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Voltammetric Behaviour of *o*-nitro aniline in Aqueous Methanol Medium at Various Electrodes

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Abstract : The voltammograms of *o*-nitroaniline (aqueous-methanol solution) in BR buffer at different pH *e.g.* 4.0, 7.0 and 9.0 exhibits the one reduction peak corresponding to 4e$^-$ change in acidic (pH=4.0) and 5 e$^-$ change in neutral (pH 7.0) and basic (pH 9.0) media. Constant current electrolysis in acidic and basic media of *o*-nitroaniline gives *o*-phenylenediamine and 2,2' diaminoazo benzene respectively which were confirmed by TLC, NMR and IR spectrum.

Key words : Electrochemical Reduction *o*-nitroaniline SS cathode, Cyclic Voltammetry and Constant Current Electrolysis.

Introduction

Numerous investigations (Zuman P. and Rupp E., 1995) have been made on the reduction of aromatic nitro compounds and number of different products has been obtained under various conditions. This is caused more by differences in the chemical follow-up reactions rather than by the the electrochemical reactions. It is well known that the reduction of Nitro compounds has played a vital role in the development of organic-electrochemistry (Fichter, 1942).

The present work deals with the electrochemical studies (cyclic voltammetry & constant current electrolysis at SS-316 electrode) of *o*-nitroaniline (Singhal *et al.*, 1997 and Nicholson, 1965) in acidic, neutral and basic media, which elucidate the mechanism, kinetics and product of electrode processes.

Constant current electrolysis at SS cathode *o*-nitroaniline gave different products (Swan, 1956) in different media, which have been studied in detail by means of various techniques and possible mechanism, have been proposed. Stainless steel electrode (SS-316) is a economically viable electrode has been used successfully in our laboratory (Yadav *et al*., 2002a and Yadav *et al*., 2002b)

Materials and Methods

All the reagents, NaOH, CH$_3$COONa, KNO$_3$, *o*-nitroaniline, methanol and acetic acid, etc used were of AR grade. The solutions were prepared in double distilled water. *o*-nitroaniline re-crystallized from methanol,(M.P.-71.5° C) was used for reduction purpose. Prior to electrolysis, TLC, which gave single spot, was used to check the purity of the compound.

Cyclic voltammograms were recorded on a fully computer controlled Basic Electrochemistry System - ECDA 001(supplied by conserved, Mumbai, India), using 3-electrode cell assembly with 1mm diameter glassy carbon as working electrode,

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Ag/AgCl as reference electrode and Pt wire as counter electrode.

In aqueous media, 1.0 mM concentration of depolarizer and KNO_3 was used as supporting electrolyte to maintain the ionic strength of the solution at 0.1 M. BR buffer was used to maintain desired pH viz. 4.0, 7.0, and 9.0.

Galvanostat, designed and made by CDPE (Centre for Development of Physics Education, Univ. of Rajasthan, Jaipur), was used for carrying out controlled current electrolysis. Stainless steel (SS 316) electrode was used as cathode. The solution was stirred by a Remi 2LH hot plate cum stirrer throughout the electrolysis.

FT-IR spectra of *o*-nitroaniline and the products were obtained and compared for analysis, identification and characterization.

The preparative electrolysis of 200 ml 0.1M *o*-nitroaniline was carried out at constant current (at 1 amp. For 24 hours) in alkaline solution containing (1M CH_3COONa +0.5MNaOH) as well as in acidic media containing (1MCH_3COONa +1MCH_3COOH pH=4) in 1:1 CH_3OH: H_2O

After electrolysis the methanol was removed from the solution by distillation at reduced pressure (30 mm Hg). The catholyte was then extracted repeatedly with ether layer. The ether layer was collected in watch glass and was allowed to evaporate. After evaporation product was then recrystallized with absolute alcohol and pure crystals were obtained.

Results and Discussion

Most cyclic voltammograms were recorded with an initial potential E_i of 1300mV and final (switching) potential Es of -2000 mV at different scan rates viz.50, 100, 200, 500 and 1000 mV/sec, and double cycle voltammograms were also recorded to monitor the fate of products generated in first cycle.

A prominent cathodic peak of *o*-nitroaniline at scan rate of 50 mV/sec and pH=7,4 and 9 were appeared at -650mV, -519 mV and -775 mV respectively .As the sweep rate was gradually increased to 100, 200, 500 and 1000 mV/sec peak potential gradually shifted towards higher values as is expected for an irreversible electron transfer processes.

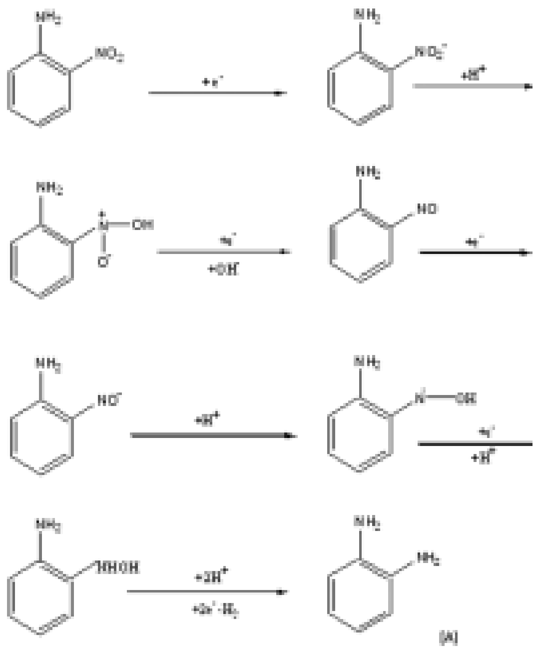
Table-1 summarizes the voltammetric data for *o*-nitroaniline in acidic, basic as well as in neutral media. Constant values of $I_{pc}/v^{1/2}$ and linear nature of I_{pc} vs. $v^{1/2}$ plots indicates that the reduction of *o*-nitroaniline is a diffusion-controlled process.

Above mentioned electrolytically reduced product was obtained in reasonably good yield. Single spot TLC checked the purity of compounds. The product of electrolysis in acidic and basic media has mpt. 103° and 134° respectively which is in good agreement to the reported mpt. of *o*-phenylene diamine (1, 2-diamino benzene) and 2, 2'-diamino azo benzene respectively.

The identity of *o*-phenylene diamine [A] was further confirmed on the basis of spectroscopic analysis. IR and NMR data given below:

IR Data

3080(s) cm^{-1} shows C-H stretching band; 1650 - 1440 (b, s) cm^{-1} shows aromatic ring; 3440(s) cm^{-1}shows asymmetrical N-H stretching, 3330(s) cm^{-1} symmetrical N-H stretching and1620 (b) cm^{-1} bending N-H stretching.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O-
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N—OH
+e-
+H+
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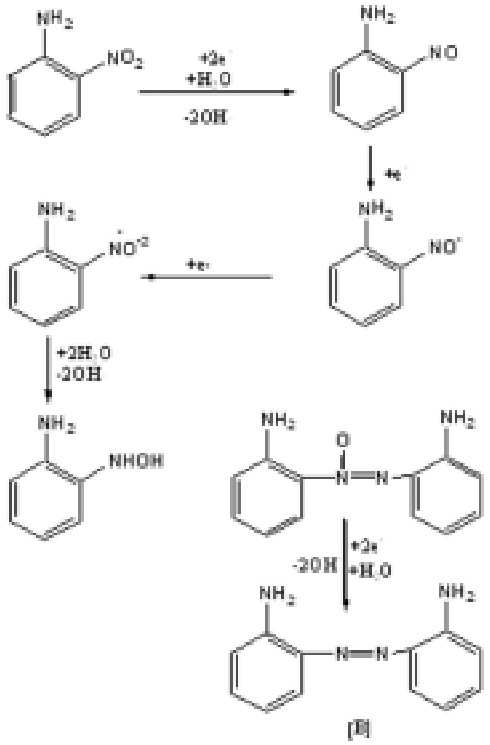
+2H+
+2e- -H2
NH2

(A)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NO
+e-
NO-
+e-
NO-2
+2H2O
-2OH
NHOH
O
N=N
+2e-
+H2O
-2OH
N=N

[B]

Table-1 : Effect of sweep rate on voltammetric parameters of o -Nitroaniline (1mM methanolic solution containing BR buffer)

Initial potential Ei : 1300mV
Switching potential Es : -2000mV

Working Electrode : Glassy Carbon
Reference Electrode : Ag/AgCl/KCl
Auxiliary Electrode : Platinum

S.No.	Media (BR Buffer) pH	Sweep Rate (mV/s)	Ep (mV/s)	Ep1/2 (mV/s)	αn_a	Ei (mV/s)	lpa (mA)	$lpa/v^{1/2}$
1	7.0	50	-650	-541	0.000438	-450	122	0.122
2	7.0	100	-641	-542	0.000482	-401	187	0.187
3	7.0	200	-656	-545	0.00043	-434	236	0.236
4	7.0	500	-730	-614	0.000411	-487	542	0.542
5	7.0	1000	-773	-637	0.000351	-513	697	0.697
6	9.0	50	-775	-609	0.000287	-560	88	0.088
7	9.0	100	-765	-610	0.000308	-530	139	0.139
8	9.0	200	-812	-641	0.000279	-478	242	0.242
9	9.0	500	-871	-659	0.000225	-564	317	0.317
10	9.0	1000	-854	-649	0.000233	-559	398	0.398
11	4.0	50	-519	-353	0.000287	-429	46	0.046
12	4.0	100	-603	-436	0.000286	-426	102	0.102
13	4.0	200	-617	-423	0.000246	-434	100	0.101
14	4.0	500	-697	-378	0.00015	-517	146	0.146
15	4.0	1000	-719	-421	0.00016	-528	160	0.160

NMR Data

2H d 6.37, 2H d 6.21 and 4H d 3.9

The formation of 2, 2'-diamino azo benzene [B] was also confirmed by spectroscopic analysis. The corresponding data are as follows:

IR Data

3080(s) cm^{-1} shows C-H stretching band; 1650 - 1440 (b, s) cm^{-1} shows aromatic ring; 1 and 1500 - 1400 cm^{-1} is assigned for azo (-N=N-) group.

NMR Data

2H d 7.68, 2H d 7.21, 2H d 6.82, 2H d 6.60 and 4H d 3.7.

On the basis of kinetic parameter, number of total electrons change during reduction and product of bulk electrolysis the most probable mechanism for the reduction of *o*-nitroaniline is given as follows:

1. Suggested mechanism for the electrochemical reduction of *o*-nitroaniline at SS-316 steel electrode at pH 4.0

2. That occurring under condition of low proton availability (basic and neutral condition)

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