

ELECTROREDUCTION OF m-NITROANILINE TO m-PHENYLENE DIAMINE USING Ti^{3+} / Ti^{4+} REDOX SYSTEM

M D RAVI, V N SIVASANKARAN PILLAI,

Department of Applied Chemistry, University of Cochin, Cochin-682 002, INDIA
and

P N ANANTHARAMAN,

Central Electrochemical Research Institute, Karaikudi-623 06, INDIA

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Conditions for the electroreduction of m-nitroaniline to m-phenylenediamine were optimised using Ti^{3+} / Ti^{4+} redox system. Galvanostatic and voltammetric studies were made to understand their reduction behaviour with and without Ti^{3+} / Ti^{4+} redox system.

Key words: Electroreduction, m-nitroaniline, Ti^{3+} / Ti^{4+} redox system

INTRODUCTION

In the preparation of m-phenylenediamine from m-nitroaniline by catalytic reduction [1], the yield was very low due to slight volatility of the nitroaniline. Electrolytic preparation of m-phenylenediamine from m-nitroaniline using stannous chloride in hydrochloric acid medium has been studied [2], where the evolution of chlorine gas is a problem.

Many nitrocompounds were reduced to their respective aminocompounds using the Ti^{3+} / Ti^{4+} redox system [3]. Since it was thought that the cost of production would be less if the number of faradays were 6 instead of 12 for the production of m-phenylenediamine starting from m-nitroaniline instead of m-dinitrobenzene, this investigation was taken up and this presents the results of the same.

EXPERIMENTAL

It was observed that the amine group of m-nitraniline gives some insoluble compounds with titanium and hence m-nitraniline was acetylated and m-nitroacetanilide was used.

Preparation of m-nitroacetanilide

m-Nitroaniline (20g) was taken in a 500 ml round bottomed flask. Acetic anhydride (21ml) and glacial acetic acid (21ml) were added to it and the whole mixture was refluxed over a flame for about half an hour. It was then poured into 500 ml cold water while stirring continuously. After it got cooled, it was filtered and the crude product was washed and dried. It was again recrystallised from methanol and the pure acetyl compound thus obtained was used. The m.p. was 425K (literature value 155°C) and the yield was 80%.

Titanyl sulphate was prepared by the method described earlier [4].

Preparation of catholyte for the electro-reduction of m-nitroacetanilide

About 12.5g titanyl sulphate was dissolved in 500ml of supporting electrolyte viz. 20% H_2SO_4 (v/v). The solution was heated to 80°C and allowed to stand for overnight in a measuring cylinder.

The supernatant liquid was used after estimating the titanium content which should be normally not less than 1% TiO_2 equivalent. Estimation was done by standard method [5].

Reduction of m-nitroacetanilide

Electrolytic cell consisted of a copper vessel of 100ml capacity which also acted as the cathode. It was provided with a PVC cover with provision for introducing ceramic porous pot, reflux condenser, thermometer and stirrer. Ceramic porous pot with a lead anode served as the anode chamber. The cell was kept in a water bath which was provided with heating arrangement. 400ml catholyte of 20% H_2SO_4 (V/V) containing 1% TiO_2 in the form of titanic sulphate was taken in the cell. 20% H_2SO_4 in the porous pot served as anolyte. m-Nitroacetanilide (20g) was added to the catholyte. The temperature of the cell was adjusted to 328-333K and after making necessary connections, a current of 5A was passed for 4 hours which being 10% excess over theoretical quantity of current. After reduction, the unreduced nitro compound, if any, was filtered and the solution was estimated for amine content by titration by diazotisation method.

The above reduction was continued by adding 180g nitro compound and current was passed as above. Afterwards the solution was filtered to remove any unreduced nitro compound. M.P. of the acetyl derivative of the free base was found to be 463K (literature value 464K), thus confirming diamino compound. The experiment was carried out at different current densities and the results are given in Table I.

Table II shows the results of experiments under different temperature ranges.

For depolarisation studies under galvanostatic conditions a H type cell having ceramic partition was used. Identical conditions were used to study the depolarisation characteristics and the results are shown in Fig. 1. The cell was kept in a bath whose temperature was maintained between 328 and 333K.

Cyclic voltammetric studies

The working electrode (copper) was connected to the saturated

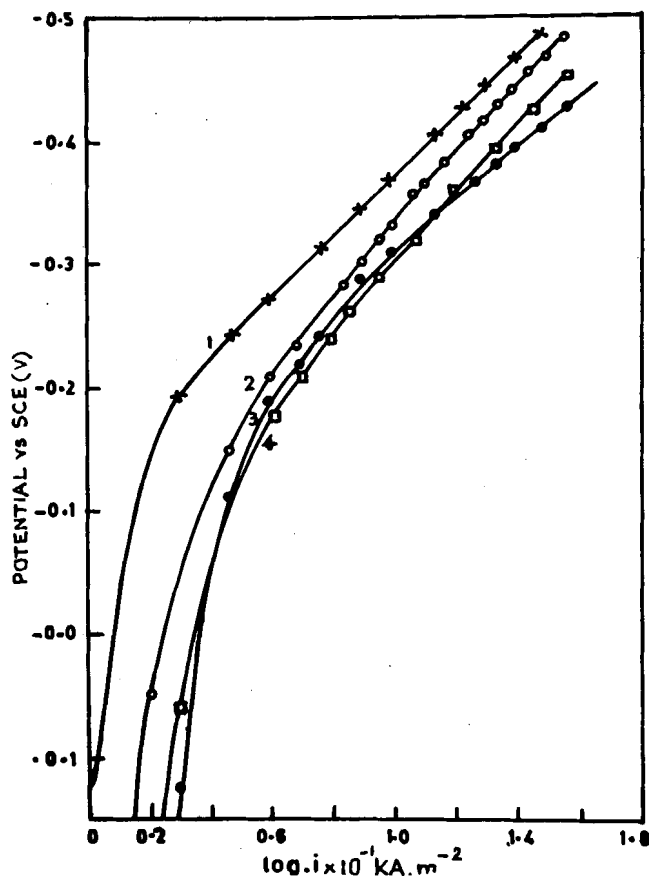


Fig. 1: Depolarisation studies at copper cathode using (1) 20% H_2SO_4 (2) 20% H_2SO_4 + m-nitroacetanilide (3) 20% H_2SO_4 + $Ti(SO_4)_2$ of concn 0.1% TiO_2 and (4) 20% H_2SO_4 + m-nitroacetanilide + $Ti(SO_4)_2$ of concn 0.1% TiO_2

TABLE-I: Reduction of m-nitroacetanilide at various current densities

Conditions: Catholyte 400 ml of 20% H_2SO_4 (v/v) containing 1% TiO_2 ; Cathode: Copper of area 2.9 dm^2 ; Anolyte: 20% H_2SO_4 (v/v); Anode: lead of area 0.8 dm^2 , Temp. 328-333K; Diaphragm: Ceramic porous pot

Current density $KA.m^{-2}$	Qty. of current passed (A.hr)	Wt. of nitro compound taken (g)	Wt. of un-reduced nitro compound recovered (g)	Wt. of diamine obtained (g)	Current efficiency (%)	Yield (%)
17	200	200	-	108.1	80	90
34	200	200	-	103.2	77	86
51	140	140	20	59.4	65	82

calomel electrode (SCE) through KCl bridge. Samples of m-nitroacetanilide used in these studies were obtained by recrystallising twice from methanol. 1M m-nitroacetanilide stock solution was prepared using methanol as solvent.

Ti^{IV} sulphate solution was prepared from TiO_2 and H_2SO_4 using the method described earlier [4]. 2M H_2SO_4 was used as the background electrolyte in all studies.

During each experiment the electrode was placed in the cell with background electrolyte and purified nitrogen gas (by passing through alkaline pyrogallol and water for 30-45 minutes) was bubbled. The electrode under such conditions gave reproducible results at least for one hour. The electrode once deteriorated was removed, mechanically polished and cleaned same as before.

RESULTS AND DISCUSSION

Table I shows the effect of current density on the yield and current efficiency. Even though the reduction was not much pronounced in terms of yield it was found that low current density such as $17KA.m^{-2}$ gave better yield and current efficiency. At higher current density such as $51KA.m^{-2}$ hydrogen evolution was pronounced and reduction was found to be incomplete resulting in low current efficiency.

Table II shows the effect of temperature on reduction. It is evident from the results that the reduction above 338K gave better results with a yield of 90.2% and current efficiency of 82.1%. This was due to the fact that solubility of m-nitroacetanilide was more at high temperature; the reduction became faster and complete reduction was observed. On the contrary at low temperature such as less than 323K the reduction was incomplete; the yield and current efficiency were low. A current efficiency of 76.8% and yield of 86% were obtained at the temperature range 328-333K.

Fig.1 shows the depolarisation characteristics under galvanostatic conditions for the reduction of m-nitroacetanilide. It was observed that the cathode potential shifted less sharply to more negative values at higher current densities perhaps due to hydrogen

TABLE-II: Reduction of m-nitroacetanilide at various temperatures.
 Conditions: Same as in Table I except C.D. $34KA.m^{-2}$

Temp. (K)	Qty. of current passed (A.hr)	Wt. of nitro compound taken (g)	Wt. of un-reduced nitro compound (g)	Wt. of diamine obtained (g)	Current efficiency (%)	Yield (%)
318-323	58.9	60	10	19.5	49	65
328-333	200	200	-	103.2	77	86
338-343	58.9	60	-	32.5	82	90

evolution. It is clear from the figure that the presence of titanium (IV) brings down the potential to less negative values even at high current densities.

Voltammetry of $Ti^{(IV)}$ sulphate in $2M H_2SO_4$

It was found that when small concentrations of $Ti^{(IV)}$ was added

to $2M H_2SO_4$ a very small wave was noticed. On increasing the $Ti^{(IV)}$ concentration to 120mM, the reduction started at $E_p = -0.175V$ vs SCE and a well defined wave appeared at $E_p = -0.525V$ vs SCE. The wave height increased sharply with further increase in concentration of $Ti^{(IV)}$ to 160mM and 200mM as shown in Fig.2.

Voltammetry of m-nitroacetanilide in $2M H_2SO_4$

In $2M H_2SO_4$, m-nitroacetanilide showed a well defined single

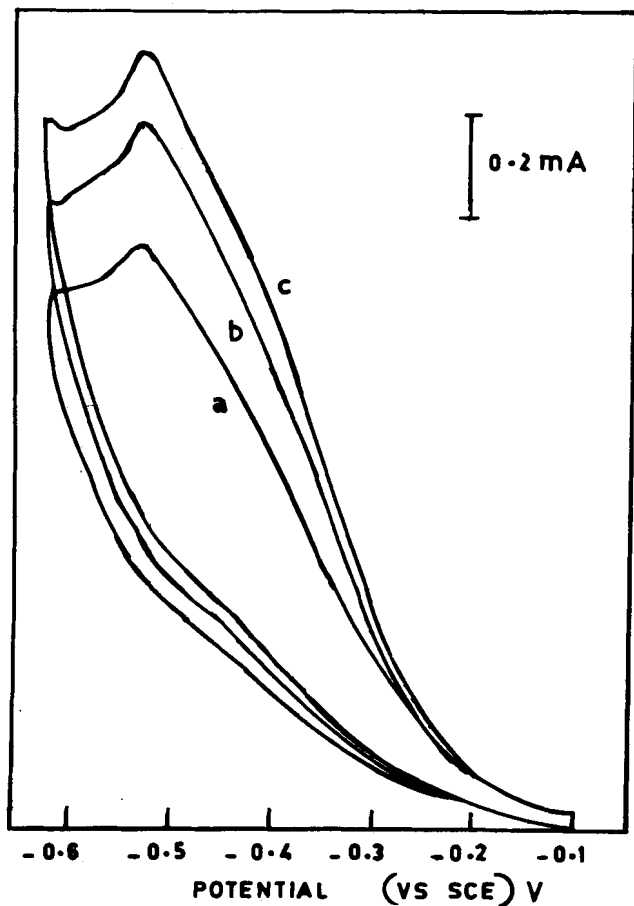


Fig.2: Cyclic voltammogram for the reduction of $Ti(SO_4)_2$ in $2M H_2SO_4$; Sweep rate $10 mv. sec^{-1}$; Temp. $398 \pm 1K$ (a-c) 120, 160, 200 mM $Ti(SO_4)_2$

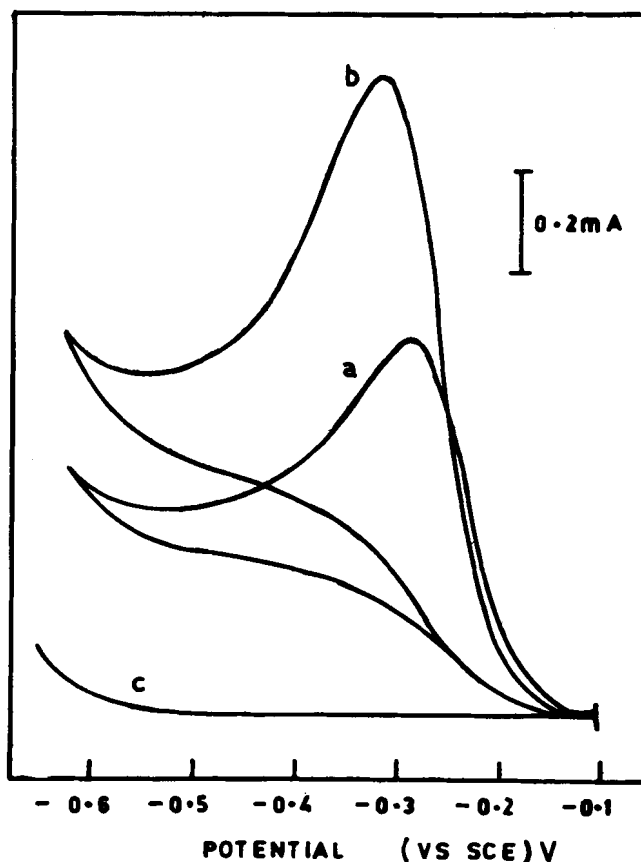


Fig.3: Cyclic voltammogram for the reduction of m-nitroacetanilide in $2M H_2SO_4$; Sweep rate $10 mv. sec^{-1}$; Temp. $398 \pm 1K$ (a-b) 10, 20 mM m-nitro acetanilide

irreversible wave with a peak potential of $-0.3V$ vs SCE as shown in Fig.3. The peak potential shifted cathodically with increase in concentration.

Voltammetry of m-nitroacetanilide in presence of titanium (IV) sulphate

In presence of m-nitroacetanilide and titanium (IV) sulphate the cyclic voltammogram clearly showed two waves. The first wave corresponded to potential at which m-nitroacetanilide reduction occurred i. e. at $-0.3V$ SCE as shown in Fig. 4.

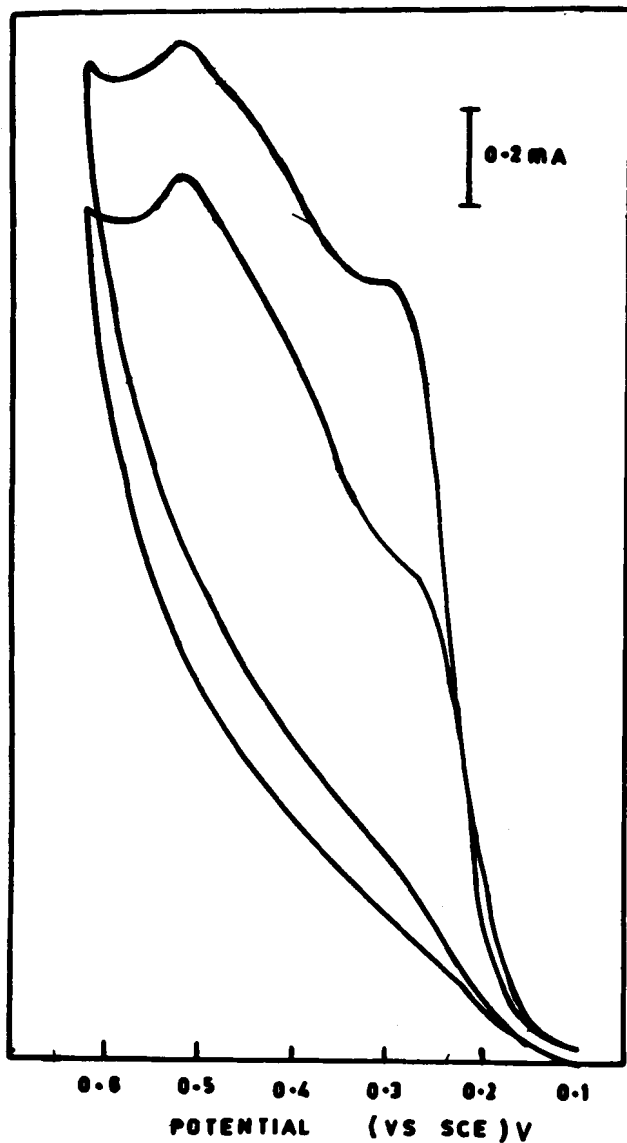
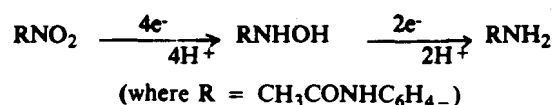
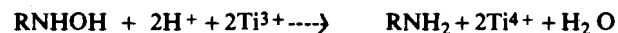


Fig.4.: Cyclic voltammogram for the reduction of (a-b) 10 and 20 mM m-nitroacetanilide in 2mM $Ti(SO_4)_2$: Sweep rate 10 mv. sec⁻¹; Temp. $398 \pm 1k$

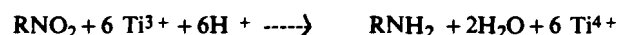
Based on the following reaction scheme the observed facts are correlated as follows:



The voltammogram of m-nitroacetanilide in 2M H_2SO_4 vs SCE results is the formation of RNHOH. The second stage reduction of RNHOH takes place at more negative potential than the hydrogen evolution potential at copper cathode. So the wave for 2 electron reduction does not appear in the voltammogram. Since the reduction potential of Ti^{4+} is found to be $-0.525V$ vs SCE which is less than the hydrogen evolution potential of copper, it would enhance the reduction of RNHOH and the reaction may be represented as



In addition to this the following solution phase reduction also can take place:



These reactions can explain for the improved reduction efficiency of m- nitroacetanilide.

CONCLUSION

From the current density studies it is evident that a current density of 17 kA. m^{-2} gives good yield of amino compound and current efficiency. Above 50 KA. m^{-2} the yield decreases. The favourable temperature for the reaction seems to be $338-343K$.

From voltammetric studies it may be concluded that in H_2SO_4 medium m-nitroacetanilide undergoes an irreversible reduction involving the transfer of four electrons. The process is controlled by diffusion. When both $Ti(IV)/Ti(III)$ and m- nitroacetanilide are present the reduction of m-nitroacetanilide is mediated through $Ti(III)$.

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