

## Electrochemical reduction of 2-nitrobenzidine in methanol-water mixtures<sup>§</sup>

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**Abstract.** The electroreduction of 2-nitrobenzidine (2-NB) in buffered methanol-water mixtures in the composition range 20-80% (v/v) and pH range 2.80-12.00 gave a single six-electron diffusion-controlled irreversible wave. On the basis of the results obtained, a diphenoquinone-diimine intermediate is suggested in the mechanism of 2-NB reduction in methanol-water mixtures.

**Keywords.** 2-Nitrobenzidine; voltammetric techniques; reduction mechanism; electroreduction.

### 1. Introduction

Aromatic nitro compounds follow two distinct pathways of reduction depending on the nature of the substituents in the phenyl ring (Stocesova 1949; Shreve and Markham 1949; Heyrovsky and Vavrika 1970): (i) a two-step reduction process wherein the hydroxylamine first formed in a four-electron reduction step is further reduced at a more negative potential to the corresponding amine by a two-electron uptake, and (ii) a single step reduction process wherein the hydroxylamine formed as in (i) undergoes dehydration to give the quinoneimine intermediate which is subsequently reduced at a more positive potential to the corresponding amine.

Recently, some interesting reports have appeared on the electrochemical reduction of various nitro substituted biphenyl derivatives in protic and dipolar aprotic media (John Koshy *et al* 1974, 1978, 1981, 1982; Hlavaty *et al* 1979, 1983; Voigtlander *et al* 1983). In view of the importance of some nitro substituted benzidines in the field of analytical and industrial chemistry (Braithwaite 1958; Kuhn 1959; Aravamuthan *et al* 1982), we have taken up in detail the study of the electrochemical behaviour of these compounds at the mercury cathode in different media. In continuation of our work from this laboratory in N,N-dimethylformamide solutions (Aravamuthan *et al* 1984), we report in this paper the results obtained from the electrochemical reduction of 2-NB (NB-nitrobenzidine) in buffered methanol-water mixtures (pH 2.80-12.00) at various compositions (20-80% v/v) of methanol.

### 2. Experimental

2-NB was prepared according to the literature procedure (Kovar 1964) and its purity tested by m.p. (141°C), IR, TLC and mass spectrometry. Methanol (Rechem) was

<sup>§</sup> Dedicated to Prof. K S G Doss on his eightieth birthday.

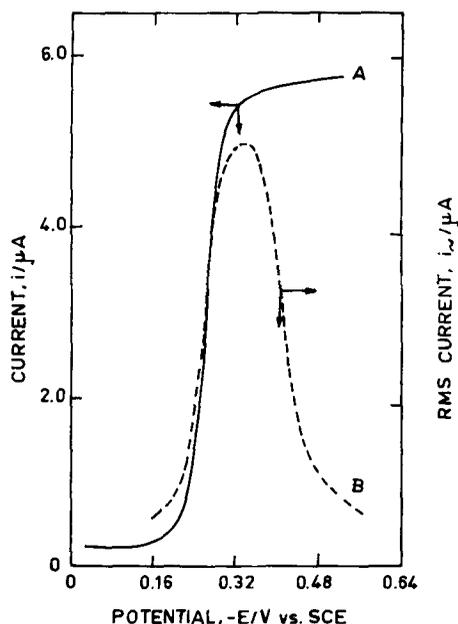
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purified by standard methods (Robert 1977–78). Potassium chloride (GR) was used as the supporting electrolyte without further purification. Britton–Robinson (BR) and Clark–Lubs (CL) buffers (Britton 1955) were used to control the pH of the experimental solutions.

The polarographic measurements made in the present work using a three electrode assembly were similar to those described previously (John Koshy *et al* 1978). The dropping mercury electrode (DME) used in 0.1 M aqueous potassium chloride supporting electrolyte at 55 cm height of the mercury column (height uncorrected for back pressure) had the following capillary characteristics under open circuit conditions:  $m = 0.8814 \text{ mg}\cdot\text{sec}^{-1}$ ,  $t = 7.0 \text{ sec}$ . Details of the microcoulometric experiments employed in the present investigation and the method of evaluating the total number of electrons ( $n_{\text{app}}$ ) in the electro-reduction have been described earlier (John Koshy *et al* 1974). A microburette type hanging mercury drop electrode (HMDE, Metrohm EA 290) was used as the working electrode in cyclic voltammetric (CV) experiments. The area of the electrode was calculated to be  $0.022 \pm 0.003 \text{ cm}^2$  in aqueous methanol containing 0.1 M potassium chloride. All measurements were carried out at 30°C.

### 3. Results and discussion

Figure 1 shows typical polarograms of 2-NB ( $5.0 \times 10^{-4} \text{ M}$ ) obtained in buffered 20% (v/v) methanol-water mixture containing 0.1 M potassium chloride supporting electrolyte. It is seen from figure 1 that 2-NB gives a single well-defined d.c. wave



**Figure 1.** d.c polarogram (A) and a.c polarogram (B) of 2-NB ( $5.0 \times 10^{-4} \text{ M}$ ) in 20% (v/v) buffered (pH 3.08) methanol-water mixture containing 0.1 M KCl supporting electrolyte.

and the a.c. polarogram shows a single peak corresponding to the d.c. step. This observation is true for all the compositions of methanol studied at different pH values. The d.c. wave was found to be diffusion-controlled in the composition range 20–80% (v/v) methanol and in the pH range 2.80–12.00 as indicated by the linearity of the plots passing through the origin of (i) limiting current *versus* concentration of 2-NB and (ii) limiting current *versus* square root of the height of the mercury column. A slope of 0.5 in the  $(\log i - \log h)$  linear plot further confirmed the diffusion-controlled nature of the limiting current in buffered methanol solutions. The electrode process was found to be irreversible on the basis of larger wave slopes  $(E_{3/4} - E_{1/4})$  obtained for a six-electron process ( $n_{app} = 6$  in the present work was confirmed subsequently by micro-coulometry) and larger negative a.c. summit potential ( $E_s$ ) values in all methanol solutions of varying compositions and pH.

The electrochemical reduction of 2-NB in buffered methanol solutions is strongly dependent on the pH of the medium. The half-wave potential ( $E_{1/2}$ ) varies linearly with pH becoming more negative as the pH is increased which indicates proton participation in the electrode process. It is also found that  $E_{1/2}$  varies with the composition of methanol shifting it to more negative values as the methanol content is increased. This is attributed to the 'inhibition' of the electrode process caused by the adsorption of methanol molecules at the mercury-solution interface (Maironovsky 1968).

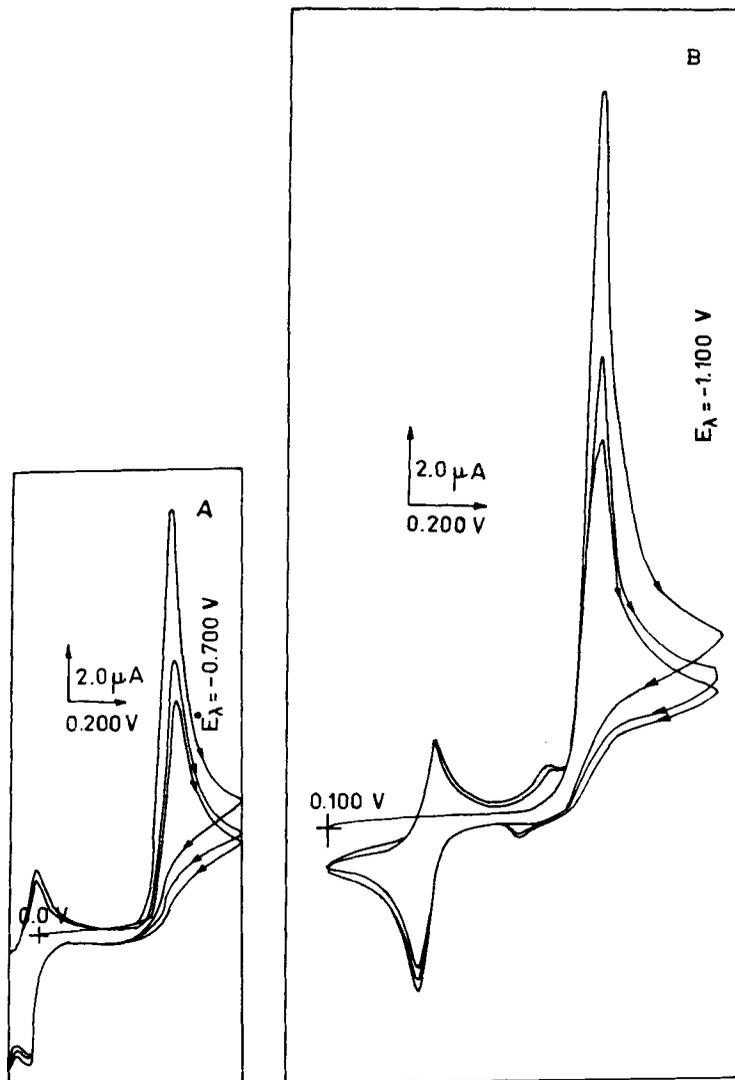
The total number of electrons ( $n_{app}$ ) participating in the reduction of 2-NB in buffered methanol-water mixtures was determined by microscale controlled-potential electrolysis experiments (John Koshy *et al* 1974). The coulometric data presented in table 1 for different compositions of methanol at various pH values indicate that a total of six electrons are involved in the reduction of 2-NB.

Figure 2 shows typical cyclic voltammograms of 2-NB obtained at 0.100 V sec<sup>-1</sup> sweep rate in 20% (v/v) methanol-water mixtures in acid (figure 2a) and alkaline (figure 2b) regions. It is found that a single cathodic peak appears in the forward scan at all compositions of the methanol-water mixture in the pH range 2.80–12.00.

**Table 1.** Microcoulometric data for 2-NB ( $5.0 \times 10^{-4}$  M) reduction in buffered methanol solutions at various compositions.

Percentage composition of methanol (v/v)	Applied potential ( $-E$ vs Hg pool electrode/V) at the plateau of the wave		
	pH		$n_{app}$
20	3.08	0.600	6.05
	6.85	0.900	5.95
	11.60	1.100	6.02
60	3.50	0.700	5.95
	6.34	0.950	5.92
	10.42	1.100	6.02
80 <sup>a</sup>	4.81	0.900	5.95
	6.99	1.100	5.98
	10.23	1.400	5.94

<sup>a</sup> in CL buffer



**Figure 2.** Cyclic voltammograms of 2-NB ( $5.0 \times 10^{-4}$  M) in buffered 20% (v/v) methanol-water mixture containing 0.1 M KCl supporting electrolyte at pH 4.94 (A) and 10.81 (B) [switching potentials,  $E_A$  and starting voltages are indicated in the figures; sweep rate,  $v = 0.100$  V  $\text{sec}^{-1}$  in both the cases].

The peak potential corresponds to the d.c. polarographic step. The cathodic peak is said to be diffusion-controlled as evidenced by the linearity of the plot passing through the origin of  $i_p^c$  versus  $v^{1/2}$ . A sweep reversal past the cathodic peak gives no anodic peak which confirms the irreversible nature of the electrode process. In alkaline media, during continuous cycles a reversible one-electron 'redox couple' appears at a potential just positive to the cathodic peak (figure 2b). This is attributed to a single electron addition to give the radical anion of 2-NB which is stable only in alkaline solutions. A similar observation has been made by Voigtlander *et al* (1983) for 2,2'-dinitrobenzophenone.

It may be mentioned that during the reverse scan in CV experiments, an anodic peak first appears at more positive potentials which gives rise to the cathodic peak in the forward scan (figure 2). Since the anodic peak is observed during the first reverse scan itself, it might have resulted from the oxidation of the reduction product of 2-NB formed at the electrode surface and the oxidised product is once again reduced to the initial reduction product. The peak separation ( $\Delta E_p$ ) of 0.030 V corresponds to a reversible two-electron 'redox couple' and this may be attributed to the following reaction:

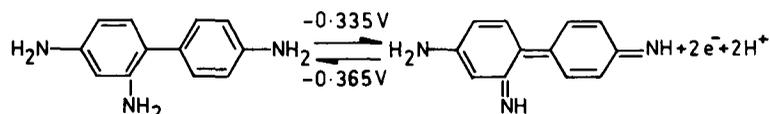


Chart 1.

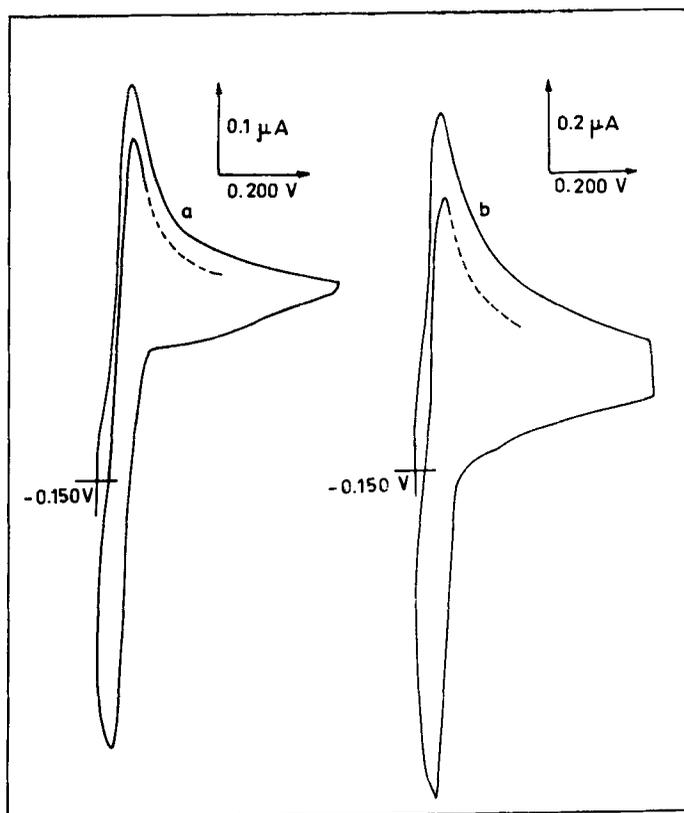
In acidic solutions of methanol (pH < 4.50), it is quite likely that the 'redox couple' might be observed at more positive potentials than the zero volts *versus* SCE, but in view of the possible oxidation of mercury and the chloride ion of the supporting electrolyte, sweep experiments were not extended to more positive potential scales.

The presence of diphenylquinonediimine intermediate during the reduction of 2-NB was confirmed by CV experiments carried out on 2-aminobenzidine. 2-aminobenzidine was prepared by the chemical reduction of 2-NB using tin and hydrochloric acid. The product was recrystallised and characterised by m.p. (observed 132°C, literature value 134°C, Tauber 1890) and IR techniques. Figure 3 shows typical cyclic voltammograms of 2-aminobenzidine ( $1.09 \times 10^{-3}$  M) in buffered (pH 11.75) 50% (v/v) methanol-water mixtures containing 0.1 M KCl. It is found that a peak separation ( $\Delta E_p$ ) of 0.035–0.040 V which corresponds to a reversible two-electron 'redox couple', is comparable to the value reported earlier for 2-NB reduction. This indicates that the 'redox couple' which appeared in the cyclic voltammogram of 2-NB is due to the oxidation of 2-aminobenzidine.

The reason for observing the cathodic peak in the forward scan (figure 3) for 2-aminobenzidine is due to the starting potential, namely, 0.0 V which is more positive than the potential required to oxidize 2-aminobenzidine (around  $-0.150$  V vs SCE) to the diphenylquinonediimine intermediate. Hence, during the start of the experiment the oxidised form of 2-aminobenzidine is reduced to give the cathodic peak. Though the concentration of 2-aminobenzidine taken was much higher ( $1.09 \times 10^{-3}$  M), the smaller current obtained in the cyclic voltammogram is due to the low concentration of the oxidised compound formed at the electrode surface.

This point has been repeatedly checked by the following experiments:

- i. On holding the potential at 0.0 V for few seconds, the cathodic current was found to increase; on the other hand, when the potential was held at a more negative value the peak height was found to decrease.
- ii. The cyclic voltammograms of 2-aminobenzidine at sweep rates  $0.050 \text{ V sec}^{-1}$  and  $0.100 \text{ V sec}^{-1}$  in the same buffered (pH 11.75) medium (50% v/v methanol) were also taken keeping the starting voltage at  $-0.800$  V *versus* SCE and scanning the potential *backwards* (anodically polarised). In this case, as expected, the anodic



**Figure 3.** Cyclic voltammograms of 2-aminobenzidine ( $1.09 \times 10^{-3}$  M) showing diphenoquinonediimine species in 50% (v/v) buffered (pH 11.75) methanol-water mixtures at sweep rates,  $\nu = 0.050$  V sec $^{-1}$ (a) and  $0.100$  V sec $^{-1}$ (b). Starting voltages are indicated in the figure.

peak first appeared followed by the cathodic peak while the anodic peak current is found to be more than what has been observed earlier.

Based on the polarographic, coulometric and CV experiments, the ECE-type of mechanism is suggested for 2-NB reduction in buffered methanol-water mixtures (chart 2).

It may be pointed out that since the formation of 2-aminobenzidine occurs at a more positive potential ( $E_2$ ) than the potential ( $E_1$ ) at which the 2-hydroxylaminobenzidine is formed from the parent compound, a single wave is observed (figure 1) in the present investigation (Stocesova 1949; Par Michel le Guyader 1966). In the mechanism cited above it is inferred that in acidic media, the protonated form of 2-NB is reduced to 2-aminobenzidine via the protonated diphenoquinone diimine intermediate while in neutral and alkaline solutions, the unprotonated form of 2-NB is reduced. The identification of the reduction product of 2-NB from macroscale controlled-potential electrolysis through spectral means was not successful due to the 'film formation' on the mercury surface which is responsible for discontinuity and sudden fall in the electrolysis current. In the case of buffered alkaline solutions although such behaviour was not observed, it was found that the

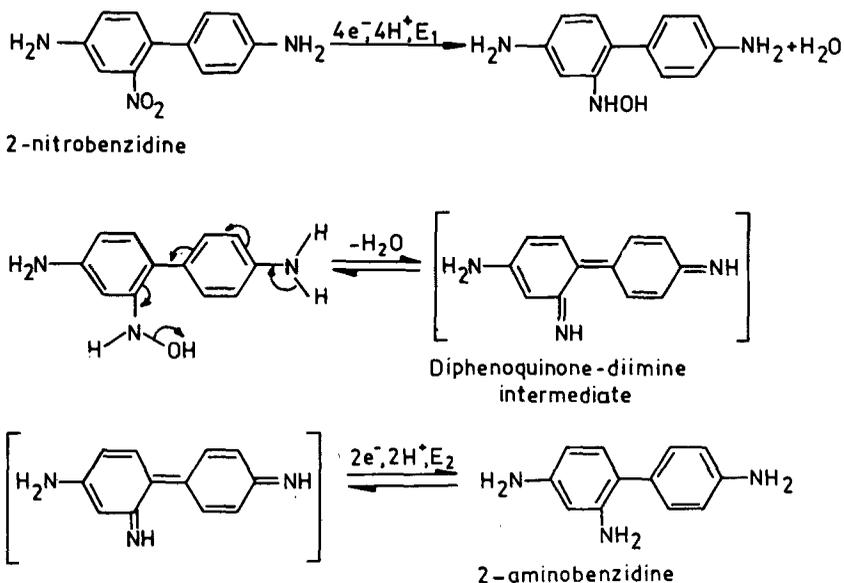


Chart 2.

solution after electrolysis changed its colour rapidly due to possible aerial oxidation when taken out of the cell.

### Acknowledgements

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