

ELECTROCHEMICAL REDUCTION OF *m*-NITROBENZENE SULPHONIC ACID TO METANILIC ACID USING Ti^{4+}/Ti^{3+}

P THIRUNAVUKKARASU, S THANGAVELU and K S UDUPA

Central Electrochemical Research Institute, Karaikudi - 623 006, INDIA

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Electrochemical reduction of *m*-nitrobenzene sulphonic acid has been studied on a copper cathode in presence of Ti^{4+}/Ti^{3+} redox reagent. Effect of concentration of the reactant, current density and temperature on the current efficiency and product yield was found out. Voltammetric data were also collected for the above system to understand the kinetics of the reduction of *m*-nitrobenzene sulphonic acid on copper cathode.

Key words: Electrochemical reduction, *m*-nitrobenzene sulphonic acid, metanilic acid, Ti^{3+}/Ti^{4+} redox couple

INTRODUCTION

Electrochemical reduction of aromatic nitrocompounds [1-6] has been studied extensively in aqueous, aqueous alcoholic and nonaqueous media using polarographic technique. It has been reported that the reduction of nitrocompounds in aqueous medium (1) gives two polarographic waves; the first wave representing a four electron reduction with the formation of phenylhydroxylamine and the second wave being a two electron reduction of phenylhydroxylamine with the formation of corresponding primary amine. The reduction of nitrocompounds has also been reported on copper electrode [7-9]. The reduction of nitrocompounds in the presence of Ti^{4+}/Ti^{3+} redox system has paved the way for the improved conversion efficiency. A detailed review [10] has been published on this indirect reduction of aromatic nitrocompounds with the use of Ti^{4+}/Ti^{3+} redox catalyst.

In an earlier study on the electrochemical preparation of metanilic acid—an organic intermediate used mainly in the manufacture of various dyes [11] and drugs—direct reduction of *m*-nitrobenzene sulphonic acid has been studied on a copper electrode. It has been reported [9] that the current efficiency could not be achieved above 60-70% in these experiments.

In the present work, voltammetric studies on the reduction of *m*-nitrobenzene sulphonic acid has been carried out with copper electrode both in the presence and absence of the Ti^{4+}/Ti^{3+} redox catalyst and on the basis of the reduction behaviour, preparative scale electrolysis has been attempted.

EXPERIMENTAL

Cyclic voltammetric study

A high purity copper rod (99.99%) of 6mm dia, inserted tightly into a teflon holder was used as the stationary working electrode. The electrode contact was made by connecting threaded copper rod tightly with the electrode material inside the teflon rod. A platinum foil was used as counter electrode and saturated calomel (SCE) was used as reference electrode.

An H-type cell with a sintered glass frit separating the working

and counter electrode compartment had provisions to introduce gas inlets into and over the solutions, working electrode, thermometer and salt bridge.

Sodium salt of *m*-nitrobenzene sulphonic acid was purified and solution was prepared using double distilled water. The titanous sulphate solution in 4N H_2SO_4 was prepared by heating equimolar quantities of TiO_2 powder and H_2SO_4 at 598-623K for 15 minutes and digesting the material in sulphuric acid [12].

The copper disc electrode was mechanically polished to mirror finish, degreased with trichloroethylene, rinsed with double distilled water and placed inside the cell. Purified hydrogen gas was passed inside the cell for deaeration. The electrode was then activated by applying a potential range cyclically for about five minutes in the background electrolyte. Potentials were applied to the cell from potential scan generator through potentiostat and current was recorded in a x-y recorder.

Preparative scale electrolysis

The electrochemical cell used for preparative scale electrolysis was a one litre beaker having a wooden lid with provisions for inserting the rotating copper electrode (2.5cm dia), ceramic porous pot diaphragm and thermometer. 500 ml of 2M H_2SO_4 was used as catholyte and the same concentration of H_2SO_4 was used as anolyte. 3.5% TiO_2 concentration in the form of $Ti(SO_4)_2$ was added to the catholyte and during electrolysis, *m*-nitrobenzene sulphonic acid as sodium salt was added in equal instalments after sufficiently building up the Ti^{3+} concentration in the electrolyte each time. After the passage of theoretical current, the experiment was stopped and metanilic acid content was estimated by bromination method [13]. The solution was then cooled to 283K and isolated the precipitated product.

RESULTS AND DISCUSSION

Voltammetry of *m*-nitrobenzene sulphonic acid in the absence of Ti^{4+}/Ti^{3+} redox system

Fig.1 shows the typical cyclic voltammogram recorded for the reduction of 2mM sodium salt of *m*-nitrobenzenesulphonic acid on copper electrode in 2M H_2SO_4 solution at 323K. Single peak

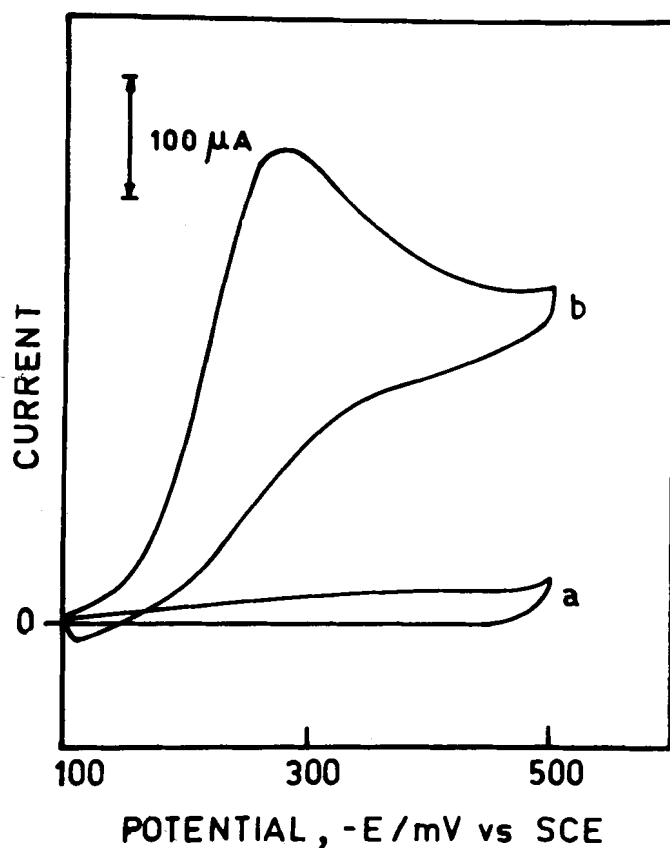


Fig. 1: Cyclic voltammogram for the direct reduction of 2mM concentration of sodium salt of m-nitrobenzene sulphonic acid on copper disc cathode: Temp. 323K Scan rate 40 $mV s^{-1}$

shaped wave is observed around -0.275V at 40 $mV s^{-1}$ and no anodic wave is observed on the reverse scan. As it has been established that under the above conditions, nitrobenzene gives a four electron single wave, the wave observed in the present case is also a four electron wave with the formation of phenylhydroxylamine and copper being a low hydrogen overvoltage electrode further reduction of phenylhydroxylamine is a competitive reaction with hydrogen evolution.

Effect of sweep rate on the voltammetric behaviour of m-nitrobenzene sulphonic acid is shown in Fig. 2. The peak current i_p is found to increase linearly with square root of sweep and $i_p/V^{1/2}$ is fairly constant. This indicates that the reduction process is diffusion controlled. i_p is also found to increase linearly with the concentration of m-nitrobenzenesulphonic acid.

Peak potential, (E_p) is found to shift in the cathodic direction with sweep rate (Fig. 2) and also with increasing concentration of the nitro compound. All these observations with no anodic wave on the reverse scan suggest that the reduction process is an adsorption involved irreversible process.

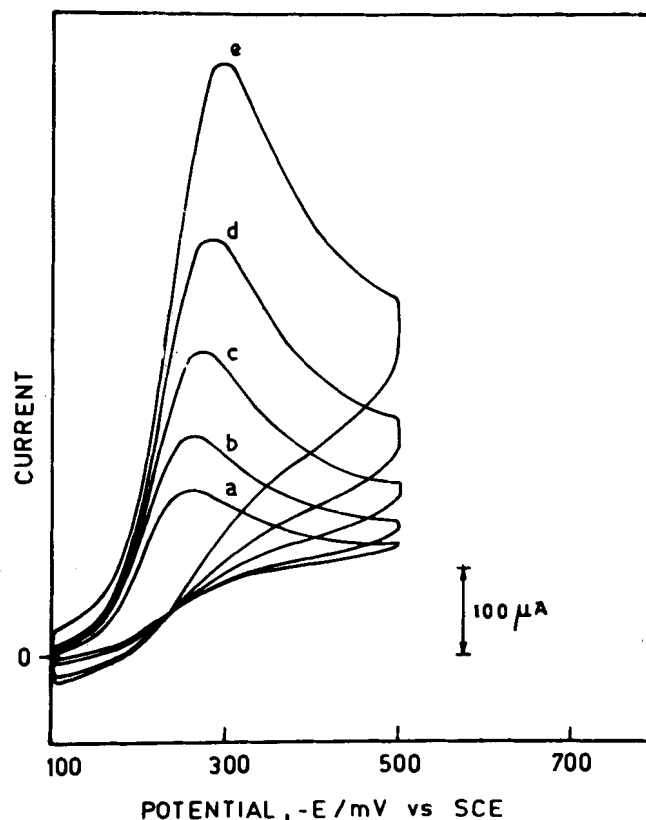


Fig. 2: Effect of sweep rate on the reduction of 2mM concentration of m-nitrobenzene sulphonic acid on copper disc cathode: Temp. 308K; Scan rate: (a) 10 $mV s^{-1}$ (b) 20 $mV s^{-1}$ (c) 40 $mV s^{-1}$ (d) 80 $mV s^{-1}$ (e) 160 $mV s^{-1}$

Voltammetry of Ti^{4+}/Ti^{3+} sulphate both in presence and absence of m-nitrobenzene sulphonic acid

Fig. 3 shows the voltammograms recorded for the reduction of 120 mM titanous sulphate present in 2M H_2SO_4 solution at 323K. The voltammograms are polarographic type limiting waves and as the sweep rate is increased the wave is found to merge with hydrogen evolution current. Fig. 4 shows the reduction of various concentrations of m-nitrobenzenesulphonic acid in presence of 120 mM of $Ti(SO_4)_2$ in 2M H_2SO_4 at 323K. As the concentration of m-nitrobenzenesulphonic acid is increased from 2mM to 8 mM, gradual increase in the limiting current for the reduction of Ti^{4+} is observed and becomes almost constant at 8 mM. At the same time gradual appearance of another limiting wave for the direct reduction of m-nitrobenzenesulphonic acid at less negative potential (-0.350 V vs SCE) is noticed. These observations indicate that at lower concentration of nitro compound, redox catalytic reduction is predominant and at higher concentrations of nitro compound, direct reduction of nitro compound is also taking place.

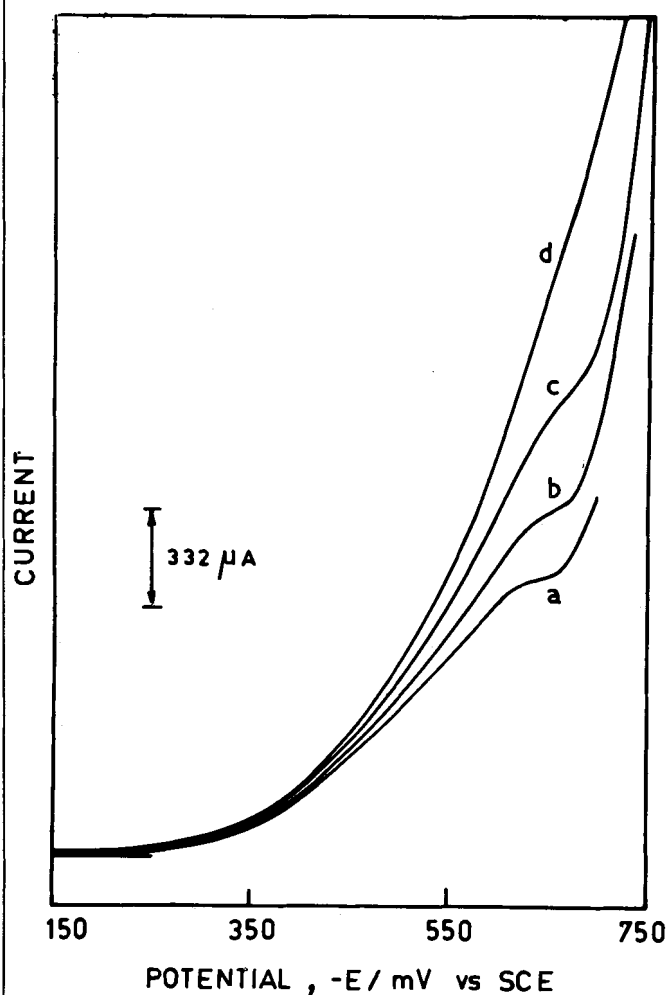


Fig.3: Effect of sweep rate on the reduction of 120mM $Ti(SO_4)_2$ on copper disc cathode: Temp. 323K; Scan rate: (a) 10 mV s^{-1} (b) 20 mV s^{-1} (c) 40 mV s^{-1} (d) 80 mV s^{-1}

TABLE-I: Effect of temperature on the indirect reduction of *m*-nitrobenzenesulphonic acid using Ti^{4+}/Ti^{3+} redox catalyst
Cathode: Cylindrical copper; Catholyte: 500 ml of 2M H_2SO_4 ; Current density: 10 A.dm^{-2} ; Anode: Lead; Anolyte: 15% by wt H_2SO_4 ; Diaphragm: Ceramic porous pot diaphragm; Depolarizer: 45g; TiO_2 : 3.5%

S. No.	Temperature (K)	Cell voltage (V)	Estimated product (g)	Current efficiency (%)
1	303-313	4.0	22.4	65
2	313-318	3.8	26.3	76
3	318-323	3.6	30.4	88
4	323-333	3.4	32.6	94
5	333-343	3.2	32.4	94

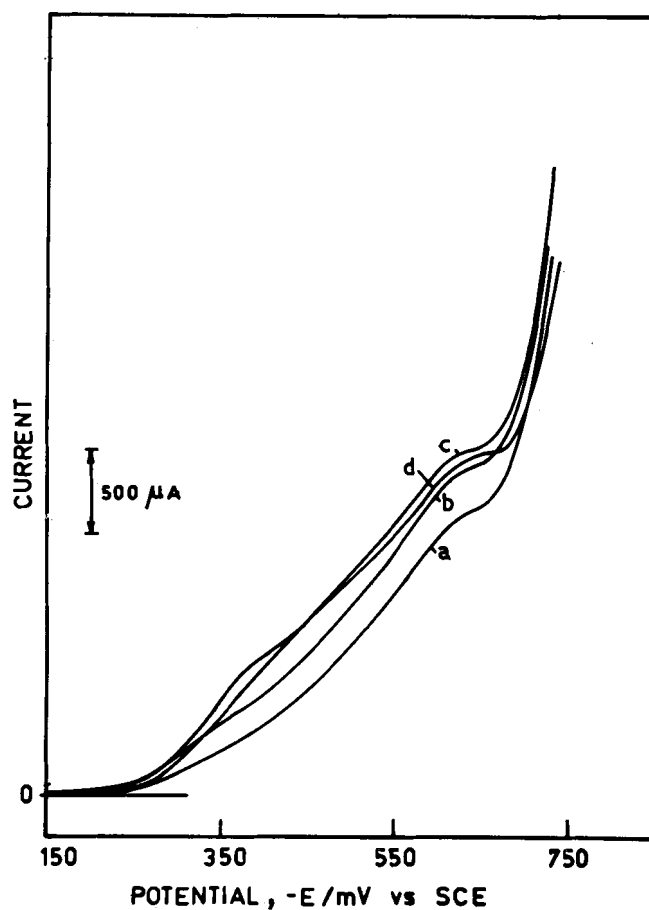


Fig.4: Effect of concentration of *m*-nitrobenzene sulphonic acid in the presence of 120 mM $Ti(SO_4)_2$: Temp.323K; Scan rate: 10 mV s^{-1} ; (a) 2 mM (b) 4 mM (c) 6 mM (d) 8 mM

However under these conditions, further reduction of phenylhydroxylamine to amine may occur favourably with Ti^{3+} species generated at the electrode surface. From these studies, it is understood that the para-rearrangement and other coupling reactions of phenylhydroxylamine can be avoided by the fast catalytic reduction of the same to amine especially at lower concentrations of nitro compound or by instalment addition of the nitro compound to the electrolyte containing sufficient concentration of Ti^{3+} species.

Effect of temperature on the catalytic reduction of *m*-nitrobenzene sulphonic acid is also studied and is shown in Fig. 5. The experimental temperature is varied from 303K to 323K. At lower temperature, for a fixed concentration of nitro compound and Ti^{4+} the wave formation for the direct reduction of nitro compound is very distinct and the wave height for the Ti^{4+} reduction is lower. As the temperature is increased from 303K to 323K,

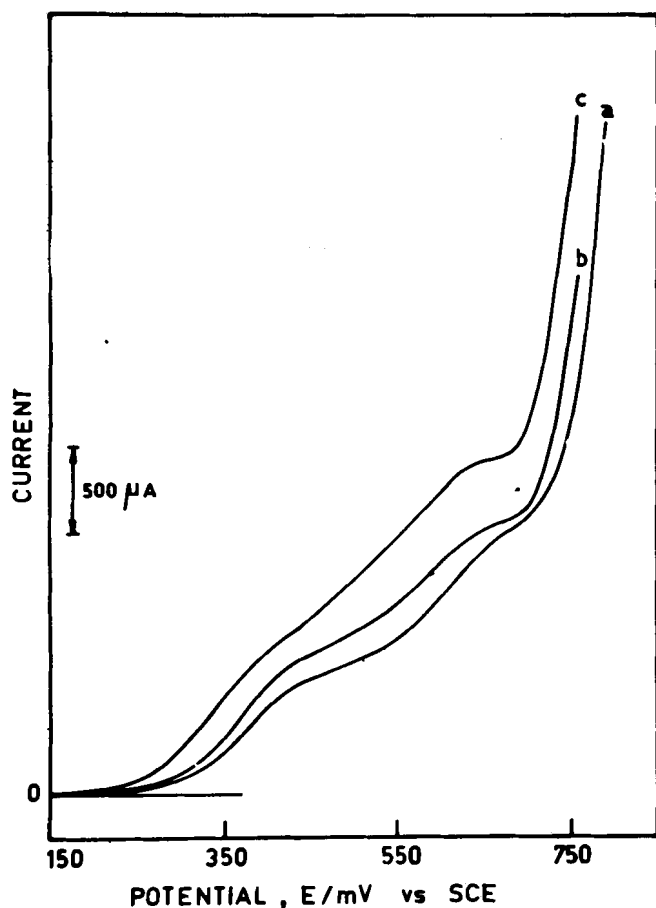


Fig.5: Effect of temperature on the reduction of 8mM sodium salt of m-nitrobenzene sulphonic acid in the presence of 120 mM $Ti(SO_4)_2$: (a) 303K (b) 313K (c) 323K

the wave height for the reduction of Ti^{4+} is enhanced. The increase of the wave height at higher temperature is due to the faster rate of regeneration of Ti^{4+} and by increased rate of the chemical reaction between the nitrocompound and Ti^{3+} species.

Preparative scale electrolysis

Preparative scale electrolysis was carried out under different conditions and Table-I shows the effect of temperature on the current efficiency and estimated product yield in the reduction of sodium salt of m-nitrobenzenesulphonic acid in presence of $Ti(SO_4)_2$. As the temperature of electrolysis increased, the current efficiency was found to increase upto 323-333K. At a lower temperature range of 303-313K, there was not much difference in the current efficiency obtained with and without Ti^{4+}/Ti^{3+} redox catalyst. As observed in voltammetric study, in preparative electrolysis also the rate of the catalytic chemical reaction between the nitrocompound and Ti^{3+} species was found to be increased at

higher temperature (Table I). The temperature range of 323-333K was chosen as the optimum temperature and employed for further experiments.

Table II shows the effect of current density on the current efficiency. It shows that under the chosen experimental conditions

TABLE-II: Effect of current density on the reduction of m-nitrobenzene sulphonic acid:

Depolariser: 45 g TiO_2 : 3.5% ; Temperature = 323 - 333K; (other conditions same as in Table I)

S. No.	Current density ($A.dm^{-2}$)	Cell voltage (V)	Estimated product yield (g)	Current efficiency (%)
1	4	3.0	33.4	96
2	6	3.1	33.2	96
3	8	3.2	33.2	96
4	10	3.4	32.6	94
5	15	4.0	28.1	80
6	20	4.5	25.3	73

the current efficiency was found to be almost constant up to 8 $A.dm^{-2}$. A few experiments were also done using the same electrolyte after the product isolation. The electrolyte was reused five times after isolating the product each time. The sulphuric acid concentration and $Ti(SO_4)_2$ concentration were maintained by make up. The overall product yield was 80-85%.

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