1330 (C-N), 1270-1205 (C-O), 1065-920b (O-H), 880-825 (*p*-position)	8.9 (1H),5.1 (2H) 6.7 (2H),5.5 (2H)	*p*-amino benzoic acid	92.6

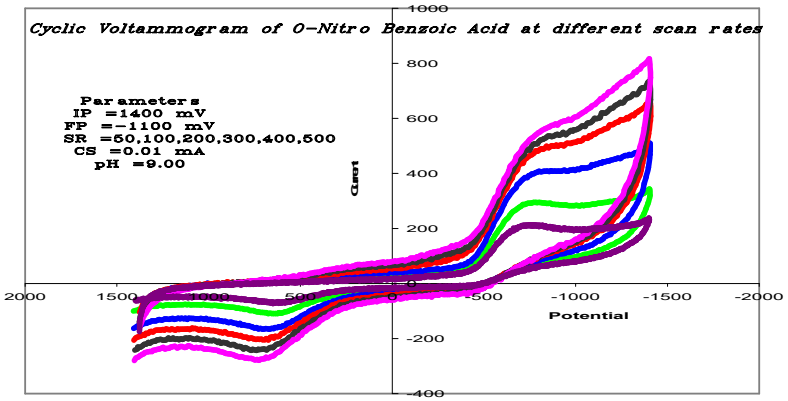


Fig.-3: Cyclic Voltammograms of *o*-nitrobenzoic acid at pH 9 with Different Scan Rates

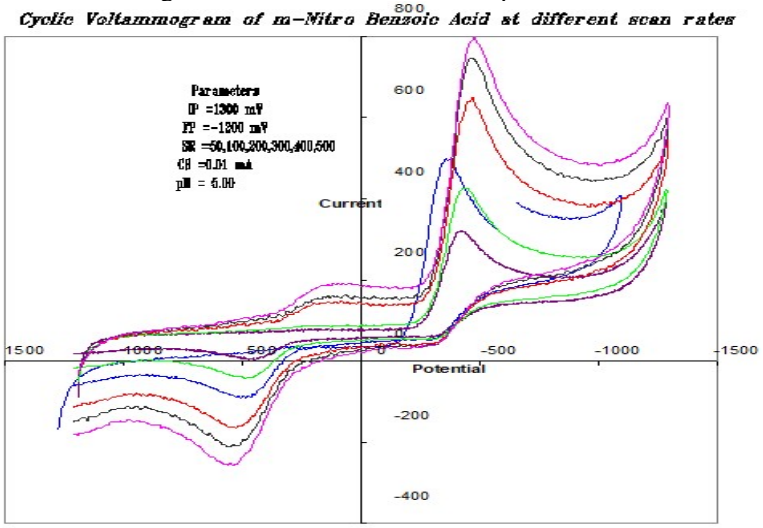


Fig.-4: Cyclic Voltammograms of *m*-nitrobenzoic acid at pH 5 with Different Scan Rates

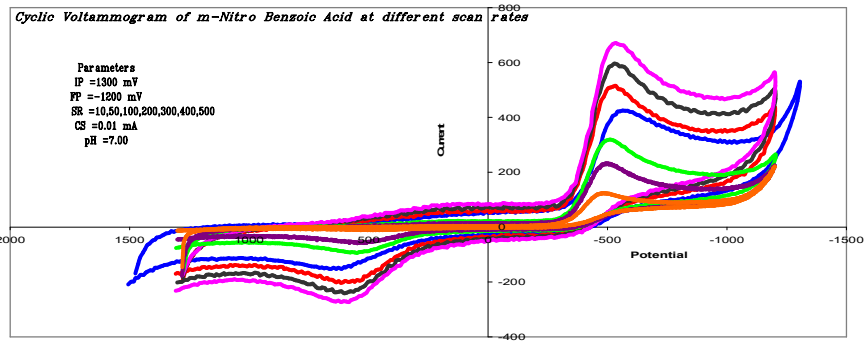


Fig.-5: Cyclic Voltammograms of *m*-nitrobenzoic acid at pH 7 with Different Scan Rates

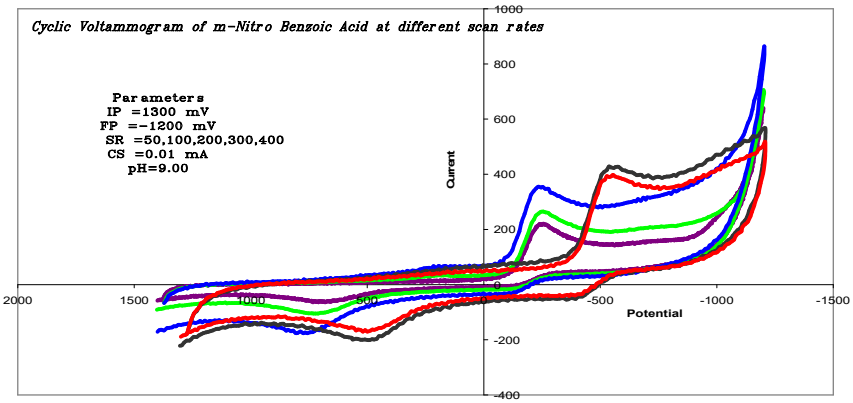


Fig.-6: Cyclic Voltammograms of *m*-nitrobenzoic acid at pH 9 with Different Scan Rates

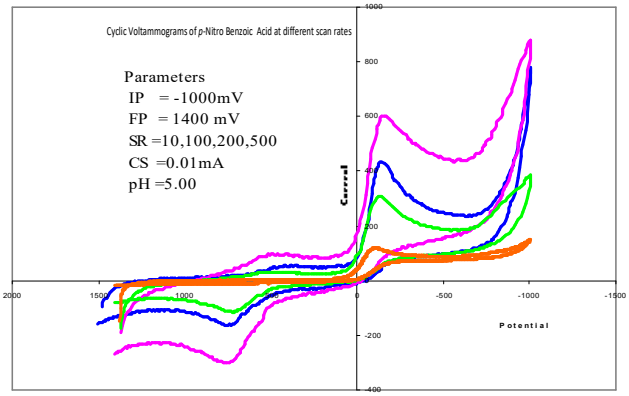


Fig.-7: Cyclic voltammograms of *p*- nitrobenzoic acid at pH 5 with Different Scan Rates

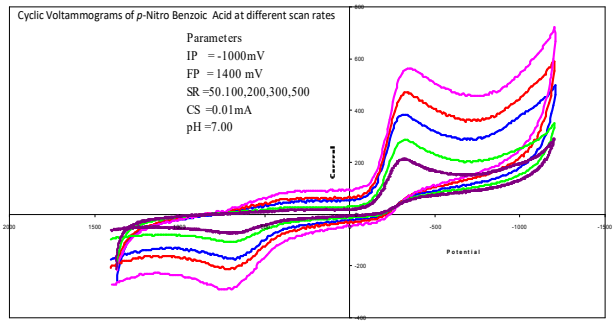


Fig.-8: Cyclic Voltammograms of *p*-nitrobenzoic acid at pH 7 with Different Scan Rates

Table-6: Characterization Table for Reduction of *p*-nitrobenzoic Acid in Alkaline Medium

Name of Substrate	IR (cm^{-1})	NMR (δ)	Product Identified	Yield (%)
p-nitro-benzoic acid	3850-3290(O-H),3100-3050 (aromatic =C-H),3060 (C-H), 1720(C=O),1552-1455(N=N) 1365-1330(C-N),1270-1205(-C-O),1065-920b (O-H),880-825 (*p*-substitution)	6.5-8.5 (8H) 9.2-11.2 (2H)	4,4'-dicarboxy azobenzene	90.4

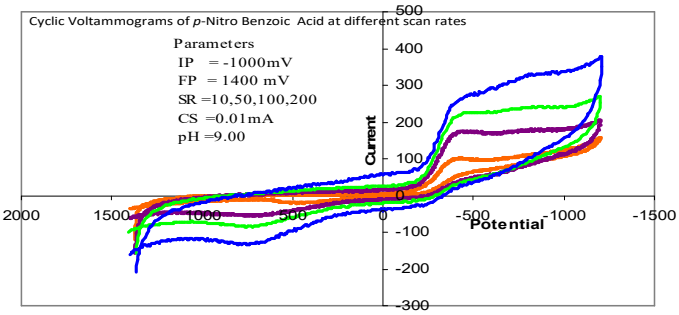


Fig.-9: Cyclic voltammograms of *p*-nitrobenzoic acid at pH 9 with Different Scan Rates

Tables-7, 8 and 9 summarize voltammetric data for *o*-, *m*- and *p*-nitrobenzoic acids respectively; in acidic, neutral and basic media. Data are given here show the effects of scan rates. The linear nature of I_{pc} vs. $\sqrt{V}$ plots and constant values of $I_{pc}/\sqrt{V}$ indicates that the reduction of nitrobenzoic acids studied is diffusion-controlled process.

Table-7: Cyclic Voltammographic Characterizations of *o*- nitrobenzoic Acid

Initial Potential E_i =1400 mV, Final Potential E_s =-1100 mV

S. No.	pH	Scan Rate (in mV/sec)	Peak Potential (E_p) (in mV)	Half Peak Potential ($E_{p/2}$) (in mV)	Cathodic Peak Potential (I_{pc}) (in µA)	$I_{pc}/\sqrt{V}$	Effect of Scan Rate	Remark
1.	5	100	-412	-272	92	9.2	cathodic shift of peak potential as increasing scan rates	Reduction is Irreversible
2.	5	200	-430	-288	136	9.6		
3.	5	300	-435	-299	162	9.3		
4.	5	500	-449	-310	214	9.5		
5.	7	100	-598	-447	89	8.9	as increasing scan rates peak potential shift towards negative direction	Reduction is Irreversible
6.	7	200	-622	-459	118	8.1		
7.	7	300	-635	-486	151	8.7		
8.	7	400	-655	-491	178	8.9		
9.	9	100	-822	-592	111	11.1	shift in negative direction of peak potential with increase in scan rates	Reduction is Irreversible
10	9	200	-844	-600	159	11.2		
11	9	300	-894	-644	205	11.8		
12	9	400	-922	-657	242	12.1		

Table-8: Cyclic Voltammographic Characterization of *m*- nitrobenzoic Acid

Initial Potential E_i =1300 mV, Final Potential E_s =-1200 mV

S. No.	pH	Scan Rate (in mV/sec)	Peak Potential (E_p) (in mV)	Half Peak Potential ($E_{p/2}$) (in mV)	Cathodic Peak Potential (I_{pc})(in µA)	$I_{pc}/\sqrt{V}$	Effect of Scan Rate	Remark
1.	5	50	-353	-261	59	8.3	shift in negative direction of peak potential with increase in scan rates	Reduction is Irreversible
2.	5	100	-373	-275	84	8.4		
3.	5	200	-374	-282	123	8.6		
4.	5	300	-392	-291	155	8.8		
5.	5	400	-395	-300	178	8.9		
6.	7	50	-522	-416	65	9.1	as increasing scan rates peak potential shift towards negative direction	Reduction is Irreversible
7.	7	100	-530	-421	93	9.3		
8.	7	200	-585	-431	136	9.6		
9.	7	300	-595	-437	168	9.7		
10	7	400	-598	-439	199	9.9		
11	9	50	-280	-186	73	10.3	cathodic shift of peak	Reduction is

12	9	100	-294	-188	106	10.6	potential as increasing scan rates	Irreversible
13	9	200	-298	-194	151	10.7		
14	9	300	-302	-198	187	10.7		
15	9	400	-310	-199	216	10.8		

Table-9: Cyclic Voltammographic Characterization of *p*- nitrobenzoic Acid
Initial Potential E_i =1400 mV, Final Potential E_s =-1000 mV

S. No.	pH	Scan Rate (in mV/sec)	Peak Potential (E_p) (in mV)	Half peak potential ($E_{p/2}$) (in mV)	Cathodic peak potential (I_{pc}) (in μA)	$I_{pc}/\sqrt{V}$	Effect of Scan Rate	Remark
1.	5	100	-141	-50	77	7.7	cathodic shift of peak potential as increasing scan rates	Reduction is Irreversible
2.	5	200	-161	-56	111	7.8		
3.	5	500	-177	-65	177	7.9		
4.	7	100	-345	-226	81	8.1	as increasing scan rates peak potential shift towards negative direction	Reduction is Irreversible
5.	7	200	-358	-231	116	8.2		
6.	7	300	-365	-237	146	8.4		
7.	7	500	-369	-244	189	8.5		
8.	9	100	-487	-327	86	8.6	shift in negative direction of peak potential with increase in scan rates	Reduction is Irreversible
9.	9	200	-502	-337	126	8.9		

Effect of pH

Effect of pH can be explained based on cyclic voltammogram obtained at the different pH values. Typical cyclic voltammograms of *o*-, *m*-acid and *p*-nitrobenzoic acids at varying pH (5.0, 7.0, and 9.0) are given in Figs.-10, 11 and 12 respectively. In these cyclic voltammograms prominent cathodic peaks appear which show that reduction of nitrobenzoic acids is possible in all three media (acidic, neutral and basic). Although in the acidic medium the electrode gets corrode the electrodes are economically viable & can be used as sacrificial cathode.

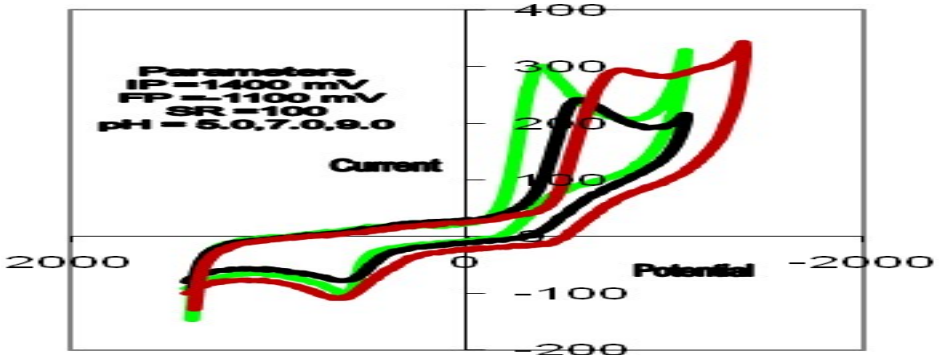


Fig.-10: Cyclic Voltammograms of *o*-nitrobenzoic Acid at Different pH

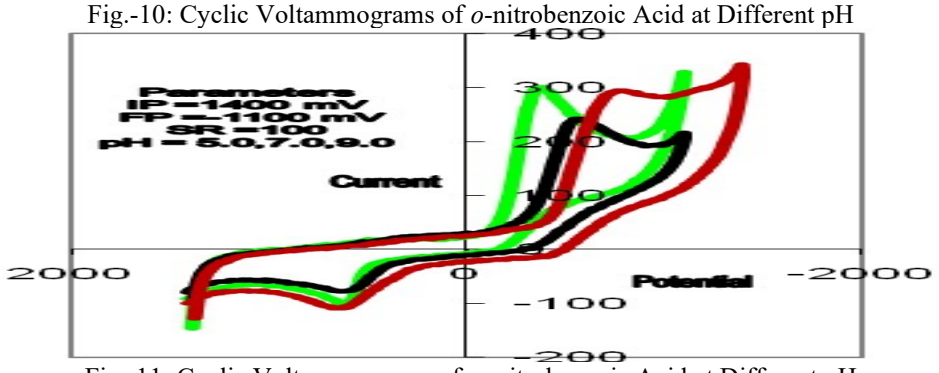


Fig.-11: Cyclic Voltammograms of *m*-nitrobenzoic Acid at Different pH

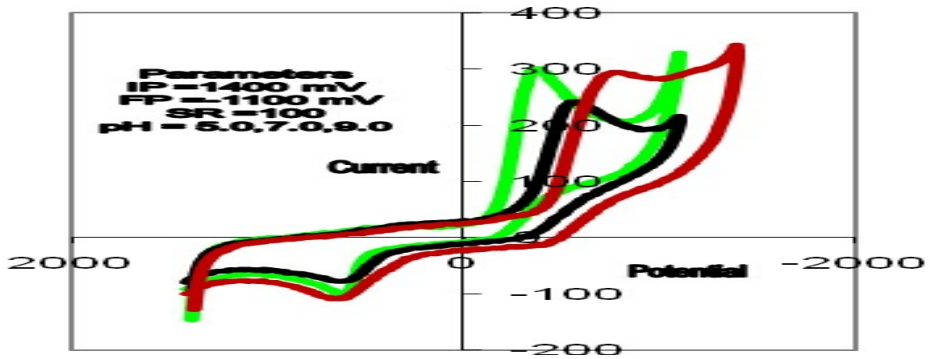
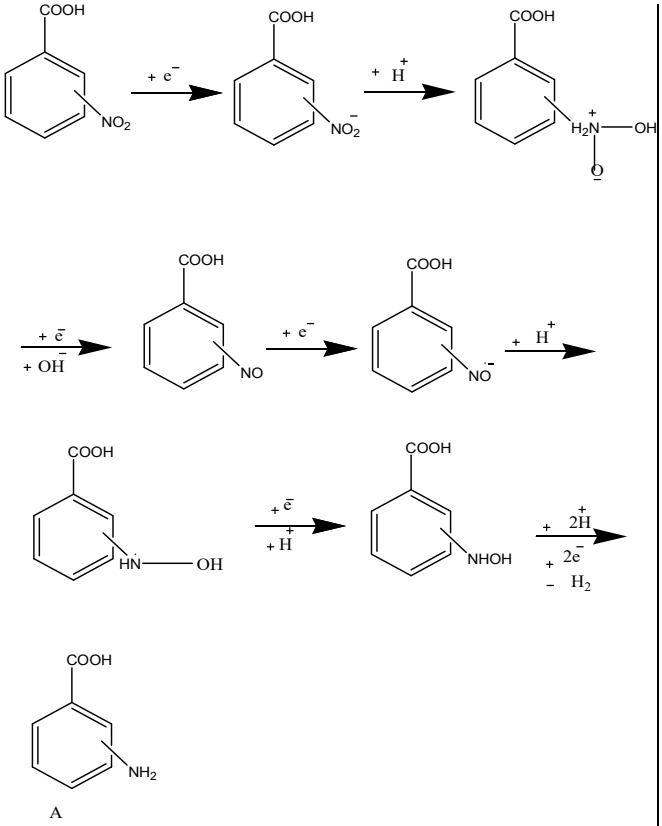
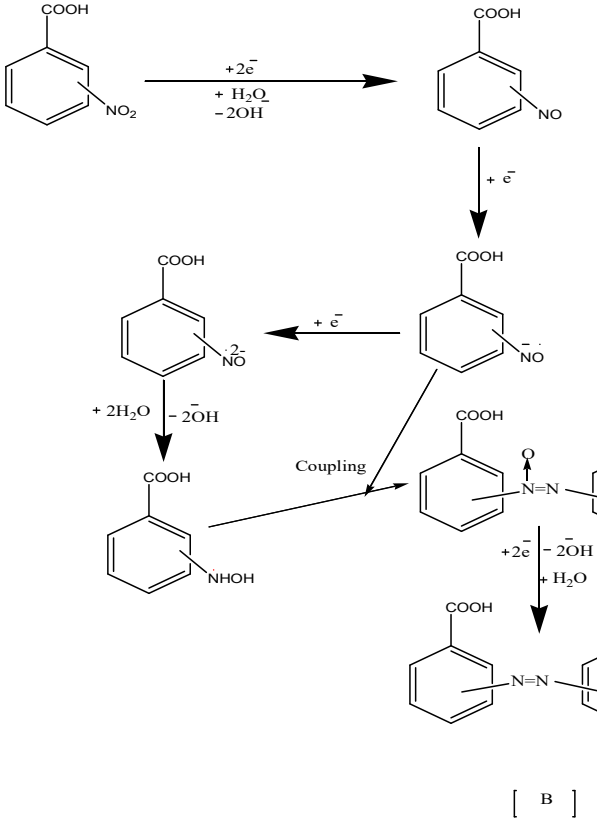


Fig.-12: Cyclic Voltammograms of *p*-nitrobenzoic Acid at Different pH

Based on cyclic voltametric studies following mechanism can be proposed:



Scheme-1: Proposed mechanism of *o*-,*m*-and *p*-nitrobenzoic acid in acidic medium



Scheme-2: Proposed mechanism of *o*-,*m*-and *p*-nitrobenzoic acid in alkaline medium

CONCLUSION

1. Electrochemical reduction of *o*,*m* and *p* benzoic acid on glassy carbon electrode is diffusion-controlled process at different pH confirmed by constant values of $I_{pc}/\sqrt{V}$.
2. Using stainless steel electrode (SS-316) in constant current electrolysis the *o,m* and *p* nitro benzoic acids give *o,m* and *p* aminobenzoic acids in acidic medium and 2,2',3,3'and 4,4'-dicarboxyazobenzene in alkaline medium. The resulting products were confirmed by IR and NMR spectroscopic techniques.
3. Stainless steel electrode (SS-316) is a very cost-effective electrode as compared to other electrodes.

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