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Comparative evaluation of electroreduction of nitrobenzene and *m*-dinitrobenzene on Ti/TiO_2 electrodes in H_2SO_4

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Cyclic voltammetric studies of nitrobenzene and *m*-dinitrobenzene in 1M H_2SO_4 on thermally coated Ti/TiO_2 electrodes indicate heterogeneous redox catalysis for both these compounds. Significant adsorption and blocking effect of these compounds are noticed at higher concentrations. *m*-Dinitrobenzene (MDNB) exhibits greater inhibitive adsorption when compared to nitrobenzene. These effects, however, do not significantly influence the yield and current efficiency of the reduction of these two nitro compounds to their corresponding amines. Under optimum experimental conditions yields of over 87% nitrobenzene reduction and over 83% *m*-dinitrobenzene reduction could be achieved. The electrolyte could also be reused by recovering the amines as their sulphates at lower temperatures.

1. Introduction

Extensive polarographic [1, 2] and cyclic voltammetric measurements [3] on the reduction of nitrobenzene have been reported. During preparative electrolysis in aqueous acidic solutions at 80–90 °C the intermediate phenylhydroxylamine can undergo chemical transformation to *p*-aminophenol [4]. Preparative electrolysis of nitrobenzene under galvanostatic against potentiostatic conditions [5] on low vs high-over voltage cathodes [6] and even Nafion® based solid polymer electrolyte (SPR) electrodes have been reported [7].

For the electroreduction of nitrobenzene to aniline copper is the electrode material of choice [8]. The Ti^{4+}/Ti^{3+} redox system further improves the yield of aniline [9], as shown in the subsequent publications in the case of other aromatic nitro compounds. A brief note on the heterogeneous redox catalysis of nitrobenzene reduction by Ti/TiO_2 electrode was reported earlier [10]. A further study of the cyclic voltammetric as well as preparative electrolytic behaviour of nitrobenzene on the standardized thermally-coated electrode was also reported [11]. Preparative electrolysis at 80–90 °C on this electrode gives a good yield of *p*-aminophenol [12], although there is significant dissolution of electrode material.

Comparatively few polarographic studies on the electroreduction of *m*-dinitrobenzene have been reported [13, 14]. Formation of phenylhydroxylamine intermediates [15] during preparative scale electroreduction was also reported for this compound. Direct reduction of this compound to the corresponding *m*-phenylenediamine [16–18] is also improved by the Ti^{4+}/Ti^{3+} redox system [9]. Heterogeneous redox catalysis for this compound on the Ti/TiO_2 electrode has not been reported so far.

In the present work cyclic voltammetric as well as constant current electrolysis studies were carried out to evaluate the relative efficiency of the Ti/TiO_2 electrode towards the electroreduction of nitrobenzene and *m*-dinitrobenzene to their corresponding amines. The results are also compared with those on the conventional copper cathode.

2. Experimental details

2.1. *Ti/TiO_2 electrode preparation*

Titanium metal strip used in cyclic voltammetric and expanded mesh used in preparative electrolysis were sand blasted and treated with 50% HCl at 90 °C for an hour to obtain a rough surface for good adherence of the oxide coating. This material was dipped in a solution of 0.05M titanylacetylacetonate in isopropanol containing 5.0–7.5% (v/v) HNO_3, and the adherent film was dried in an oven at 100–110 °C. It was then placed in a muffle furnace at 500–550 °C for 25 min. The above method of coating was repeated at least five times to get a good coating of TiO_2 over the titanium.

2.2. *Cyclic voltammetric studies*

In the cyclic voltammetric studies an aqueous SCE and a platinum foil served as reference and counter electrodes, respectively, while a Ti/TiO_2 (area 0.28 cm^2) served as the working electrode. Purified nitrogen gas was used for deaeration.

2.3. *Preparative scale experiments*

A one litre capacity glass beaker covered with a lid with provision for introducing the porous diaphragm,

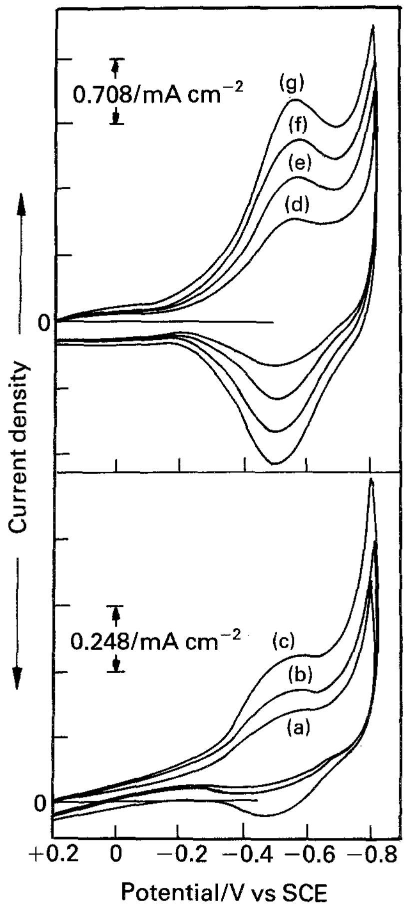

Fig. 1. Cyclic voltammetric behaviour of Ti/TiO_2 electrode in 1 M H_2SO_4 at different sweep rates. Sweep rates: (a) 5, (b) 10, (c) 20, (d) 50, (e) 100, (f) 150 and (g) 200 mV s^{-1}.

thermometer, condenser and electrodes was used as the preparative cell. About 500 ml of 10–20% (v/v) H_2SO_4 was used as catholyte as well as anolyte. Ti/TiO_2 cathode of 84 cm^2 surface area and lead anode of 18 cm^2 surface area were employed. Although passage of dissolved Pb^{2+} ions from the anode compartment through the porous pot diaphragm and deposition on Ti/TiO_2 cathode would be expected, no such cathode poisoning effect was noticed during preparative electrolysis and even during continuous experiments involving reuse of electrolytes. The glass cell was placed in a water bath for maintaining the required temperature. After electrolysis the aniline content was estimated by the bromination method [19] and *m*-phenylenediamine content by the diazotization method [20].

3. Results and discussion

3.1. *Cyclic voltammetric studies*

Typical cyclic voltammetric curves obtained from activated Ti/TiO_2 electrodes in 1 M H_2SO_4 in the sweep rate range 5–200 mV s^{-1} are presented in Fig. 1. The peak current value increases with sweep rate but i_p/V is not constant as would be expected for surface processes. The ΔE_p value remains around 60 mV s^{-1}. The nonzero ΔE_p value at slow sweep rate and the decreasing i_p/V value with sweep rate may be due to partial control by surface diffusion of redox couple in the oxide film. Such surface processes are common in thin film redox system [21–23].

At low concentrations the cathodic reduction peak potential of nitrobenzene and *m*-dinitrobenzene are very close to the reduction potential of the Ti/TiO_2 electrode itself.

Figure 2 shows typical cyclic voltammograms at a relatively slow (10 mV s^{-1}, Fig. 2A) and high (100 mV s^{-1}, Fig. 2B) sweep rate at different concentrations of nitrobenzene. At slow sweep rates the anodic peak current during the reverse sweep is totally absent. At higher sweep rates, however, even at fairly high concentration of nitrobenzene, a small but noticeable anodic peak current still remains in the reverse sweep. As would be expected, the cathodic peak current increases with nitrobenzene concentration. The reduction peak potential generally shifts

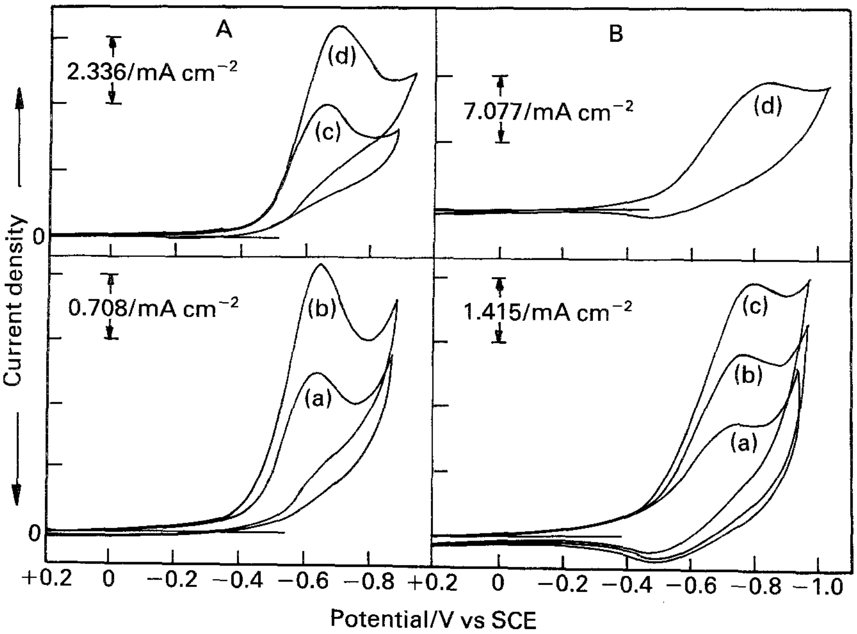

Fig. 2. Concentration effect on the electroreduction of nitrobenzene on Ti/TiO_2 electrode in 1 M H_2SO_4 at sweep rates 10 mV s^{-1} (A) and 100 mV s^{-1} (B). Concentrations: (a) 4, (b) 8, (c) 15 and (d) 30 mM.

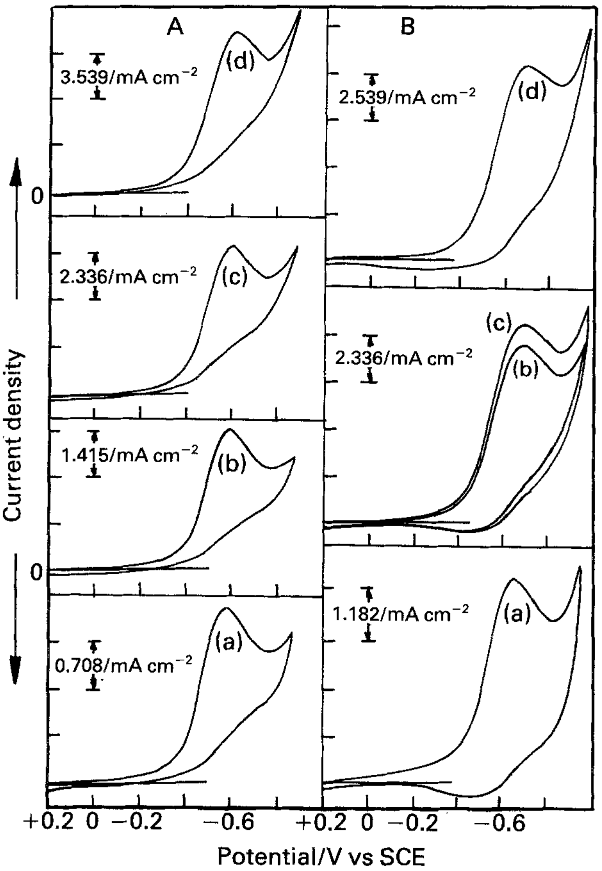

Fig. 3. Concentration effect on the electroreduction of *m*-dinitrobenzene on Ti/TiO$_2$ electrode in 1 M H$_2$SO$_4$ at sweep rates 10 mV s^{-1} (A) and 100 mV s^{-1} (B). Concentrations: (a) 4, (b) 8, (c) 15 and (d) 30 mM.

in the negative direction with increasing nitrobenzene concentration both at slow and high sweep rates [11].

At slow sweep rates the cathodic peak current due to *m*-dinitrobenzene increases with increasing concentration and no noticeable anodic peak current is observed in the reverse sweep (Fig. 3A). At higher (100 mV s^{-1}) sweep rate (Fig. 3B) the anodic peak current on the reverse sweep is again clearly evident. Another important feature in this figure is the relatively slower increase in the cathodic peak current with increasing concentration (Fig. 3).

Nitrobenzene and *m*-dinitrobenzene exhibit different polarographic reduction potentials in aqueous solutions [24]. However, on Ti/TiO$_2$ electrode both these compounds are reduced in the same potential region. This can happen only if both compounds are reduced by a chemical reaction between the compounds and a common electrogenerated reducing agent, namely surface bound Ti^{3+} species. All these compounds are reduced by a heterogeneous redox catalytic pathway on Ti/TiO$_2$ electrodes under the present experimental conditions.

With increasing concentration of the nitro compounds, the reduction peak potential is found to shift negatively. The negative shift in the case of *m*-dinitrobenzene is found to be greater than the shift in the case of nitrobenzene at both low and high concentrations (Fig. 4). These results suggest that MDNB is adsorbed more strongly on the Ti/TiO$_2$ electrode surface when compared to nitrobenzene. This is in conformity with the general trend of increased adsorption with increasing molecular size or molecular weight.

The cathodic peak currents obtained at 10 and 200 mV s^{-1} for the electroreduction of the two nitro compounds are compared in Fig. 5. At low concentration (Fig. 5A) the peak currents are found to increase linearly for both these compounds. The peak current value for MDNB is found to be only slightly higher than that due to nitrobenzene. At high concentrations (Fig. 5B) the peak current due to MDNB trends to decrease with further increase in concentrations (Fig. 5). This may either be due to a relatively slower heterogeneous redox reaction for MDNB or the emergence of severe blocking effects in the case of MDNB at higher concentrations.

3.2. *Preparative electrolysis*

Beck *et al.* [11] have previously reported the optimum conditions for the preparation of phenylhydroxylamine from nitrobenzene. The results of the preparative electrolysis for the reduction of nitrobenzene to

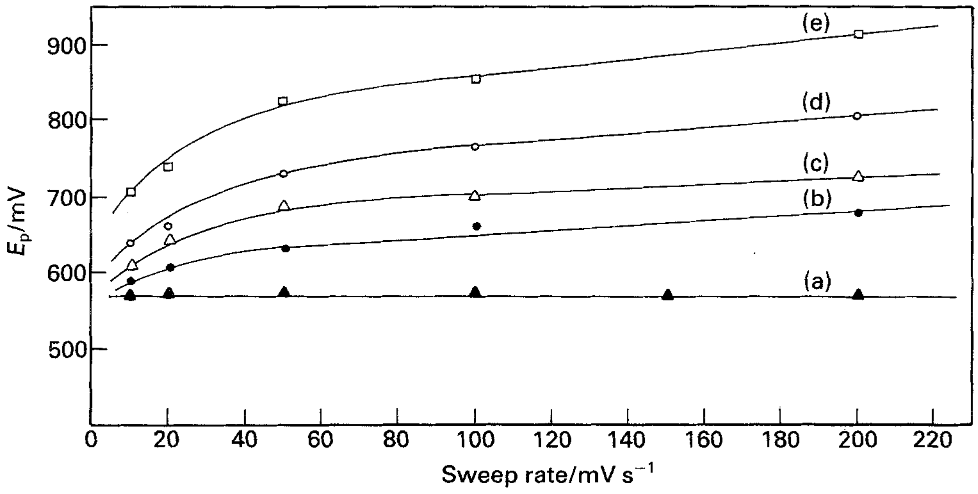

Fig. 4. The effect of sweep rate on the cathodic peak potential of nitrobenzene (b,c) and *m*-dinitrobenzene (d,e) at 4 mM (b,d) and 30 mM (c,e) of the nitro compounds. The peak potential in the absence of nitro compound (a) is also presented for comparison.

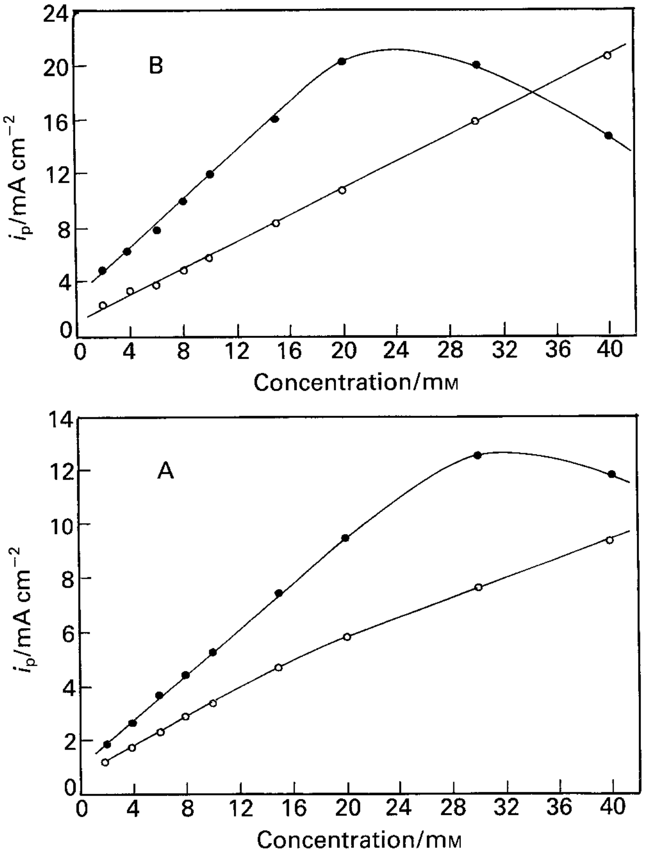

Fig. 5. The effect of peak current on different concentrations of nitrobenzene (○) and *m*-dinitrobenzene (●). Sweep rates: (a) 10 and (b) 200 mV s^{-1}.

aniline are summarized in Table 1. The concentration of H_2SO_4 was varied from 5–20 (v/v), it was found that 10% H_2SO_4 (v/v) gave maximum yield and current efficiency (CE) (Experiments 1–3). At lower acid strength nitrobenzene remains practically unreduced. At higher acid strength the yield and CE decreased, probably due to competitive hydrogen evolution. Results of preparative electrolysis experiments at different temperature indicate that 40–50 °C is the optimum temperature (Experiments 2, 4 and 5). Optimum current density for the galvanostatic electrolysis is found to be 5 A dm^{-2} (Experiments 2, 6 and 7).

Table 1. Galvanostatic reduction of nitrobenzene and m-*dinitrobenzene at a Ti/TiO$_2$ electrode*

Conditions:
Amount of nitrobenzene taken: 12 g
Amount of *m*-dinitrobenzene taken: 11 g
Cell voltage: 2.5–3.5 V

Expt.	*Acid strength (H_2SO_4)/%*	*Current density /A dm^{-2}*	*Temperature /°C*	*Recovered reactant/g*	*Weight of amine estimated/g*	*Estimated yield of amine/%*	*Current efficiency /%*
Nitrobenzene							
1	5	5.0	40–50	1.08	7.27	88.05	78.56
2	10	5.0	40–50	–	8.66	95.48	93.62
3	20	5.0	40–50	0.96	7.76	92.97	83.86
4	10	5.0	30–40	5.70	3.86	81.10	54.74
5	10	5.0	50–60	–	8.55	94.28	92.43
6	10	2.5	40–50	4.80	4.52	83.60	69.86
7	10	7.5	40–50	4.36	4.61	79.79	61.89
8*	10	5.0	40–50	5.16	3.40	65.72	51.73
m-dinitrobenzene							
9	10	5.0	70–80	3.82	3.68	79.72	64.79
10	20	5.0	70–80	–	6.52	92.21	91.07
11	30	5.0	70–80	–	6.48	91.65	90.48
12	20	5.0	50–60	3.68	3.97	84.36	69.10
13	20	5.0	60–70	1.71	5.18	86.74	77.13
14	20	2.5	70–80	1.39	4.97	80.45	73.99
15	20	7.5	70–80	3.26	4.16	83.60	61.94
16*	20	5.0	70–80	5.28	2.68	72.88	54.15

* At copper cathode

Table 2. Reuse of electrolyte in the electroreduction of nitrobenzene and m-*dinitrobenzene*

Conditions for Experiments 1–5
Catholyte: 400 ml 10% H_2SO_4 (v/v)
Anolyte: 100 ml 10% H_2SO_4 (v/v)
Bath temperature: 40–50 °C
Cell voltage: 5.0–6.0 V

Conditions for Experiments 6–10
Catholyte: 400 ml 20% H_2SO_4 (v/v)
Anolyte: 100 ml 20% H_2SO_4 (v/v)
Bath temperature: 70–80 °C
Cell voltage: 4.0–5.0 V

Expt.	*Weight of nitro-compound taken /g*	*Weight of amine sulphate/g*	*Weight of amine obtained on neutralization/g*	*Weight of amine estimated in mother liquor/g*	*Total amine recovered /g*	*Yield /%*
Nitrobenzene						
1	126	148.46	81.34	1.78	83.12	87.25
2	126	148.59	81.50	1.56	83.06	87.19
3	126	148.97	81.51	1.64	83.15	87.26
4	126	148.04	81.02	1.80	82.82	87.25
5	126	148.59	81.48	1.65	83.13	87.26
m-Dinitrobenzene						
6	38.3	58.69	19.21	1.02	20.23	82.27
7	46.8	69.82	23.62	1.64	25.26	83.95
8	46.8	68.99	23.86	1.08	24.94	82.88
9	46.8	69.76	23.75	1.20	24.95	82.92
10	46.8	69.68	23.59	1.41	25.00	83.08

Under the optimum conditions arrived at from the above experiments, continuous galvanostatic electrolysis was carried out adding nitrobenzene in regular instalments until the electrolyte solution became supersaturated with aniline sulphate. Then the electrolyte was cooled to 15–20 °C and the aniline sulphate was filtered. The electrolyte was adjusted for acid strength and reused for further reduction of nitrobenzene. The overall experimental results obtained by using the same electrolyte five times are summarized in Table 2 (Experiments 1–5). The average yield obtained in these experiments was always greater than 87%.

In the case of MDNB, requiring 12 electrons and 12 protons for complete reduction, a relatively higher acid strength is found to be necessary for efficient reduction. Experiments 9–16 in Table 1 clearly indicate that the yield and CE improve substantially when 20% H_2SO_4 (v/v) is used as the electrolyte. When compared to nitrobenzene, MDNB is slightly less soluble in aqueous media. Hence, a fairly high electrolyte temperature (70–80 °C) is required for improved electroreduction. Once again 5 A dm^{-2} is found to be the optimum current density for this reaction.

Under these optimum experimental conditions the same electrolyte was again reused five times for reducing MDNB by recovering the *m*-phenylenediamine sulphate after each stage. These results are summarised in Table 2 (Experiments 6–10). The overall yield in these experiments was maintained around 83%.

The results in Table 1 (Experiments 9–16) also indicate that Ti/TiO_2 electrodes yield slightly better results when compared to copper electrodes.

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