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Kinetics of Electrochemical Reduction of N-Nitrosodimethylamine by Voltammetric Techniques in Aqueous Solution

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The kinetics of the electro-reduction of N-nitrosodimethylamine (NDMA) was studied using controlled potential coulometry, linear scan voltammetry (LSV) and cyclic voltammetry (CV). Controlled potential coulometry showed that two moles of electrons were required for the reduction of one mole of NDMA. LSV studies were done to determine the transfer coefficient (α) and the standard exchange current density (j_{00}). These were obtained from plots of overpotential (η) versus $ln\ (i_p\text{-}i)/i$. The value of α was found to be 0.28 and did not depend on the concentration of NDMA. j_{00} was found by extrapolation of a plot of j_0 versus c to c = 1 mol dm^{-3} and its value was found to be 1 x 10^{-12} A cm^{-2}. CV studies were done at different scan rates, for different concentrations of NDMA, and from these studies α and the diffusion coefficient D were obtained. The values found for α and D were respectively 0.30 and 1 x 10^{-7} cm^2 s^{-1}.

Keywords: N-nitrosodimethylamine, electrode kinetics, linear scan voltammetry, cyclic voltammetry, transfer coefficient, standard exchange current density, Butler-Volmer equation.

1. INTRODUCTION

Nitrosoamines are present in a variety of environments [1-5], for instance in air, water, foods, blood, industrial and consumer products, and because they are carcinogenic compounds [5-9] a large amount of research has been done on them. In a doctoral programme on water pollution and water purification [10-13], one of the aspects studied was the development of a sensitive differential pulse polarographic (DPP) method and its use for the determination of the concentrations of nitrosoamines in various natural water samples. As an extension of this study, the kinetics of the electro-reduction of the most potent and prevalent nitrosoamine, N-nitrosodimethylamine (NDMA), was investigated. Its

structure is $(CH_3)_2$ N-N=O. This comprised the determination of the moles of electrons transferred in the electroreduction, the transfer coefficient (α) and exchange current (i_0). In order to determine the value of n in the stoichiometric equation, NDMA + n e^- → P, controlled potential coulometry [14] was used and the product formed was identified by UV/VIS spectroscopy.

Two electrochemical techniques namely linear scan voltammetry (LSV) and cyclic voltammetry (CV) [14,15] have been previously used to determine the transfer coeficient α and the exchange current i_0. α and i_0 are the two most important parameters in electrode kinetics and a large number of research studies have been done to determine them for many electrode reactions [16-25].

In the present study, the main objectives were to identify the product P formed, the number of electrons (*n)* involved in the electrochemical reduction of one mole of N-nitrosodimethylamine (NDMA), determine the transfer coefficient (α) and the standard exchange current density j_{00} (which are the two most important parameters in electrode kinetics) for the electro-reduction of NDMA using controlled potential coulometry, linear scan voltammetry (LSV) and cyclic voltammetry (CV) techniques.

2. EXPERIMENTAL

2.1 Chemicals and reagents

A 1M stock solution of N-nitrosodimethylamine (NDMA, molar mass 74.08 g mol^{-1}) was prepared by dissolving 7.408 g of the compound in water in a 100.0 cm^3 volumetric flask. Different aliquots of this solution were used to prepare solutions of various concentrations of NDMA. A 0.10 M NaOH solution was used as a supporting electrolyte. A cadmium sulphate solution (1.00 x 10^{-3} M) was used for checking the operation of the instrument.

Deaeration of the solutions was done using high purity nitrogen gas. Triple-distilled mercury used as the working electrode in experiments had a purity of 99.999%. Dimethylamine (DMA) was obtained from Fluka. All measurements were made at room temperature and deionized water was used for making all the solutions.

2.2 Instrumentation

A BAS-100B/W Electrochemical Workstation was used for the studies (manufacturer: Bioanalytical Systems Inc., BAS, USA). It is a microprocessor-based electrochemical analyzer that had three-electrodes. The working electrode (WE) was mercury which could be used as a controlled growth mercury electrode (CGME), dropping mercury electrode (DME) or stationary mercury drop electrode (SMDE). The reference electrode (RE) was silver/silver chloride (Ag/AgCl) and the auxiliary electrode (AE) was a platinum wire. A CARY 50 UV/VIS spectrophotometer was used for recording spectra of DMA and electrolysed NDMA solutions.

2.3 Procedure for a typical run

2.3.1 Controlled potential coulometry

10.0 cm^3 of a solution of NDMA, in 0.10 M NaOH as supporting electrolyte, was placed in the coulometric cell. The potential of the working electrode (mercury pool) was fixed at -1.9 V which ensures reduction of NDMA whose reduction potential is – 1.7 V. Two Ag/AgCl/Cl^- electrodes were used: one as the reference electrode and the other as auxiliary electrode. High purity nitrogen gas was then used for purging and stirring the solution.

The end-current ratio in the instrument was set at 1% to ensure completion of electrolysis and sensitivity was set to the automatic mode. The current and the total charge passed at any time were recorded. The experiment was carried out in triplicate.

2.3.2 Linear scan voltammetry (LSV)

10.0 cm^3 of a solution of NDMA of known concentration, in 0.10 M NaOH as supporting electrolyte, was placed in a voltammetric cell. The solution was purged with high purity nitrogen and the potential was recorded every five minutes until it reached a constant value. This was taken to be the reversible potential (E_{rev}).

The BAS-100B/W Electrochemical Workstation was used for recording the voltammograms. The potential scan was started at -1.00 V (initial potential, E_i). It was linearly increased in a negative direction at a scan rate of 100 mV/s and was stopped at -1.90 V, the final potential (E_f). The voltammograms were recorded in duplicate. A new SMDE was used for each run.

2.3.3 Cyclic voltammetry (CV)

The NDMA solutions were prepared in 0.10 M NaOH as the supporting electrolyte. 10.0 cm^3 of the solution of NDMA was transferred to a voltammetric cell and the solution was purged with high purity nitrogen gas. The potential of the cell was recorded every 5 minutes until E_{rev} was reached.

The potential scan started at -1.30 V (initial potential, E_i), and was linearly increased in a negative direction. The direction of the scan was reversed at -1.80 V (the switching potential, E_λ) and then stopped at -1.30 V (final potential, E_f). A new SMDE, size 12, was used for each run. Several scan rates were used to record voltammograms (CV) of each NDMA solution. The voltammograms for each NDMA solution were recorded in duplicate.

3. RESULTS AND DISCUSSION

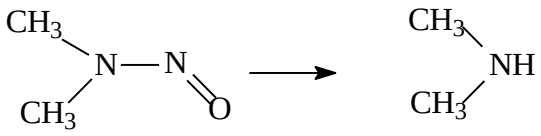
3.1 Results from coulometric studies

The charge (Q) needed for the reduction of all the NDMA present in 10.0 cm^3 solutions, at five different concentrations, are shown in columns 3, 4 and 5 of Table 1, and the mean charge is given in

column 6. The experiments were done in triplicate. From the values of *Q*, the moles (*n*) of electrons needed to reduce one mole of NDMA was calculated using the equation $n = Q/ F\ n_{NDMA}$ and these results are given in the last column of the table.

The result obtained ($n = 2$) is in agreement with the findings of Lund [26] and Odziemkowski et al [27] who reported that two moles of electrons were required in the electrochemical reduction of secondary N-nitrosoamines in alkaline solution. Similar studies [28] on the electrochemical reduction of N-nitrosodi-n-propylamine (NDPA) by constant potential coulometry also showed that two moles of electrons were required for the reduction of one mole of NDPA**.**

UV/VIS spectroscopy helped in the identification of the reduction product. Since the reduction of N-nitrosoamines generally gives amines [26-28] it was thought that the reduction of N-nitrosodimethylamine (NDMA) would probably give dimethylamine (DMA) as shown below:

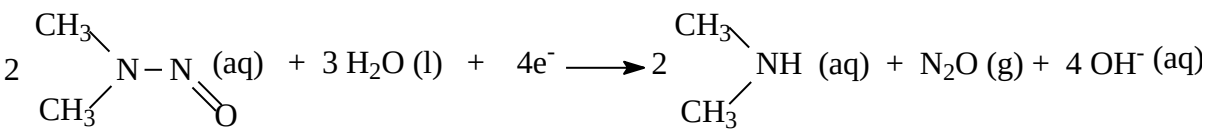


To check this, UV/VIS spectra of DMA and the electrolyzed solution of NDMA were compared. Figure 1 shows the UV/VIS spectrum for a 1.00×10^{-3} mol dm^{-3} solution of DMA and for the solution obtained after the electrolysis of 1.00×10^{-3} mol dm^{-3} NDMA. The spectra are similar which suggests that the product formed by the reduction of NDMA is DMA.

Table 1. Charge (*Q)* and moles of electrons (*n*) required to reduce 1 mole of NDMA in solutions of various concentrations.

c_{NDMA}/ mol dm^3 x 10^{-3}	n_{NDMA}/ 10.0 cm^3 x 10^{-5}	Q/C Replicate 1	Q/C Replicate 2	Q/C Replicate 3	Q/C Mean	*n*
1.00	1.00	2.30	1.75	1.83	1.96	2.03
2.00	2.00	4.29	4.26	4.29	4.28	2.22
3.00	3.00	5.71	6.27	6.04	6.01	2.07
4.00	4.00	8.12	7.45	8.02	7.86	2.04
5.00	5.00	9.78	9.43	9.48	9.56	1.98

From the results of coulometric studies ($n = 2$) and UV/VIS spectral data (product is DMA), the equation for the reduction of NDMA ($C_2H_6N_2O$) at a stationary mercury drop electrode (SMDE) may be written as



This is consistent with the results that were obtained by Odziemkowski et al [27].

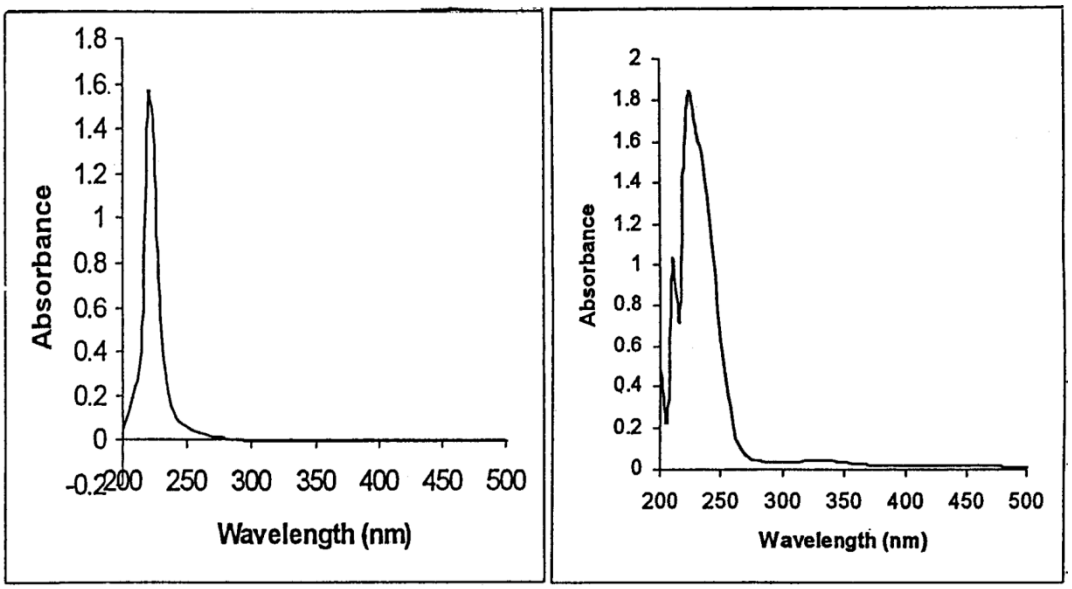


Figure 1. UV/VIS spectra of solutions of DMA and electrolyzed solution of NDMA

3.2 Results from LSV studies

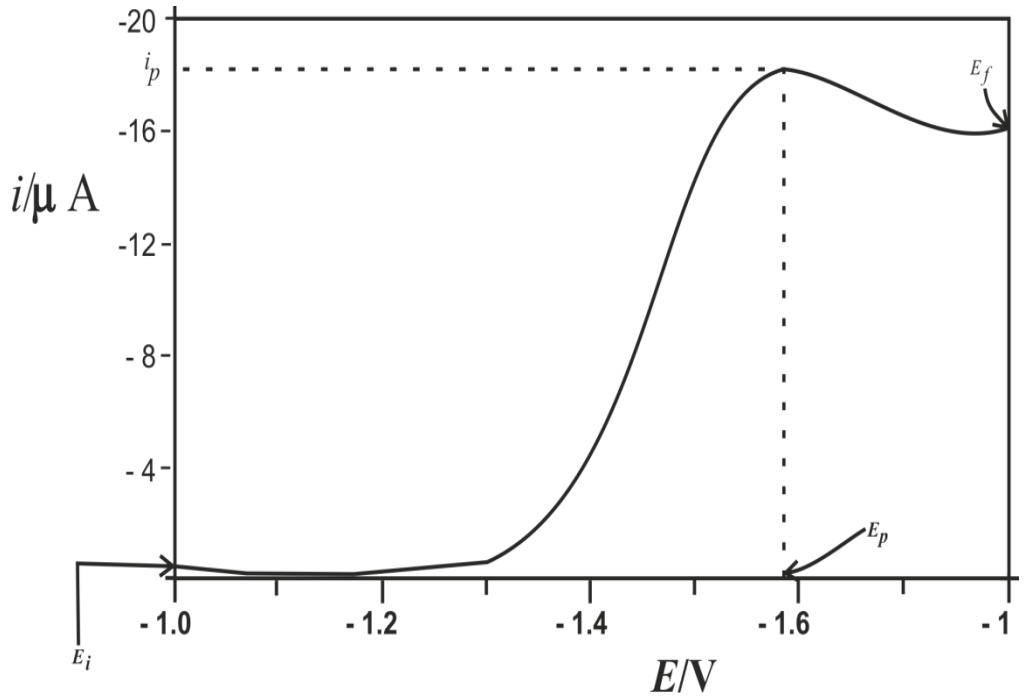


Figure 2. A typical linear scan voltammogram of a 1.00 x 10^{-3} mol dm^{-3} NDMA solution.

Using LSV voltammograms (Figure 2), α and i_0 have been obtained using the following theoretical equation [14,15,29]:

$$-\eta = \frac{RT}{\alpha nF} ln \frac{i_o}{i_l} + \frac{RT}{\alpha nF} \ln\left(\frac{i_l - i}{i}\right) \quad (1)$$

where i and i_l are respectively the current and limiting current and η is the overpotential which is defined by $\eta = E_i - E_{rev.}$ This equation indicates that a plot of η versus $ln\ (i_l - i)/i$ should give a linear graph from which α and i_0 can be obtained from the gradient ($RT/\alpha nF$) and intercept ($RT/\alpha nF$) $ln\ (i_0/i_l)$. Equation (1) is based on the assumption that α does not depend on the applied potential. Though many research studies have shown that this assumption is not strictly correct [30-32], the error caused by this assumption will not be significant in our studies since they were done at the low applied potentials.The scan rate used for LSV studies was 100 mV/s. This scan rate was selected because preliminary studies showed that around this scan rate the values of α (obtained from the voltammograms) were essentially independent of scan rate (α should, theoretically, not depend on scan rate).

Linear scan voltammograms were obtained, in duplicate, for seven solutions of NDMA within the concentration range 2.00 x 10^{-4} – 5.0 x 10^{-3} mol dm^{-3}. From each voltammogram (see Figure 2) the data obtained were the peak current (i_p) and the current (i) at various potentials (E_i) for the initial part of the voltammogram. All currents were corrected for residual currents which were obtained from blank runs.

Plots of η versus $ln\ (i_p - i)/i$ were made for each of the seven solutions studied (see Figure 3).

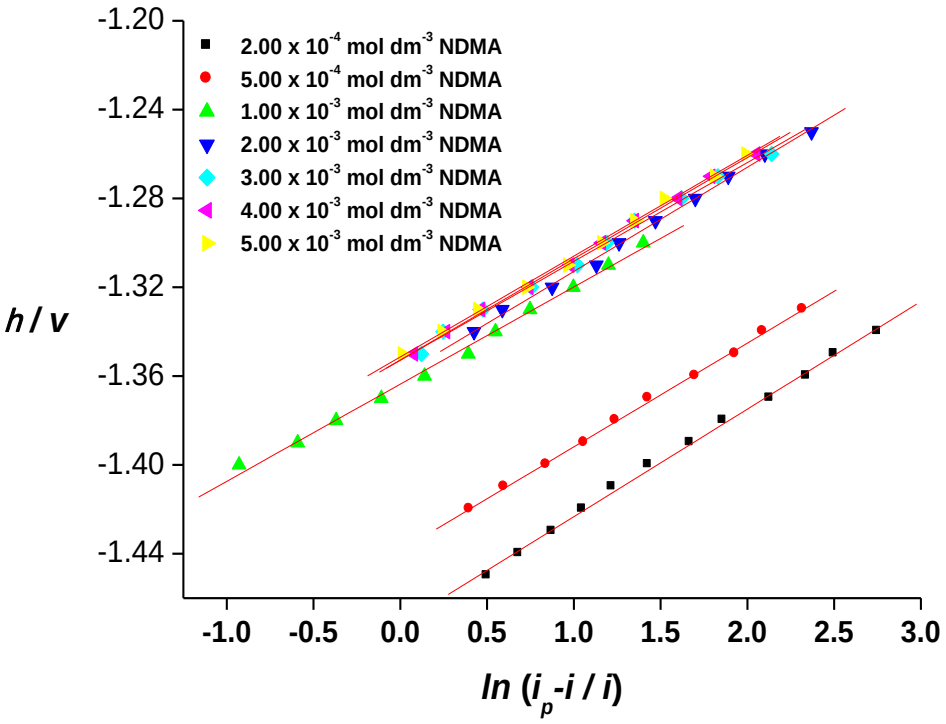


Figure 3. LSV plots of η versus $ln\ (i_p-i)/i$ for various concentrations of NDMA

The method of least squares [12] was used to draw the best line through the experimental data and then α and i_0 were calculated using Equation (1). The results for α and i_0 for various concentrations of NDMA are shown in Table 2.

Table 2. Values of α, i_o and j_o at various concentrations of NDMA (LSV studies).

c_{NDMA} / mol dm^{-3} x 10^{-3}	α	i_o / A x 10^{-18}	j_o / A cm-2 x 10^{-17}
0.20	0.28	0.038	0.15
0.50	0.28	0.11	0.44
1.00	0.28	0.49	2.0
2.00	0.28	1.1	4.4
3.00	0.28	1.5	6.0
4.00	0.28	2.2	8.8
5.00	0.28	2.8	11

Column 2 in the table shows that α was 0.28 for all the solutions studied. This is to be expected since α is a kinetic parameter and hence should not vary with solution concentrations. This value for α indicates that the fraction of electrical energy (nFE) supplied to the working electrode that favours the cathodic reaction (reduction of NDMA) is 0.28. The fraction of the electrical energy that favours the reverse reaction (oxidation of DMA to NDMA) will therefore be 1 – 0.28 = 0.72.

The exchange current densities j_o that were obtained for various concentrations of N-nitrosodimethylamine (NDMA) are also shown in Table 2 (column 4). They were obtained from the exchange current i_o (see column 3) by dividing it by the area (A) of the electrode surface.

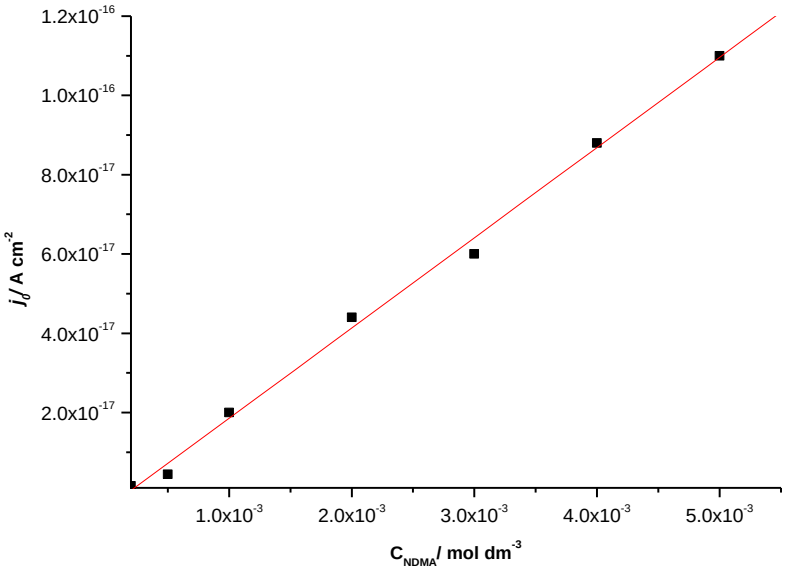


Figure 4. A plot of j_0 versus c_{NDMA} for data given in Table 2. Extrapolation of the graph to c = 1.0 mol dm^{-3} gives j_{00} as 1 x 10^{-12} A cm^{-2}.

The data in Table 2 also shows that exchange current densities (j_o) increase, as is to be expected, with increase in the concentration of NDMA. To compare exchange current densities of different electrodes it is therefore necessary to compare standard exchange current densities (j_{oo}) which are exchange current densities when concentrations (c) are 1.00 mol dm^{-3}. Unlike the exchange current density, the standard exchange current density is a constant for an electrode reaction at any given temperature. The standard exchange current density (j_{oo}) for the electro-reduction of NDMA was found by the extrapolation of the plot of j_0 versus c (Figure 4) to be 1 x 10^{-12} A cm^{-2}.

Values for j_{00} that are less than 10^{-5} A cm^{-2} indicate very slow rate of electron transfer and hence irreversible electrode reactions [14,29]. The electrode reaction NDMA → DMA is therefore highly irreversible. These results are essentially in agreement with those of Pulidori et al [28] who reported that the electroreduction of N-nitrosoamines is irreversible at the DME.

3.3 Results from CV studies

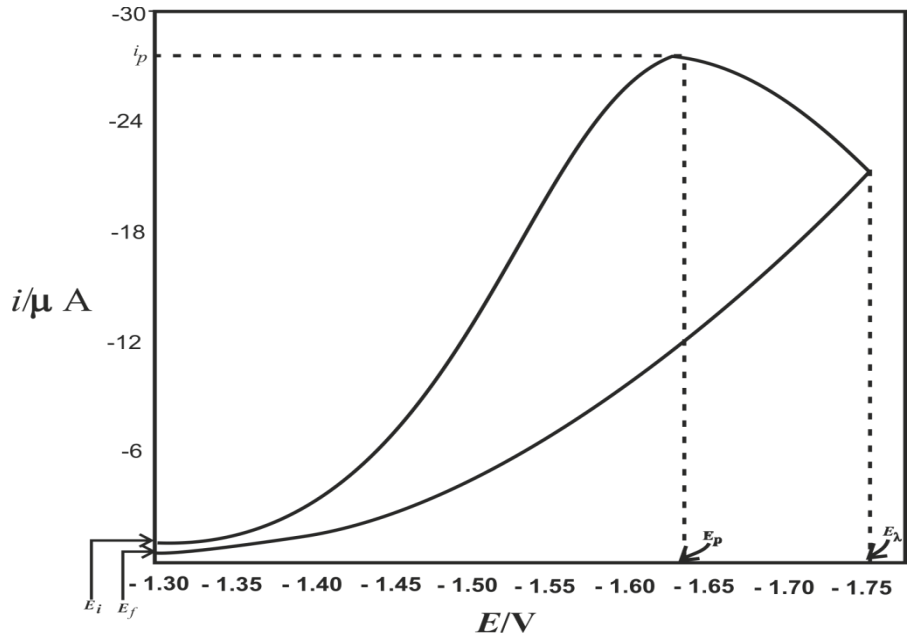


Figure 5. A cyclic voltammogram of a 1.00 x 10^{-3} NDMA solution

Cyclic voltammetric studies at different scan rates were also used to determine α. A typical cyclic voltammogram (CV) obtained for NDMA is shown in Figure 5 with cathodic peak potential (E_p) and cathodic peak current (i_p). The dependence of peak potential (E_p) and peak current (i_p) on scan rate (v) is given respectively by the theoretical equations [14,15]:

$$E_p = -\frac{RT}{2\alpha nF} \ln v + k \qquad (2)$$

$$i_p = \left(2.99 \times 10^5\right) n(\alpha n)^{\frac{1}{2}} A D^{\frac{1}{2}} c_o^* v^{\frac{1}{2}} \qquad (3)$$

from which α and the diffusion coefficient D can be obtained respectively from the gradient of plots of E_p versus $ln\ v$ and i_p versus $v^{1/2}$. Cyclic voltammograms (Figure 5) were recorded, at different scan rates (v), for seven solutions of NDMA within the concentration range 2.0 x 10^{-4} mol dm^{-3} to 5.0 x 10^{-3} mol dm^{-3}. The data obtained from each voltammogram were cathodic peak potential (E_p) and cathodic peak current (i_p).

To obtain α, E_p was plotted versus $ln\ v$. Five of these plots are shown in Figure 6. The transfer coefficient α was obtained from the gradient ($-RT/2\alpha nF$) of the plots (see Equation 2). The method of least squares [12] was used to draw the best straight line through the points to obtain α. The results, for various concentrations of NDMA, are given in Table 3 and show that $\alpha = 0.30$ and that it does not depend on concentration.

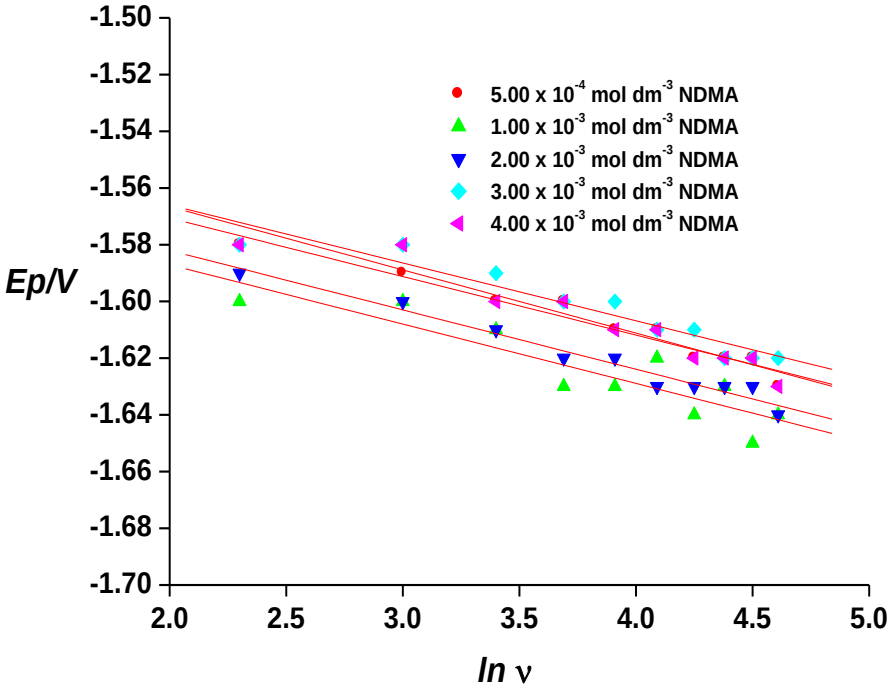


Figure 6. E_p versus $ln\ v$ plots for various concentrations of NDMA.

Table 3. α at various concentrations of NDMA (CV studies).

c_{NDMA} / mol dm^{-3} x 10^{-3}	α
0.20	0.30
0.50	0.30
1.00	0.30
2.00	0.31
3.00	0.32
4.00	0.30
5.00	0.30

To calculate the diffusion coefficient (D) of NDMA, i_p was plotted versus $v^{1/2}$, for various concentrations of NDMA (Figure 7). The best line was drawn through the points using the method of least squares. From the gradients of the plots, which is equal to (2.99×10^5) $n\,(\alpha n)^{½}\,AD^{½}\,c_o^*$ (see Equation 3), D was calculated, for each concentration of NDMA, using the known values for n, α, A and c_o^*: (n = 2, α = 0.28, and A = 0.0249 cm^2). The results are given in Table 4 which shows that the average value of D is 9.7 x 10^{-8} cm^2 s^{-1}. This value is smaller than that obtained by Pulidori et al [28] for the electroreduction of N-nitrosodipropylamine (NDPA) in alkaline solution (8.8 x 10^{-6} cm^2 s^{-1}) and by Gorski and Cox [33] for the oxidation of nitrosoamines on a modified glassy carbon electrode (8.8 x 10^{-6} cm s^{-1}).

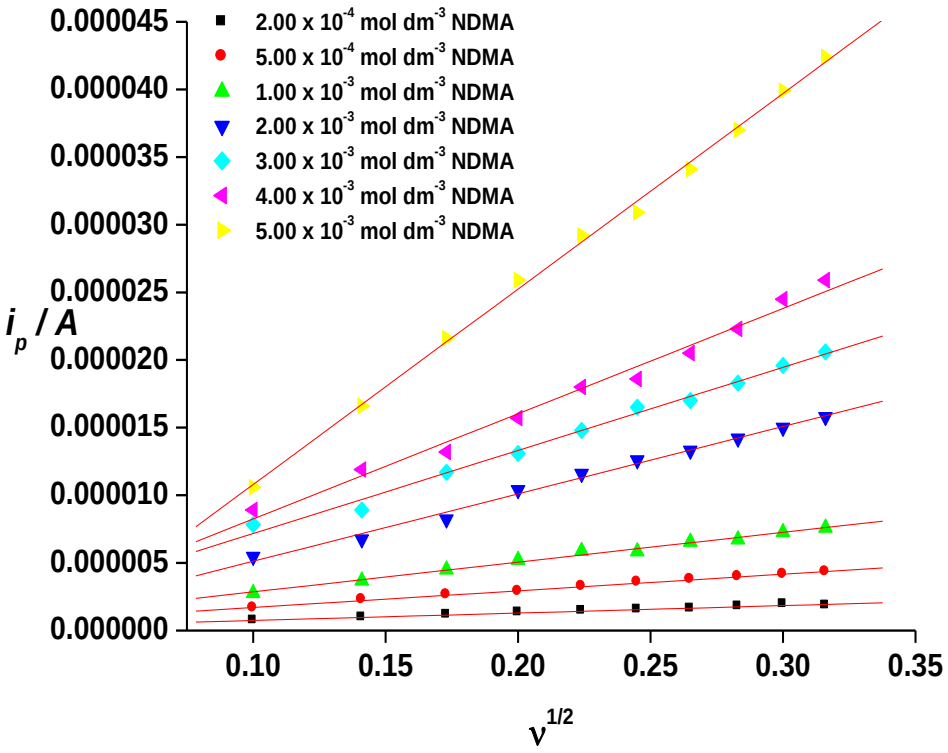


Figure 7. Plots of i_p versus $v^{1/2}$ for various concentrations of NDMA.

Table 4. *D* at various concentrations of NDMA (CV studies).

10^6 c_{NDMA}/mol cm^{-3}	α	10^5 Gradient	10^8 D/cm^2 s^{-1}
0.3	0.296	0.546	6.3
0.5	0.311	1.23	10.9
1.0	0.307	2.20	8.7
2.0	0.307	4.98	11.3
3.0	0.315	6.15	7.5
4.0	0.288	7.78	7.4
5.0	0.295	14.5	15.9

4. CONCLUSIONS

The kinetics of the electro-reduction of N-nitrosodimethylamine (NDMA) in alkaline solutions was investigated. Controlled potential coulometric studies showed that two moles of electrons were required for the reduction of one mole of NDMA and UV/VIS spectra of DMA and the reduction product indicated that the major product of the reduction was dimethylamine (DMA). From linear scan voltammograms (LSV), the transfer coefficient (α) and exchange current density (j_0) were calculated from plots of η versus $ln\ (i_p\text{-}i)/i$. The transfer coefficient (α) was found to be independent of concentration and its average value was 0.28. The exchange current density (j_0) was found to increase from 1.5×10^{-18} A cm^{-2} for a 2.00×10^{-4} mol dm^{-3} solution to 1.1×10^{-16} A cm^{-2} for a 5.00×10^{-3} mol dm^{-3} solution. From j_0 values, the standard exchange current density (j_{00}) was obtained by extrapolating a plot of j_o versus c_{NDMA} to unit concentration (1.00 mol dm^{-3}) , and this was found to be 1×10^{-12} A cm^{-2}. The low value for j_{00} implies that the electrode reaction is irreversible. Cyclic voltammograms were also used to determine α from plots of peak potential (E_p) versus $ln\ v$, for various concentrations of NDMA. The mean value of α was found to be 0.30 and this essentially agrees with that obtained from LSV studies (0.28). The diffusion coefficient was also obtained from the cyclic voltammograms and its average value was found to be 1×10^{-7} cm^2 s^{-1}.

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