ELECTROREDUCTION OF m-NITROANILINE TO m-AZOANILINE AT LEAD AND AMALGAMATED LEAD ELECTRODES

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Electrolytic reduction of nitroanilines has been studied at amalgamated gold [1], amalgamated gold ring disk [2,3], mercury and platinum [4] electrodes. Different reduction products, such as o-(hydroxylamino) aniline, o-phenylene-diamine, m-(hydroxylamino) aniline, p-phenylendiamine, were obtained under different conditions by these workers from their respective nitroanilines. Electrodes used in these studies were either costly or created environmental pollution problems such as mercury) and hence of little use for obtaining the products on a large scale. Keeping this in view, study of the electroreduction of nitroanilines at cheap metal (lead, copper, nickel) electrodes and their amalgamated forms was undertaken.

We have already reported the electroreduction of p-nitroaniline to p-phenylenediamine at amalgamated copper, Nickel [5], lead and amalgamated lead electrodes. Results of the electroreduction of m-nitroaniline at lead and amalgamated lead electrodes are presented in this communication.

Effect of parameters such as current density, temperature, depolarizer ratio, medium concentration and nature of cathode material has been studied.

EXPERIMENTAL

Reagents and Apparatus

m-Nitroaniline used was of (SISCO CHEM) laboratory grade and other chemicals were of AnalaR grade. All solutions were prepared in conductivity water. Aqueous sulphuric acid was used as catholyte and anolyte. Calomel electrode with potassium chloride salt bridge was used. Electrolysis was carried out at constant current. Experimental procedure used was same as reported earlier [5].

Isolation

After passing the current, the catholyte was neutralized with 10% sodium hydroxide solution. Orange-yellow coloured m-azoaniline was precipitated. It was filtered and washed with ice cold water and dried. Crude m-azoaniline was purified by recrystalization with alcohol.

Analysis

Recrystalized m-azoaniline was characterized by thin layer chromatography (TLC) and spectral analysis. A single clear spot obtained on silica gel-G (TLC) plate in iodine chamber using chloroform as solvent, clearly indicated the purity of the product. The stretching vibrations of azo (-N=N-) group in KBr were observed in the region of 1630-1575 cm^{-1}. It was further supported by elemental analysis, melting point and ^1H NMR studies. In $CDCl_3$, a siglet at δ = 7.60 ppm is present between azo and amino groups, multiplet in the range of 6.81-7.30 of the phenyl protons. The siglet of the amino protons is also present at δ = 3.75 ppm.

RESULTS AND DISCUSSION

Polarization curves obtained by plotting potential vs log c.d. are given in Figures 1 and 2. Different current densities were chosen

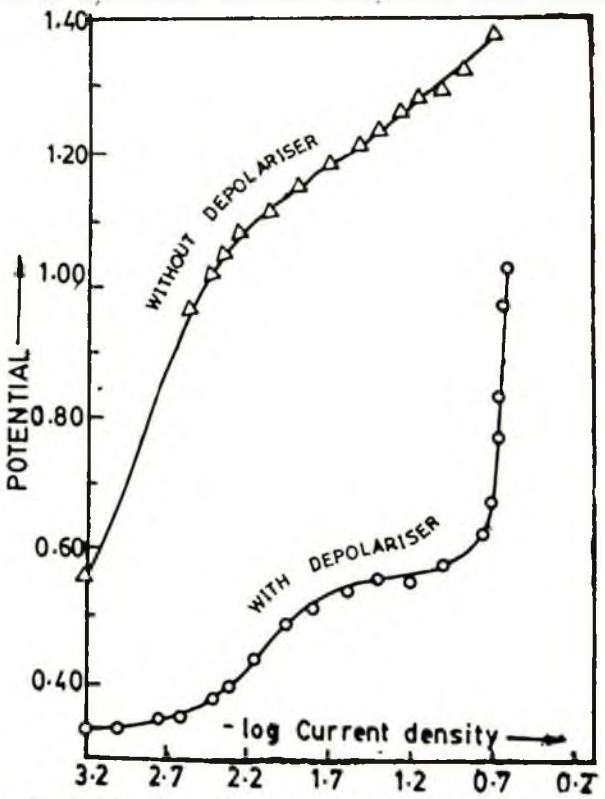


Fig.1 Cathodic polarization Curves at Lead Electrode without depolarizer (10% H_2SO_4) with depolarizer (10% H_2SO_4 + m-Nitroaniline) Temperature 30 + 1° C

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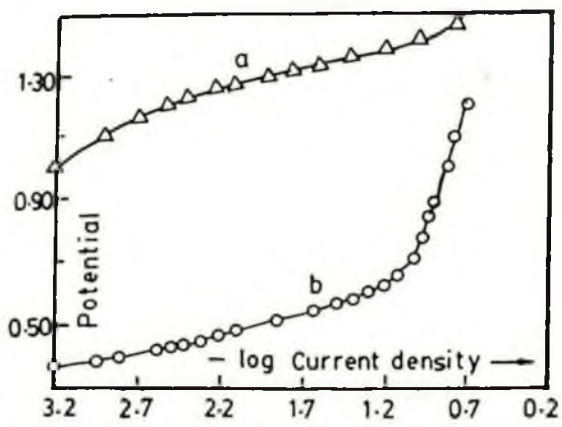


Fig. 2 Cathodic polarization curves at Amalgamated Lead electrode at Temp. 30°C
a. Without m - Nitro aniline
b. With m - Nitro aniline

from the polarization curves to investigate the proper current density at which yield is maximum.

From Table 2 it can be easily inferred that favourable current densities for the reduction

TABLE 1

ANALYTICAL DATA

Analytical Technique	Observed value	Literature value
Elemental analysis	H = 5.69% C = 67.86%	H = 5.66% C = 67.92%
Melting Point	139° C	138-40° C
Infrared spectra	1630-1575 cm^{-1}	1630-1575 cm^{-1}

TABLE 2

EFFECT OF CURRENT DENSITY, TEMPERATURE 30 ±1° C. DEPOLARIZER RATIO 1:40 H_2SO_4 CONCENTRATION 10%

S.No.	Cathode	Current density Amp/cm^2	Yield %
1.	Lead	0.0833	60
2.	-	0.1166	75
3.	-	0.1547	70
4.	Amalgamated Lead	0.0974	65
5.	-	0.1244	80
6.	-	0.1461	60

TABLE 3

EFFECT OF EXPERIMENTAL PARAMETERS

Temperature		Depolarizer Ratio		Effect of medium	
Dipol ratio 1:40 $[H_2SO_4]$ 10%		Temp. = 30 ± 0.1 $[H_2SO_4]$ 10%		Temp. = 30 ± 1° C Depol ratio 1:50	
Temp. ± 1° C	Yield %	Depol ratio	Yield %	H_2SO_4	Yield %
Lead cathode C.D. density 0.1166 Amp/cm^2					
15	70	1:40	75	5	70
30	75	1:50	80	10	80
45	65	1:60	80	15	80
Amalgamated lead cathode C.D.=0.1244 Amp/cm^2					
15	75	1:40	80	5	75
30	80	1:50	90	10	90
45	70	1:60	90	15	90

under study are 0.1166 amp/cm^2 for lead and 0.1244 amp/cm^2 for amalgamated lead cathode. Effect of parameters such as temperature, depolarizer ratio, medium concentration on percentage yield was now investigated and the results are given in Table 3.

From the result of the present investigation, it is clear that a good yield of m-azoaniline is obtained at these electrodes investigated. By this method m-azoaniline can be prepared in the purest form.

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