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Electrosynthesis of toluidines using thermally coated Ti/TiO$_2$ electrodes

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Cyclic voltammetric and preparative scale investigations on the electroreduction of (*o*-nitrotoluene (ONT), *m*-nitrotoluene (MNT), *p*-nitrotoluene (PNT) and 2,4-dinitrotoluene (DNT) to their corresponding toluidines in 1 M H_2SO_4 using thermally coated Ti/TiO$_2$ electrode are reported. In the cyclic voltammetric time scales inhibitive adsorption which decreased in the order i_p ONT > i_p MNT > i_p PNT > i_p DNT was noticed. The heterogeneous redox catalytic currents were also found to decrease in the same order. In preparative electrolysis, these inhibitive effects became unimportant. Yields around 90% were achieved for all four nitro compounds. The thermally coated Ti/TiO$_2$ electrode could be reused at least five times without any loss in yield and current efficiency.

1. Introduction

Very few recent investigations on the polarographic and voltammetric studies of nitrotoluenes and dinitrotoluene are found [1–7]. In preparative electrolysis, use of rotating disc electrodes [8], catalytic Raney nickel electrodes [9], novel types of electrolytes like xylene sulphonic acid [10] and H_2SO_4–alcohol mixtures [11, 12] have been recommended for achieving high yields of toluidines. In neutral media electroreduction of *o*-nitrotoluene to *o*-toluidine proceeds through the formation of azoxytoluene intermediates.

In this laboratory use of dissolved titanous–titanic redox system in H_2SO_4 was shown to be an effective method for the electroreduction of nitrotoluenes and dinitrotoluene [15–19].

In the present work a systematic evaluation of cyclic voltammetric as well as constant current electrolysis of all the four compounds mentioned above are reported.

2. Experimental details

Thermally-coated Ti/TiO$_2$ electrodes employed in the present work were prepared according to the method evolved by Beck and Gabriel [20].

Cyclic voltammetry for the reduction studies on nitrotoluenes and dinitrotoluene was carried out in 1 M H_2SO_4 using a thermally coated Ti/TiO$_2$ strip as cathode (area 0.28 cm^2). A SCE and a platinum foil served as reference and counter electrodes, respectively. Purified nitrogen gas was used for deaeration.

Details of the divided electrolysis cell have been given previously [21]. A Ti/TiO$_2$ electrode (area 84 cm^2) and lead were used as the cathode and anode, respectively.

For experiments involving the reuse of the electrolyte, the same concentration of the acid was maintained for every reuse by adding the requisite amount of acid after standard estimation.

The toluidines were isolated as the corresponding disulphates, which were then neutralized and recrystallized from ethanol; they were confirmed from their melting points, i.r. spectra and the melting points of their diacetyl derivatives. The toluidine in solution was estimated by the standard method [22, 23].

3. Results

3.1. *Cyclic voltammetric studies*

Typical cyclic voltammograms of the thermally coated Ti/TiO$_2$ electrode in 1 M H_2SO_4 at different sweep rates are presented in Fig. 1. The electrode shows a well defined reversible surface redox process due to the TiO$_2$/TiOOH redox couple. Detailed discussion on the redox behaviour has already been reported [24–26].

The effect of sweep rate on the cyclic voltammetric behaviour of the Ti/TiO$_2$ electrode in 20 mM *o*-nitrotoluene (ONT) is presented in Fig. 2. At slow sweep rates an excellent catalytic reduction current due to the reduction of ONT is noticed (Fig. 2, curves (a)–(c)). At higher sweep rates the well defined cathodic peak completely disappears even when the cathodic limit was extended beyond −1.0 V. The hydrogen evolution potential is apparently shifted to more positive values. A small anodic peak current, due to surface bound Ti^{3+} species, is also noticed at higher sweep rates (Fig. 2, curves (d)–(g)).

In 20 mM of *m*-nitrotoluene (MNT), also at sweep rates $\leqslant 20\,\mathrm{mV\,s^{-1}}$, the cathodic reduction peak is sharp, well defined and increase with sweep rate. At higher sweep rates, once again the cathodic reduction peak disappears completely, and a small anodic peak is noticed on the reverse sweep. In all these respects the cyclic voltammetric behaviour of MNT is similar

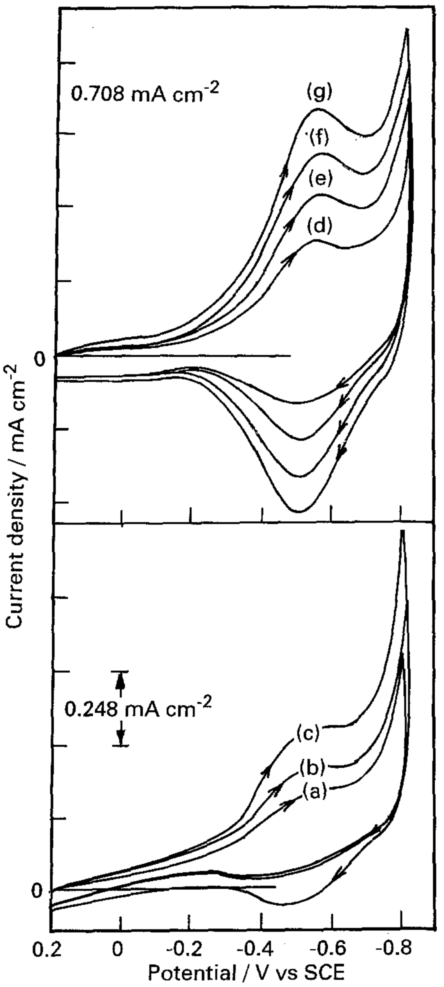

Fig. 1. Cyclic voltammetric behaviour of Ti/TiO_2 electrode in 1 M H_2SO_4 in different sweep rates. Sweep rates (a) 5, (b) 10, (c) 20, (d) 50, (e) 100, (f) 150 and (g) 200 mV s^{-1}.

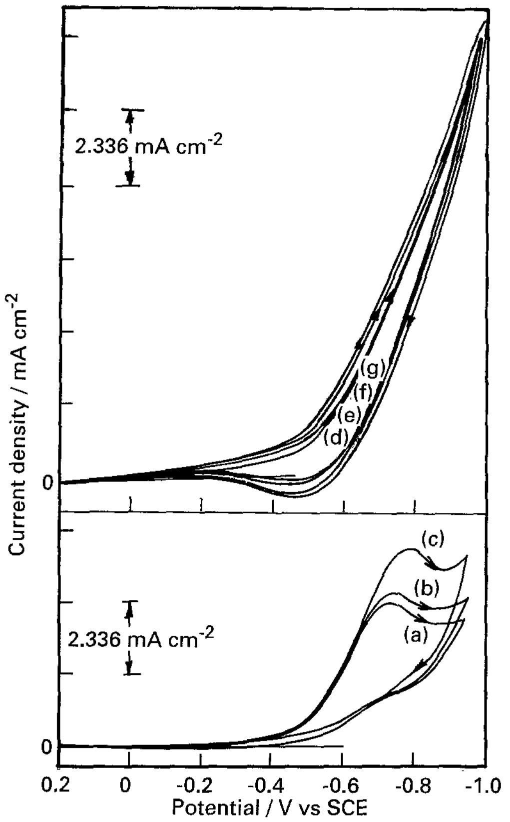

Fig. 2. Effect of sweep rate on the electroreduction of 20 mM o-nitrotoluene (ONT) on Ti/TiO_2 electrode in 1 M H_2SO_4. Sweep rates (a) 5, (b) 10, (c) 20, (d) 50, (e) 100, (f) 150 and (g) 200 mV s^{-1}.

to the cyclic voltammetric responses of ONT presented in Fig. 2.

The cyclic voltammetric behaviour of *p*-nitrotoluene (PNT) as well as 2,4-dinitrotoluene (DNT) on Ti/TiO_2 electrode in 1 M H_2SO_4 was found to be qualitatively similar in all respects. Typical cyclic voltammograms showing the effect of sweep rate in 1 M H_2SO_4 containing 20 mM of DNT for example are shown in Fig. 3. The anodic peak current, which is almost absent at slow sweep rates (Fig. 3, curves (a) and (b)), once again reappears at higher sweep rates. This type of irreversible cathodic peak at slow sweep rates, due to redox catalysis and reversible surface waves at higher sweep rates due to surface redox processes, have been noticed for a number of other nitro compounds [24–26].

In general, at slow sweep rates the cathodic peak currents due to all the four nitro compounds increased linearly with concentration (Fig. 4(a)). The slopes of the i_p against concentration plots, however, are quite different. The peak currents due to DNT are significantly smaller when compared to the other three compounds. DNT however, is found to be highly soluble in 1 M H_2SO_4 when compared to the other nitrotoluenes.

3.2. *Galvanostatic electrolysis*

Preparative scale electroreduction of all four compounds on Ti/TiO_2 electrode gave fairly high yields and current efficiencies (CE). It was found that 5 A dm^{-2} was the optimum current density (c.d.) for

Table 1. Comparison of experimental results for the electroreduction of the isomeric nitrotoluenes and of dinitrotoluene on Ti/TiO_2 electrode and copper electrode under optimum experimental conditions

Compound	*Acid strength %*	*Cell voltage V*	*Temp. °C*	*Yield %*		*CE %*	
				TiO_2	*Cu*	*TiO_2*	*Cu*
o-nitrotoluene	5	3.0	20–30	84.8	65.3	83.5	58.7
m-nitrotoluene	10	3.5	30–40	88.5	71.6	86.2	68.5
p-nitrotoluene	20	4.5	50–60	93.1	78.6	93.0	64.2
2,4-dinitrotoluene	20	4.5	65–70	94.6	77.7	92.5	52.7

Amount of nitrotoluenes taken: 14 g.

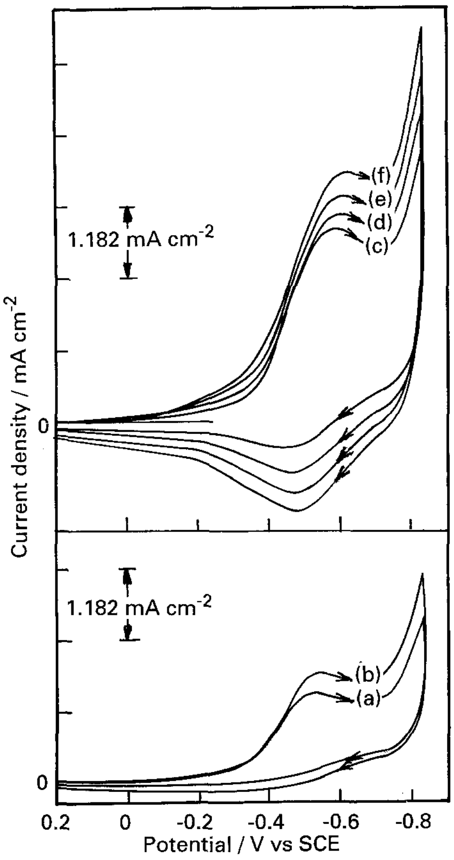

Fig. 3. Effect of sweep rate on the cyclic voltammograms obtained for the reduction of 20 mM 2,4-dinitrotoluene (DNT) on Ti/TiO$_2$ electrode in 1 M H$_2$SO$_4$. (a) 10, (b) 20, (c) 50, (d) 100, (e) 150 and (f) 200 mV s^{-1}.

all four compounds. The acid strength and the temperature range for electrolysis however, had to be optimized for individual compounds. The optimum experimental conditions for all the four compounds and the average cell voltage, yield and current efficiency are summarized in Table 1.

For ONT, the optimum acid strength was found to be 5% (v/v). For MNT which is slightly less miscible in H$_2$SO$_4$, a slightly higher optimum acid strength of 10% (v/v) was found to be necessary. For PNT and DNT, which are solid reactants, much higher acid strength of 20% (v/v) led to maximum yield.

ONT is easily miscible in H$_2$SO$_4$ at room temperature. The efficient electroreduction of this compound was thus achieved in the range 20–30° C. MNT is less soluble in H$_2$SO$_4$. Hence, a slightly higher temperature of 30–40° C and good mixing was necessary for efficient electroreduction. For PNT and DNT, which are solids at room temperature, higher temperature ranges of 50–60° C and 65–70° C were employed (Table 1).

For comparison, electroreduction of these nitro compounds under identical conditions were also carried out using copper cathodes. The results presented in Table 1 confirm that thermally coated Ti/TiO$_2$ electrodes are superior.

After the reduction the catholyte was cooled and the toluidines produced were recovered as insoluble toluidine sulphate salts CH_3–ϕ–$NH_3^+HSO_4^-$). After compensating the acid strength the electrolyte could be reused for further reduction of the same nitro compound. Typical results obtained in such reuse experiments are summarized in Table 2. These experiments indicate that the electrolyte could be reused at least five times with the yield of individual compounds ranging from 80–90%.

4. Discussion

The reduction potential for all the four nitrotoluenes are very close (−600 to −800 mV) and also close to the peak potential of the TiO$_2$/TiOOH redox (−570 mV) couple. There is a substantial increase in

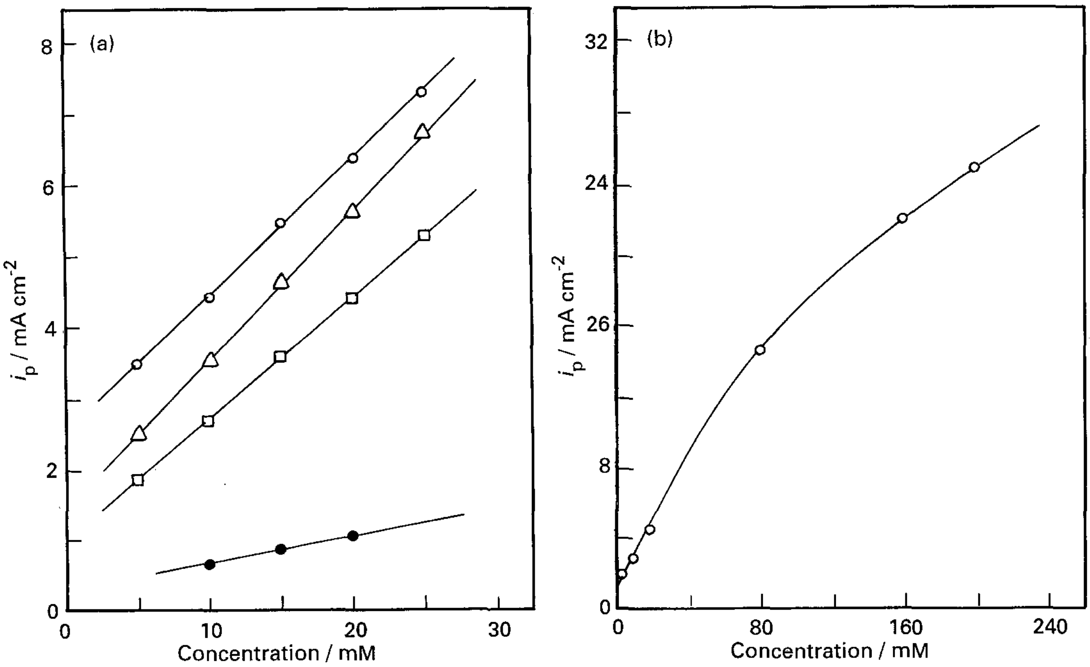

Fig. 4. i_p against concentration plots for the electroreduction of the isomeric nitrotoluenes and dinitrotoluene in slow (20 mV s^{-1} (a)) and high (100 mV s^{-1} (b)) sweep rates (○) ONT, (△) MNT, (□) PNT and (●) DNT.

Table 2. Reuse of electrolyte in the electroreduction of the isomeric nitrotoluenes and dinitrotoluene on Ti/TiO_2 electrode in H_2SO_4 medium

Experiment	*Amount of nitro compound taken /g*	*Yield of CH_3–φ–$NH_3^+HSO_4^-$ /g*	*Yield of TD* after neutralization /g*	*Yield of TD* estimated in mother liquor /g*	*Yield %*
o-Nitrotoluene					
1	45	59.28	26.27	–	74.74
2	54	68.85	31.86	–	75.54
3	54	68.99	31.70	–	75.16
4	54	68.54	31.85	–	75.51
5	54	68.78	31.98	1.72	79.89
m-Nitrotoluene					
6	40	48.80	24.62	–	76.81
7	45	56.62	28.13	–	77.33
8	45	55.94	27.51	–	77.58
9	45	56.03	27.37	–	77.19
10	45	56.14	27.39	1.72	82.28
p-Nitrotoluene					
11	60	72.85	40.58	–	86.89
12	69	80.14	47.39	–	87.92
13	69	80.93	47.88	–	88.75
14	69	80.86	47.70	–	88.51
15	69	80.76	47.91	1.02	90.79
2,4-Dinitrotoluene†					
16	84	120.83	41.48	–	79.30
17	90	126.26	44.21	–	79.33
18	90	126.92	44.24	–	79.32
19	90	126.82	44.18	–	79.33
20	90	129.80	44.22	1.13	81.27

* Toluidine.

† Approximately 6.62 g of unreduced 2,4-dinitrotoluene was isolated after each electrolysis.

the cathodic peak currents with sweep rate, at least at slow sweep rates. In the reverse sweeps the anodic peak current due to the oxidation of the remaining surface Ti^{3+} species is completely absent at low sweep rates. This indicates the involvement of heterogeneous redox catalysis by the surface bound Ti^{4+}/Ti^{3+} redox couple in the reduction of all these nitro compounds [21, 27].

The cathodic peak potentials in the absence, and in presence, of 20 mM concentration of ONT, MNT, PNT and DNT at different sweep rates are plotted in Fig. 5. The cathodic peak potentials shift only slightly in the negative direction in the presence of DNT at all the sweep rates. A slightly more negative shift is observed in the case of PNT. Cathodic shifts are substantial in the case of MNT, and even greater in the case of ONT. If the cathodic shift due to the addition of the nitro compounds is taken as a measure of the adsorbability of the corresponding compounds on to the Ti/TiO_2 electrode it may be concluded that the adsorbability decreases in the order ONT > MNT > PNT > DNT.

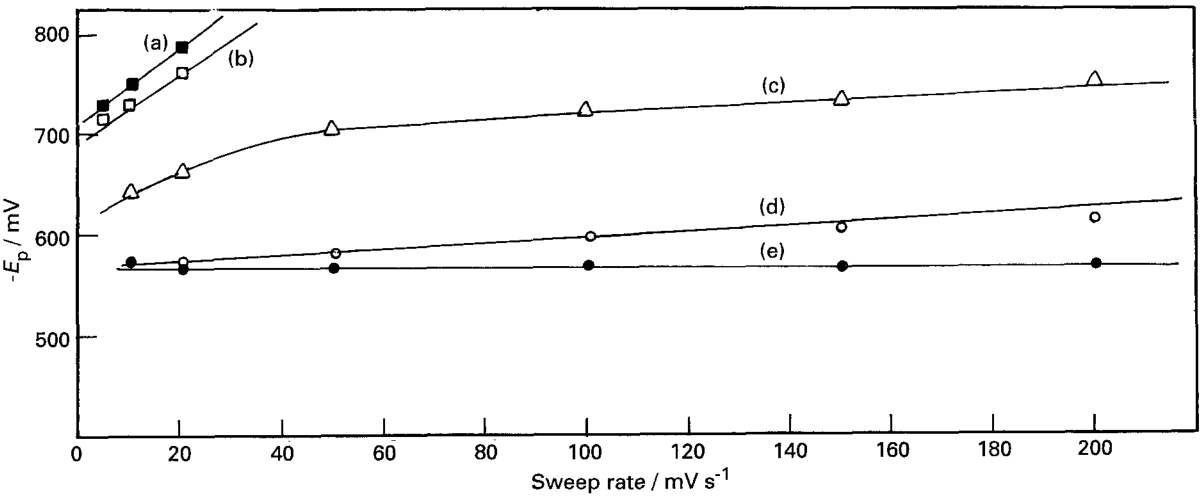

Fig. 5. Comparison of the peak potential (E_p) variation with sweep rate at concentration of 20 mM of nitrotoluenes and dinitrotoluene. (a) ONT, (b) MNT, (c) PNT, (d) DNT and (e) Ti/TiO_2 electrode.

In conventional electroorganic processes strong adsorption implies inhibition or blocking of electron transfer between the electrode and the electroactive species in solution. However, in heterogeneous redox catalysis the essential chemical reaction proceeds by close contact between the surface bound Ti^{3+} species and the nitro compound. Thus, in this case one would expect higher reduction rates with increasing adsorption. This is found to be the case, as shown in Figs 4 and 5. The heterogeneous redox catalytic cathodic peak current decreases in the same order in which the adsorptivity was found to decrease in Fig. 4 namely, i_p ONT > i_p MNT > i_p PNT > i_p DNT. The exact cause of this sequence is not apparent.

Very strong adsorption of the reactant nitro compound onto the electrode surface however, can still inhibit the electron transfer rate at least for very short time scales. This is probably responsible for the complete disappearance of the cathodic peaks in the case of strongly adsorbed ONT (Fig. 2) and MNT at sweep rates beyond $50\,mV\,s^{-1}$.

5. Conclusion

The efficiency of heterogeneous catalytic reduction of the four nitro compounds as measured by the catalytic peak currents in cyclic voltammetric studies decreases in the order i_p ONT > i_p MNT > i_p PNT > i_p DNT. It was found that the relative cathodic peak potential shift in the presence of these nitro compounds also decreases in the same order. It may be concluded that stronger adsorption or contact with the Ti/TiO_2 electrode surface simultaneously leads to better catalytic efficiency.

At high sweep rates, or shorter time scales, ONT, and to some extent, MNT adsorbs very strongly on the electrode surface and inhibits the overall electron transfer itself leading to near disappearance of the Ti^{4+}/Ti^{3+} redox peaks.

In the preparative time scale, under optimum conditions, the relative yields and CEs for these compounds decrease in the order DNT > PNT > MNT > ONT. It appears that weak adsorption leads to better efficiency. A Ti/TiO_2 electrode was found to be superior to a copper electrode.

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