THE ELECTROCHEMICAL REDUCTION OF NITRATE ION

AT VARIOUS CATHODES IN AQUEOUS ACIDIC SOLUTIONS

BY

ZAHRA POORABEDI

A thesis submitted for the degree of

Master of Philosophy

To my sweet little sister

Parirokh

UNIVERSITY OF SOUTHAMPTON

ABSTRACT

FACULTY OF SCIENCE

DEPARTMENT OF CHEMISTRY

Master of Philosophy

THE ELECTROCHEMICAL REDUCTION OF NITRATE ION
AT VARIOUS CATHODES IN AQUEOUS ACIDIC SOLUTIONS

by

Zahra Poorabedi

The electrochemical reduction of nitrate and nitrite ions has been studied under a range of conditions. It has been confirmed that in perchlorate and sulphate media, pH 0–2, the oxyanions may be reduced at some cathodes (Cu, Zn, Cd) but not at others (Hg, Pb, Ni). Rotating disc experiments and cyclic voltammetry has been used to show that at copper well formed reduction waves are observed; the electron transfer is irreversible and no electroactive intermediates may be identified, but the I-E characteristics exhibit potential regions where the process is mass transfer controlled. Halide ions inhibit the processes causing the reductions to be shifted to more negative potentials until they are masked by hydrogen evolution. In these solutions the controlled potential reduction of nitrate and nitrite requires 8F and 6F mole^{-1} respectively and leads to good material yields of ammonia. At a cadmium or zinc cathode, the reduction of the oxyanions occurs at potentials positive to metal dissolution and the I-E curves cross the $I = 0$ axis. Again, however, mass transfer controlled regions may be identified.

The reduction of nitrate at a mercury cathode does, however, take place in strongly acidic solutions (e.g. 10M H_2SO_4) or when the solutions contain certain reducible metal ions (e.g. Mo(VI), U(VI)). Polarograms of such ions in the presence of nitrate show catalytic nitrate reduction waves and the limiting current for this catalytic wave is shown to depend on pH and the presence of potential ligands in the medium.

ACKNOWLEDGEMENTS

I would like to thank the following people:

- ▲ My parents and sisters for financial support and encouragement.

- ▲ My supervisor, Dr. D. Pletcher, for his guidance and help throughout this work.

- ▲ Mr. T. Young and Mr. C. Godden for technical support.

- ▲ Mrs. W. Rogers for her care in typing this thesis.

CONTENTS

CONTENTS (continued)

CHAPTER 1

INTRODUCTION

There are several reasons for studying the electrochemical reduction of nitrate. Namely (i) to find a sensitive and reliable method for the analysis of nitrate ion in solution. Several papers have described procedures involving the indirect polarographic reduction of nitrate in the presence of metal ions or the direct reduction of nitrate ion at certain metal electrodes. The determination of nitrate and nitrite in soils and natural waters is very important; a limit of 45 ppm (7.4×10^{-4} M) nitrate has been imposed on drinking water and excessive amounts may lead to methaemoglobinaemia in humans (especially infants) by oxidation of the Fe (11) in haemoglobin by NO_3^- and NO_2^-. The methaemoglobin which is formed cannot combine with oxygen and death results. (ii) to convert nitrate into ammonia, for example by reduction at a copper cathode. (iii) to synthesise hydroxylamine which can be the product of electrolytic reduction of nitrate at cathodes such as mercury in concentrated sulfuric acid. (iv) to use nitrate as a forming agent in the manufacture of lead-acid batteries. The forming agent eliminates the dense passivating layers of lead sulfate during the production of $PbSO_4$ but is eventually removed by reduction to ammonia and hence does not effect the performance of the battery. (v) to assist the disposal of radioactive waste. Nitrate containing uranium wastes from nuclear reactors cannot be solidified into a glass. Reduction of nitrate to ammonia is a possible first step in a disposal procedure.

Electrochemical Reduction of Nitrate

Two distinct methods for the reduction of nitrate have been investigated:

(I)   Direct reduction at a metal cathode in acid solution.

(II) Reductions catalysed by a metal ion in solution either

      a)   a metal ion which itself reduces e.g. molybdenum and uranium

      b)   a highly charged cation which adsorbs at the electrode surface e.g. lanthanum, zirconium and aluminium.

1.1 Direct Reduction

The direct electrochemical reduction of nitrate has been reported to occur in several types of system. In weakly acidic aqueous solution the reduction has been said to occur at copper and cadmium cathodes but not at mercury and lead. On the other hand, in strong sulfuric acid (> 3M) the reduction takes place at most cathode materials. The final product of the reduction has variously been reported to be ammonia, hydroxylamine or gaseous

products (e.g. NO, N_2), depending on the experimental conditions, especially the cathode metal. In general, cathodes made of metals with a high hydrogen overvoltage (Hg, Pb, Sn, Zn, etc), favour the formation of hydroxylamine, while other metals, such as copper lead to the production of ammonia.

[A]   Weak Acid (<1M)

(i)   Copper

Turrentine[1] reported in 1906 that in order to reduce low concentrations of nitric acid it is necessary to use a copper cathode or introduce copper ions into the solution. Textbooks of chemistry generally report the complete reduction of dilute nitrate ion solution to ammonia after electrolysis at a copper cathode[2], but only recently there have been a few studies of this system[3-6], which clearly show the production of ammonia. It is believed[4] that the reduction of hydroxylamine occurs at a potential 0.6V more negative than that for nitrate ion reduction on a copper cathode. These workers also studied the behaviour of the current-potential curves on adding hydroxylamine sulphate to an acidic nitrate solution and found that the wave for the reduction of nitrate ion is shifted to negative potentials. It has proposed that the decrease in the rate of reaction was due to the interaction of the intermediate product of the reduction process (probably nitrite in the form of HNO_2), with hydroxylamine[4]. It is recognized that the intermediate cannot be hydroxylamine since this result is not consistant with the observation by Tafel[7], who showed that on copper cathodes hydroxylamine, unlike nitric acid, cannot be reduced. The reaction path

$$HNO_3 \longrightarrow \text{(labile compound)} \longrightarrow NH_3 \text{ (on Cu cathodes)}$$
$$\text{probably } HNO_2$$
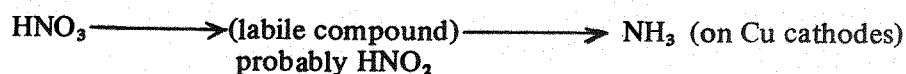
was therefore proposed.

(ii)   Cadmium

A method for the analysis of nitrate, based on its electroreduction at a rotating cadmium disc electrode has been reported recently[8]. The current-potential curves recorded for nitrate showed a reduction process immediately negative to the potential where cadmium dissolves i.e. the current-potential curve crosses the current axis without a region of zero current. A limiting current region was observed between -0.85 V and -1.3 V vs. SCE. The electrolyte used was 0.01 MHCl, because higher concentrations of acid caused the hydrogen discharge wave to be shifted to more positive potentials and interfered with the wave due to the nitrate reduction. For pH > 2 the rate of electrochemical reduction became too slow, and the value of current was not limited by the convective-diffusion

2

processes. It is shown that the plot of I_L vs. $\omega^{1/2}$ is linear only for low rotation rates of the disc electrode. Many species would interfere in this procedure (e.g. oxygen and transition metal cations which can be reduced at the electrode) and separation is required before the analysis. Davenport and Johnson have reported some further work on nitrate reduction at a rotating cadmium disc electrode[9]. Well developed current-potential curves were again observed and a limiting current region in a deaerated solution of $0.1M$ H_2SO_4 extends from $-0.80V$ to $-1.20V$. Voltammetric studies of a solution of nitrate in the presence of halides have been carried out and $I_L - \omega^{1/2}$ plots for each solution clearly showed that chloride and bromide inhibit the reduction slightly. The effect of iodide was found to be substantial, probably because iodide is strongly absorbed on cadmium cathodes[10] and blocks the active surface sites on the electrode. The effects on the nitrate reduction of the cations K^+, Mg^{++} and La^{+++} in the electrolyte was also investigated and it was found that the limiting current was decreased with increasing charge on the cation, being smallest when La^{+++} is present in the solution. According to Knoeck[11] nitrate is known to be complexed by La^{+++}. Davenport et al also showed that the reduction of nitrate occurs more rapidly at an anodized surface, compared to a mechanically polished one. The increase in current with an oxidized electrode is not simply due to roughening of the cadmium surface because when the surface was roughened the mass transfer limited current was smaller than when the polished electrode was used. It was concluded that anodizing the surface creates more active sites. Semi-stable electroactive intermediates which are produced by a kinetically controlled electrochemical reaction can be studied by using a rotating ring-disc electrode. Davenport and Johnson[9] used a RRDE which had a glassy-carbon disc plated with cadmium and a platinum ring. Nitrate was reduced at the disc at $-0.90V$ and the intermediate was detected by recording the current-potential curves at the platinum ring electrode. The current-potential curves for the intermediate formed during nitrate reduction at the Cd-plated disc electrode showed a small cathodic wave around $0.0V$ and a large anodic wave at $E > +0.8V$ at the platinum ring electrode. An anodic wave at this potential is observed on current-potential curves on solutions of both nitrite and hydroxylamine, but the NH_2OH does not show any cathodic wave at $0.0V$. Since the cathodic wave was observed in the current-potential curve of NO_2^- ion at a Pt ring electrode, they concluded that reduction of nitrate to nitrite at the rotating cadmium disc electrode is fast and the subsequent reduction of NO_2^- to NH_2OH is slower.

(iii) Deposited Copper and Cadmium on a Graphite Electrode

A procedure for the determination of nitrate is based on reduction to NO_2^- ion by passing the solution through a column that contains a Cu-Cd catalyst[12] and the colorimetric determination of nitrite. It is, however, necessary to maintain an active Cu-Cd surface and this is best achieved by generating the active surface in a reproducible way before each analysis. Bodini and Sawyer[13] based a voltammetric method for the determination of small amounts of nitrate ion ($10^{-2} - 10^{-6}$ M) on these observations; copper and cadmium metal were electrochemically deposited onto the surface of a pyrolytic graphite electrode. This method has the great advantage of achieving an active, reproducible reduction catalyst. Cyclic voltammagrams have been recorded showing a nitrate reduction peak at $-$ 1.0V vs. SCE. By use of a slow scan rate ($v = 10$ mV s^{-1}) and an excess of $CuCl_2$ in the electrolyte solution, the cyclic voltammagrams clearly exhibit two reduction peaks. The first one at $-$ 0.95V is due to NO_3^-, the second one at $-$ 1.1V to NO_2^- and hence mixtures may be determined.

[B] Strong Acid (> 1M)

(i) Copper

A study of the electrochemical behaviour of nitric acid on a copper cathode has been reported[6]. Nitric acid at concentrations of $10 - 260$ g/l was found to give ammonia as the final product. It was noted that using a concentration of nitric acid above 260 g/l caused the chemical dissolution of the copper.

(ii) Cadmium

The study of the electrochemical reduction of concentrated nitric acid on a rotating cadmium disc electrode was carried out by a Russian group[18]. Cathodic current-potential curves were reported in the potential region of $-$ 0.45V to $-$ 0.65V. The value of the limiting current was found to increase with decreasing nitrate concentration and increasing hydrogen ion concentration. Analysis of the solution after the polarization experiments and the current-potential curves suggested the following conclusions:
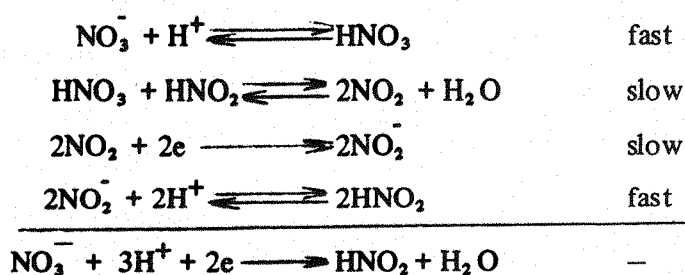
1) In all the solutions studied and in the potential region used, there is a dissolution of cadmium as well as reduction of nitrate ion.

2) The reduction of nitrate leads mainly to the formation of nitrous acid. (Very small amounts of hydroxylamine was reported to be detected in the solution).

3) The rate of the cathodic reduction of nitrate depends on:

   a) The rate of rotation of the electrode;

b) Hydrogen ion concentration;

c) Concentration of nitrates in the solution.

The plots of I_L vs. $\omega^{1/2}$ were linear and passed through the origin as required for a mass transfer controlled process. It was suggested that the decrease in the reaction rate due to the increase in nitrate concentration is caused by a change in the activity coefficient of the diffusing ions. This result is in contradiction with those reported by Davenport and Johnson[8 9] who reported that the limiting currents were higher with increasing nitrate ion concentration. The Russian group concluded that the rate of reduction is controlled by the rate of mass transport of protons to the surface. The diffusion coefficient calculated from the Levich equation and the limiting current for the solution of $1 - 4$ M nitrate ion (pH 1–3), was close to the value found for hydrogen ions in the literature. This conclusion concerning the rate determining step was supported by the fact that the rate was increased in the presence of anions capable of playing the role of proton donors i.e. $H_2PO_4^-$, CH_3COOH, etc.

(iii) Platinum

Faraday observed that in the electrolysis of dilute nitric acid solutions between platinum electrodes, hydrogen was evolved from the cathode, but with concentrated solutions no hydrogen evolution occurred[14]. The cathodic products in this case being nitrous acid and probably nitric oxide. It is found[15 16] that the smallest concentration of nitric acid which can be reduced electrochemically to nitrous acid is 18 per cent[17], at lower concentrations the only process which can take place is hydrogen evolution. The mechanism of the direct electrochemical reduction of high concentration of nitric acid at Pt electrode proposed by Vetter[19 20] is shown below:
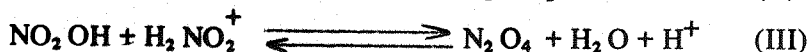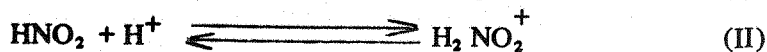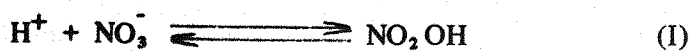
$$NO_3^- + H^+ \rightleftharpoons HNO_3 \qquad\qquad \text{fast}$$
$$HNO_3 + HNO_2 \rightleftharpoons 2NO_2 + H_2O \qquad \text{slow}$$
$$2NO_2 + 2e \longrightarrow 2NO_2^- \qquad\qquad \text{slow}$$
$$2NO_2^- + 2H^+ \rightleftharpoons 2HNO_2 \qquad\qquad \text{fast}$$

$$\overline{NO_3^- + 3H^+ + 2e \longrightarrow HNO_2 + H_2O} \qquad -$$

As soon as nitrous acid forms it decomposes by the following chemical reaction:
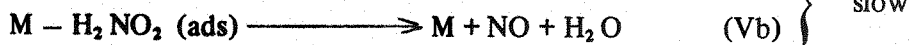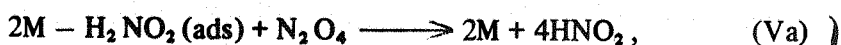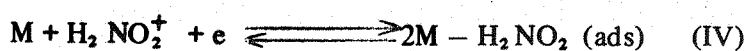
$$3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O$$

From their results it was suggested[21] that nitric acid is reduced at all electrodes to gaseous products such as nitric oxide at high concentrations of acid ($> 3N$). This conclusion is contradictory with the results of some other workers[22–24] who used a mercury electrode and

concentrated nitric acid and found hydroxylamine as being the main product. The mechanism of the reaction has been studied recently; the galvanostatic polarization curves were recorded[25] and the influence of various acids and organic solvents on the electrochemical reduction was investigated. The cathodic polarization curve for 2M nitric acid, in which nitric acid was reported to be almost completely dissociated[26], was recorded. In this condition HNO_3 is not reduced[27] and hydrogen discharge takes place at the cathode. Addition of acetone or dioxane was shown to shift the polarization curves to a more positive potential region, where reduction of nitric acid occurs. Acetic, hydrofluoric, phosphoric, or sulfuric acid were found to have the same effect, accelerating the rate of the reaction. It is believed that the mechanism of reaction involves the adsorption of the intermediates at the electrode[25]. In the near electrode layer the reactions are shown below:

$$H^+ + NO_3^- \rightleftharpoons NO_2OH \qquad (I)$$

$$HNO_2 + H^+ \rightleftharpoons H_2NO_2^+ \qquad (II)$$

$$NO_2OH + H_2NO_2^+ \rightleftharpoons N_2O_4 + H_2O + H^+ \qquad (III)$$

While at the electrode surface the following reactions are believed to occur:

$$M + H_2NO_2^+ + e \rightleftharpoons 2M - H_2NO_2 \text{ (ads)} \qquad (IV)$$

$$2M - H_2NO_2 \text{ (ads)} + N_2O_4 \longrightarrow 2M + 4HNO_2, \qquad (Va) \left. \begin{array}{c} \\ \\ \end{array} \right\} \text{ slow}$$

$$M - H_2NO_2 \text{ (ads)} \longrightarrow M + NO + H_2O \qquad (Vb)$$

It is shown that in $HNO_3 - H_2O$ system, the rate of cathodic reduction of HNO_3 depends on the concentration of undissociated acid molecules, and the presence of acetone or dioxane (in fact oxygen) increase the concentration of undissociated acid molecules, which are involved in the cathodic reduction.

(iv) Graphite

It seems likely that at high concentrations of HNO_3 most electrode materials are active towards nitrate reduction e.g. graphite electrode has also been shown to be a suitable cathode[21]. The polarization curves show that the electrochemical reduction occurs at potentials positive with respect to the standard calomel electrode., (between 0.8 and 0.0 V vs. SCE). It is reported that depending on the conditions of the electrolysis between 1 and 2.5 Faradays/mole are required for the reduction of nitric acid and during the reaction gases were evolved from the cathode; they were analysed and found to be nitrogen dioxide and carbon dioxide. Because of consumption of 1 – 2.5 Faradays for the complete reduction of one mole of acid and other observations, it is suggested that the main electrochemical process is the reduction of nitrous acid according to one of the following reactions:

6

$$2HNO_2 + 4H^+ + 4e \longrightarrow N_2O + 3H_2O \qquad (1)$$

$$HNO_2 + H^+ + e \longrightarrow NO + H_2O \qquad (2)$$
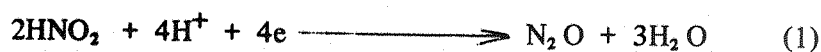
These reactions require between 1e and 2e/molecule for the reduction of nitric acid. As it was found the NO_2 was the main product of the nitrate reduction in this system and since NO is rapidly oxidized to NO_2 by air, it seems that reaction (2) is more probable. It is suggested[21] that the source of nitrous acid must be a chemical reaction with graphite.

$$HNO_3 + C \longrightarrow CO + HNO_2$$

$$2HNO_3 + C \longrightarrow CO_2 + 2HNO_2$$

The standard oxidation potential of N(V) to N(III) is + 0.94V while that of C → CO is + 0.51V and that of C → CO_2 is − 0.116V, so carbon is thermodynamically capable of reducing nitric acid[28].

(v) Mercury

The synthesis of hydroxylamine by direct reduction of nitrate ion has been studied[22-24]. Hydroxylamine can be produced by the electrolytic reduction of nitric acid in sulfuric acid using a mercury cathode[22]. The best conditions found were as follows: current density 0.25 A cm^{-2}, temperature 14 − 16°C, nitric acid concentration maintained constant at 1M by continuous addition, sulfuric acid concentration 15N at the start, decreasing to 3N at the end of the run. The remainder of the nitric acid is removed by electrolysis with a copper cathode which converts the nitrate to ammonia. Hydroxylamine sulfate can be crystallized out after the solution is made neutral. During the electrolysis, some isomonosulphohy-droxylamine sulfate $(NH_2 O SO_3 H)_2 H_2 SO_4$ is also formed. This compound may be distinguished from $NH_2 OH . H_2 SO_4$ by its ability to oxidize iodide ion to iodine in acid KI solution. It was found that the current efficiency for $NH_2 OH$ formation was increased by increasing the sulfuric acid concentration and also the nitric acid concentration up to a certain limit. It was shown however that using $H_2 SO_4$ concentration above 16N, and in the presence of nitric acid, the mercury cathode dissolves spontaneously. It was also noticed that increasing the nitric acid concentration above 1M greatly increases the formation of nitrogen oxides during the electrolysis. The electrolysis of nitric acid at the mercury cathode is effected adversely by using materials with some impurities. In this case almost 100% evolution of hydrogen occurs, and at higher HNO_3 concentration nitrogen oxides are evolved. It is proposed that the decrease in nitrate reduction occurs due to the formation of a thin white film which is visible most of the time. This film does not permit the reduction of nitric acid and causes its decomposition into oxides of nitrogen.
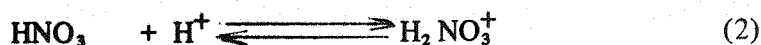
In 1947 Lazzari worked on the electrochemical reduction of nitric acid at an agitated mercury cathode in an apparatus in which cooling was possible[23]. The two lead anodes were enclosed in the porous cups. Hydroxylamine concentrations up to 70 − 100 g/l could be obtained before further reduction to ammonia became excessive, if a high current density (e.g. 0.1 A cm^{-2}) without excessive heating, was used. The yield of NH_2OH based on nitric acid was found to be 75 − 78%. Other workers[24] found that Fe^{3+} hindered the formation of hydroxylamine and when hydrogen chloride gas is passed through the cooled reduced catholyte hydroxylamine hydrochloride separated out. As a result of the study of nitric acid with mercury in sulfuric acid, the following scheme for the reaction mechanism has been suggested[29].
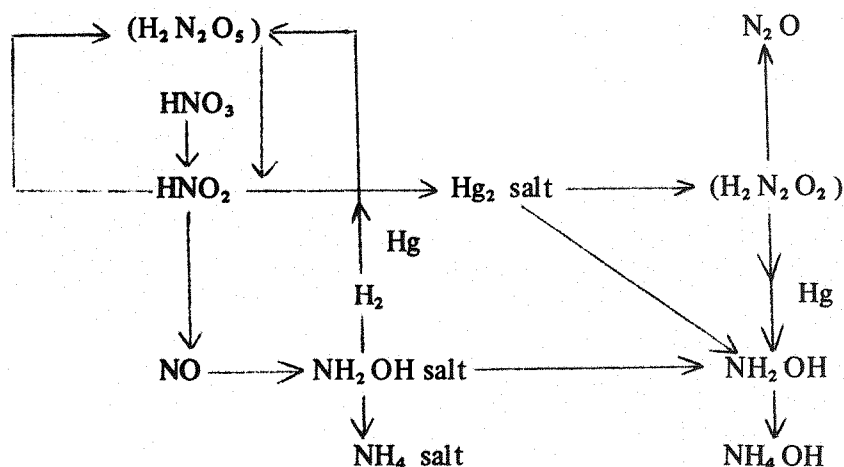
The reduction proceeds without evolution of hydrogen. The intermediates for which they had no evidence are enclosed in brackets.

It can be concluded that all electrochemical reductions of nitrate ion only occur in acidic media and the reduction product certainly depends on the cathode metal, the potential of electrode and the concentration of acid used. However we believe that the reduction process in the presence of strong and dilute acid proceed through different mechanisms. In very strong acids the following reactions can take place:

$$NO_3^- + H^+ \rightleftharpoons HNO_3 \qquad (1)$$

$$HNO_3 + H^+ \rightleftharpoons H_2NO_3^+ \qquad (2)$$

$$H_2NO_3^+ \rightleftharpoons NO_2^+ + H_2O \qquad (3)$$

Equilibrium (3) is very important in concentrated acid solutions and the cations can be reduced very easily through an electron transfer mechanism.

1.2 Indirect Reduction

[A] Reduction in the Presence of a Metal Ion which Itself Reduces e.g. molybdenum and uranium

In this kind of system, the electrode reaction is certainly the reduction of the transition metal followed by a chemical reaction between nitrate ion and the reduced form of the metal with the regeneration of the transition metal in its original oxidation state. Transition metals which have been used include molybdenum, tungsten and uranium.

(i) The study of the electrochemical behaviour of some transition metal ion in various electrolytes

The electrochemical behaviour of aquomolybdenum ions has been studied[30] in the absence of complex formation by using trifluoromethanesulfonic acid as the supporting electrolyte. It was shown that monomeric and dimeric Mo(III) ions undergo oxidation yielding dimeric Mo(V) ions. The rate of oxidation of both forms were found to be limited by chemical reactions that precede the electrode reaction. Controlled potential electrolysis of a Mo(III) solution at the potential of the limiting current region of the current-potential curve at a stirred mercury pool electrode proceeded very slowly with the consumption of 2F/mol of molybdenum and the product was analysed and found to be a dimeric form of Mo(V). It was suggested that the transient species which gave a pulse polarographic wave might be an unstable form of Mo(V) that is produced initially when Mo(III) is oxidised. The same wave was also observed in the polarogram of the reduction of Mo(VI). It was shown that the reduction product of Mo(VI) is different. The product when the potential was chosen to be in the most negative plateau region of the polarogram of a Mo(VI) solution was a green solution of dimeric Mo(III).

Kolthoff and Hodara[31] studied the polarographic behaviour of Mo(VI) in aqueous sulfuric acid solutions. It was shown that under suitable conditions two waves could be observed on the polarogram; these were proposed to be due to the reduction of Mo(VI) to Mo(V) and Mo(V) to Mo(III). They have concluded that in concentrated sulfuric acid, the first wave splits into two overlapping waves which were attributed to the existence of different forms of Mo(VI) in this acid concentration. They also observed that in acid concentration less than 0.1M, the second wave may be split into two waves, which were found to be diffusion controlled showing that there are two different Mo(V) species present and they are not in rapid equilibrium.

The polarographic study of Mo(VI) in hydrochloric acid solution has been reported[32].

The polarogram of 8.7 x 10^{-5} M molybdenum (VI) in a solution of HCl was found to show a single wave. Since no reduction wave was observed in the polarograms for Mo(V) in the same solution, it is suggested that the product of the reduction of Mo(VI) should be an oxidation state below Mo(V). The wave was analysed in different ways and it was concluded that it was a two electron reduction process, that is the conversion of Mo(VI) to Mo(IV).

Johnson and Robinson[33] investigated the polarography of molybdate solution in different acid concentrations and found that the best formed waves were observed with 0.1M sulfuric acid containing 0.2M sodium sulfate as supporting electrolyte. The polarogram of molybdate in this electrolyte showed three polarographic waves indicating the stepwise reduction of Mo(VI) and finally the rising portion due to the hydrogen evolution process. It was observed that the first reduction current is almost one third as large as the diffusion current for the overall reduction and it is suggested that at the potential of the first step Mo(VI) is converted to Mo(V). The diffusion current observed for the second and third waves were found not to be equal and the combined wave heights represent the reduction to Mo(III). Because the magnitude of the second and third waves were changing with change in acid and molybdenum concentration, it was suggested that Mo(V) is directly converted to Mo(III) rather than reduction to Mo(IV) and then Mo(III). Two mechanism can be proposed:

1) The Mo(V) formed in the first step exists in two different forms which are reducible at different potentials.

2) The reduction product Mo(III) exists in two different forms which requires different potentials to form.

With either of these assumptions the current at the plateau region of the last wave represents the completed valence change for the molybdenum solution.
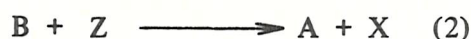
A polarogram of uranyl chloride in dilute hydrochloric acid (0.001N to 0.1N), shows two reduction waves[34]. The first one was suggested to be due to a reduction of U(VI) to U(V) and the second one corresponds to the two consecutive reductions of U(V) to U(IV) and U(III). The second wave is, however, much bigger than twice the first because it is partially a catalytic hydrogen wave.

During the investigation of the polarographic behaviour of molybdate in acidic solution, it was noted that the presence of nitrate led to an increase in the limiting current density for the reduction of Mo(V) to Mo(III), which was attributed to the catalytic nitrate reduction[33].

(ii) Catalytic polarographic currents

The nature of the catalytic polarographic current can be explained by considering an electrode process in which a substance A is reduced to another substance B at the dropping mercury electrode (Reaction (1)). The solution also contains a substance Z which is not reducible at the dropping mercury electrode at the potential at which the limiting current for A is observed.

$$A + ne \xrightarrow[\text{process}]{\text{electrode}} B \qquad (1) \qquad \text{(diffusion controlled)}$$

$$B + Z \longrightarrow A + X \qquad (2)$$

Furthermore, Z reacts with B to regenerate substance A (Reaction (2)). Because A is continuously regenerated, the limiting current due to reaction (1) is increased. The increase of current is determined by the kinetics of reaction (2) and by the diffusion process of substances A, B and Z. Delahay and Stiehl derived an equation for the catalytic current as follows:[35]

$$I_c = 0.753 \times 10^6 \; n \, m^{2/3} \; t^{2/3} \; D_A^{1/2} \; C_A \; C_Z^{1/2} \; k_2^{1/2}$$

where
$\quad I_c =$ the catalytic current in microamperes;

$\quad n =$ the number of electrons transferred in the electrochemical reaction (1);

$\quad m =$ the number of milligrams of mercury per second flowing from the capillary;

$\quad t =$ the time in seconds, of formation of each drop of mercury;

$\quad D_A =$ the diffusion coefficient of substance A in cm^2/S;

$\quad C_A =$ the concentration in moles per litre of substance A in the bulk of the solution;

$\quad C_Z =$ the concentration of substance Z in moles per litre;

$\quad k_2 =$ rate constant in litres per mole per second for reaction (2).

(iii) Catalysed Reduction of Nitrate

Polarographic results for molybdenum in sulphate medium and in the presence of nitrate ion[33] showed that the reduction current was increased in the beginning of the second wave where the reduction of molybdenum to the Mo(III) species takes place. It is concluded that nitrate is chemically reduced by the Mo(III) species formed in the vicinity of the growing mercury drop. The reoxidized form of the molybdenum then reduced again at the cathode resulting in an enhancement of the current due to the presence of nitrate.

$$Mo(VI) \ + \ 3e \longrightarrow Mo(III)$$

$$Mo(III) \ + \ NO_3^- \longrightarrow Mo(VI) \ + \ Product$$
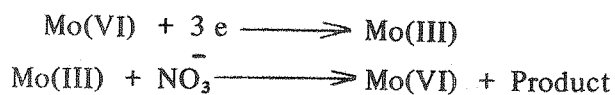
From the results it is clear that the reduction current for a molybdate-nitrate solution is limited not only by the diffusion rate, but also by the rate of chemical interaction between the nitrate and Mo(III). Because the nitrate reduction current is not diffusion controlled, the number of electrons involved in the reduction of each NO_3^- ion cannot be calculated from the Ilkovic equation.

In the presence of uranyl ion[34], nitrate is reduced at the potentials where the second wave of uranium occurs in dilute solution of hydrochloric acid. It is found that when uranyl is a catalyst for the nitrate reduction, there is a good proportionality between the diffusion current and nitrate concentration when the ratio of uranyl to nitrate is above a certain minimum.
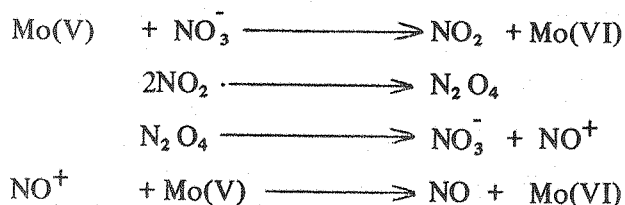
[B] Reduction in the Presence of a Highly Charged Cation

Systems involving Al^{3+}, La^{3+}, Zr^{4+} etc[36], are thought to involve a totally different mechanism. The metal ions mentioned above do not reduce but adsorb on the electrode surface and affect the electrostatic repulsion between the negatively charged electrode and the anion and promote electron transfer to nitrate.

A method for the determination of trace quantities of nitrate ion by linear scan voltammetry at a stationary mercury drop electrode has been reported[36]; 0.1M KCl was used as supporting electrolyte and the experiments were carried out in the presence of lantanium (III) in the solution.
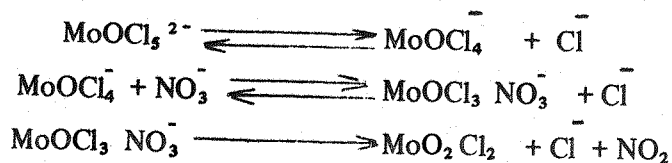
1.3   Related Chemical Reductions

Chemical reduction of nitrate ion by Mo(V) in tartrate buffer (PH 2.2 − 3.5) has been studied[37]. It was found that NO is the major product and Mo(V) monomer acts as the reactive species in this reduction reaction. The proposed mechanism is as follows:
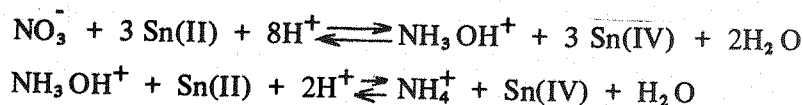
$$Mo(V) \ + \ NO_3^- \longrightarrow NO_2 \ + Mo(VI)$$

$$2NO_2 \longrightarrow N_2O_4$$

$$N_2O_4 \longrightarrow NO_3^- \ + \ NO^+$$

$$NO^+ \ + \ Mo(V) \longrightarrow NO \ + \ Mo(VI)$$

The reaction was found to be half order with respect to Mo (V) and first order with respect to nitrate.

Chemical reduction of nitrate by diammonium oxopentachloromolybdate (V) $(NH_4)_2 MoOCl_5$ in anhydrous dimethylformamide (DMF) was investigated[38]. The reaction was found to be first order in Mo(V) and nitrate ion and inhibited by Cl^-. The mechanism

12

said to involve a particular Mo(V) intermediate as shown below:

$$MoOCl_5{}^{2-} \rightleftharpoons MoOCl_4^- + Cl^-$$

$$MoOCl_4^- + NO_3^- \rightleftharpoons MoOCl_3\,NO_3^- + Cl^-$$

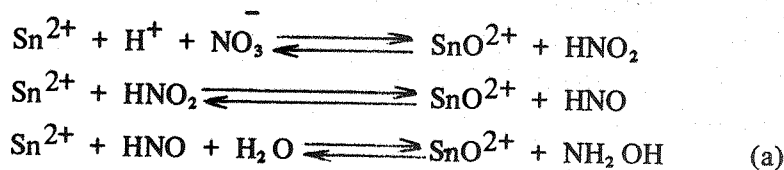$$MoOCl_3\,NO_3^- \longrightarrow MoO_2Cl_2 + Cl^- + NO_2$$

The reduction of nitrate with Sn(II) in the presence of molybdate catalyst in acid solution has also been studied[39]. The product of the reduction is found to depend on the acid used and its concentration. The reaction between nitrate and Sn(II) in the presence of molybdenum in 3.0M HCl is said to be as follows:

$$NO_3^- + 3\,Sn(II) + 8H^+ \rightleftharpoons NH_3OH^+ + 3\,Sn(IV) + 2H_2O$$

$$NH_3OH^+ + Sn(II) + 2H^+ \rightleftharpoons NH_4^+ + Sn(IV) + H_2O$$

It is believed that the nitrate reduction in HCl is much faster than in H_2SO_4. In 3.0M H_2SO_4 and 1.5M HCl plus 1.5M H_2SO_4 a different product is observed:

$$2NO_3^- + 4\,Sn(II) + 10H^+ \rightleftharpoons N_2O + 4\,Sn(IV) + 5H_2O$$

They suggested that the reason for the different products in sulfuric acid is due to the properties of the active intermediate HNO. It is assumed that stannous ion acts as a two electron reducing agent (acting as an oxygen atom acceptor); using this assumption nitrate ion may be reduced as follows:

$$Sn^{2+} + H^+ + NO_3^- \rightleftharpoons SnO^{2+} + HNO_2$$

$$Sn^{2+} + HNO_2 \rightleftharpoons SnO^{2+} + HNO$$

$$Sn^{2+} + HNO + H_2O \rightleftharpoons SnO^{2+} + NH_2OH \qquad (a)$$

HNO can react with itself in acid solution to form its anhydride

$$HNO + HNO \rightleftharpoons N_2O + H_2O \text{ (or } H_2N_2O_2) \quad (b)$$

So HNO can take part into two reactions. Reaction (1) will be favoured by low concentration of HNO and high reactivity of the reducing agent whereas the rate of the second reaction will increase as the square of the concentration of the active intermediate HNO. It is concluded that reaction (1) is dominant when $SnCl_3^-$ which is the most reactive species of Sn(II) is present in solution and that is the case when HCl is used. Although it is suggested that the effect of Sn(II) is to remove oxygen from nitrate ion (acting as an oxygen atom acceptor), it may well be that stannous ion reduces molybdenum (VI) to an active valence state towards for reduction as follows:

$$Sn(II) + Mo(VI) \rightleftharpoons Sn(IV) + Mo(IV)$$

$$2Mo(IV) \rightleftharpoons Mo(V) + Mo(III)$$
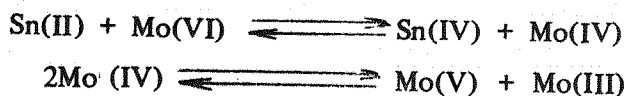
The Mo(III) species which is formed can then reduce nitrate.

Chemical reductions of nitrate are always likely to be oxygen transfer reactions:

$$M \xrightarrow[\text{Sn(II) or } e^-]{+ n e} M'$$

$$M' + NO_3^- \longrightarrow M' - O + \text{product}$$
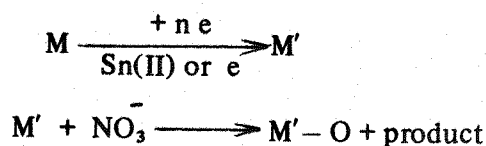
Hence for a high current density for the reduction of nitrate one needs to choose conditions for a fast oxygen transfer reaction i.e. select a metal ion which can make a strong $M-O$ bond and design ligands to assist the reaction (note effect of Cl^- mentioned above).

1.4 Purposes of this Study

While these methods for the reduction of nitrate have been investigated and seem to have some practical application, very little is known for certain about the mechanisms of the electrode processes involved. Indeed the nature of the products and hence the overall reactions taking place were almost always not known and the statements which appear in the literature are often pure speculation. Hence the objective of this project was to define the products and to investigate the mechanisms of the reactions. Certainly it was hoped to answer questions such as (a) what metals may be used as cathodes for the direct reduction of nitrate? Which property determines their suitability? (b) Which reducing agents can be generated cathodically and react rapidly with nitrate so as to produce high catalytic polarographic currents? Why do some reducing agents react with nitrate and others not, and what determines the kinetics of these reactions?

CHAPTER 2

EXPERIMENTAL

2.1 Introduction

All of the electrochemical experiments reported in this thesis involve controlled potential techniques, such as steady state current potential measurements, cyclic voltammetry, controlled potential electrolysis, rotating disc studies and polarography. All the experiments except the coulometric and rotating disc electrode experiments were carried out in quiet solutions. Solutions were de-gassed for about 15 minutes before each experiment except for controlled potential electrolysis, when the solution was stirred by N_2 throughout the experiments.

This chapter describes the electrochemical cells and electrodes, instrumentation, solution preparation, methodology of the experiments and the source and purification of chemicals.

2.2 Electrochemical Cells and Electrodes

Electrochemical experiments were carried out with two and three compartment cells.

Steady state current potential measurements were carried out using copper and cadmium wire electrodes as working electrodes. The exposed length of copper and cadmium wires were 2.5 cm. and 2.7 cm. respectively and the radii were 0.05 cm; the experiments were performed in a three compartment, three electrode cell of the type shown in Figure 2.1. The secondary electrode was platinum gauze and the reference electrode was a Radiometer type K401 saturated calomel electrode (as in all experiments).

The cell used for controlled potential coulometry was a conventional three-electrode three compartment cell as shown in Figure 2.1. The working electrodes were a copper gauze with nominal area 8.6 cm² and a cadmium wire, 48 cm. in length, formed into a flat spiral. The capacity of the working electrode compartment of the cell was approximately 30 cm³, which was reduced to about 20 cm³ by using some glass balls inside the working electrode compartment. The reference electrode was placed in a compartment separated from the working electrode compartment by an adjustable Luggin capillary inserted horizontally into the cell through a side tube. The secondary electrode was a platinum gauze, placed in a compartment separated from the working electrode compartment by a fine glass sinter.

Cyclic voltammetry and rotating disc electrode experiments were carried out using polished copper disc (area 0.16 cm²) and cadmium disc (area 0.33 cm²) working electrodes and were performed in a two compartment, three electrode cell of the type shown in
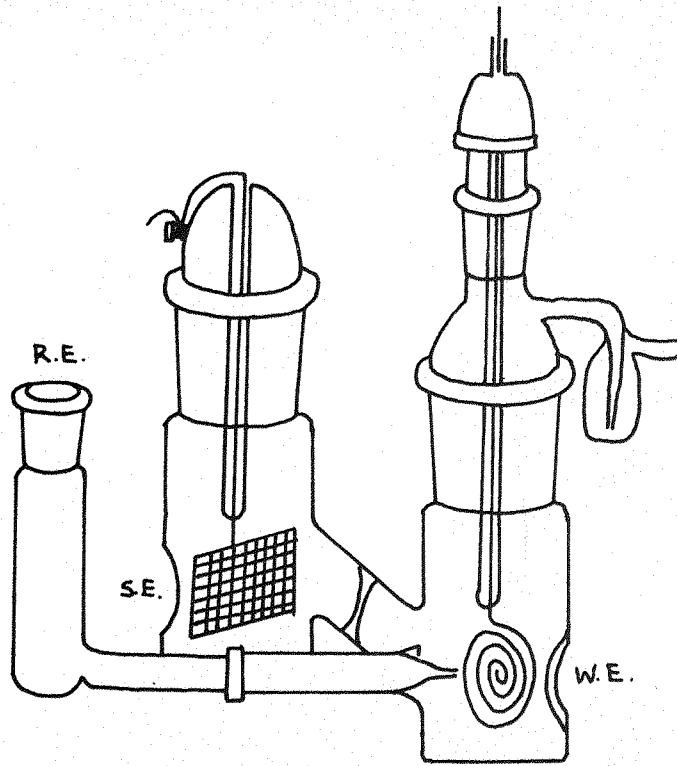
15

Figure 2.1

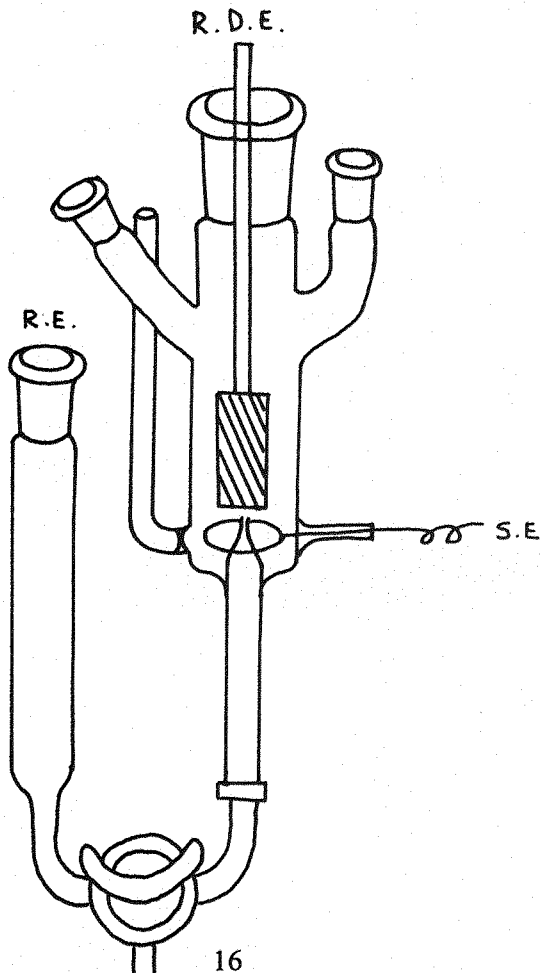R.E.

S.E.

W.E.

Figure 2.2

R.D.E.

R.E.

S.E

16

Figure 2.2. The copper and cadmium disc electrodes were inserted into the cell from the top in such a way that the surface faces vertically downward. The height of the electrode inside the cell was adjusted to make the distance between the electrode surface and the fixed Luggin capillary approximately 0.1 cm. The fixed Luggin capillary was attached to a separate reference electrode compartment. The secondary electrode was a platinum spiral placed round the working disc electrode.

Steady state current potential measurements were also carried out using a mercury drop working electrode in a cell of the type shown in Figure 2.3. It was a two compartment three electrode cell with a sitting drop of mercury as working electrode. A capillary attached to a syringe, filled with doubly distilled mercury, was fitted with a micrometer screw-gauge. The capillary was inserted into the cell vertically upwards. Mercury drops of reproducible surface area were formed on the capillary tip with the help of the micrometer. The secondary electrode was a platinum spiral round the working electrode and was inserted vertically downward into the cell. The same reference electrode was used in a compartment separated from the working electrode compartment by an adjustable Luggin capillary.

Polarographic experiments were carried out using a cell with two electrodes as shown in Figure 2.4. A mercury pool was used as the reference electrode. The working electrode consisted of a fine capillary tube down which mercury flows under a gravitational force (i.e. a head of mercury).

2.3 Electrode Pretreatment

Before each experiment with a copper wire or a copper gauze electrode they were cleaned with nitric acid, then with tap water and finally distilled water. The cadmium wire was cleaned with emery paper until the surface looked smooth, then with tap water and distilled water.

Before using the copper disc and cadmium disc electrodes, the following pretreatment was followed:

(i)   the electrode surface was cleaned by polishing it with a fine emery paper

(ii)   the electrode was then polished on a selvyet cloth first with 0.1μ
       β alumina powder until the surface looked smooth and then with 0.05μ
       γ alumina powder to make the surface mirror bright. Both β and γ polishing
       alumina and the selvyet cloth were supplied by Banner Scientific ltd.

(iii) the electrode was washed with tap water and then with distilled water.

In all the experiments carried out with mercury electrodes, doubly distilled mercury
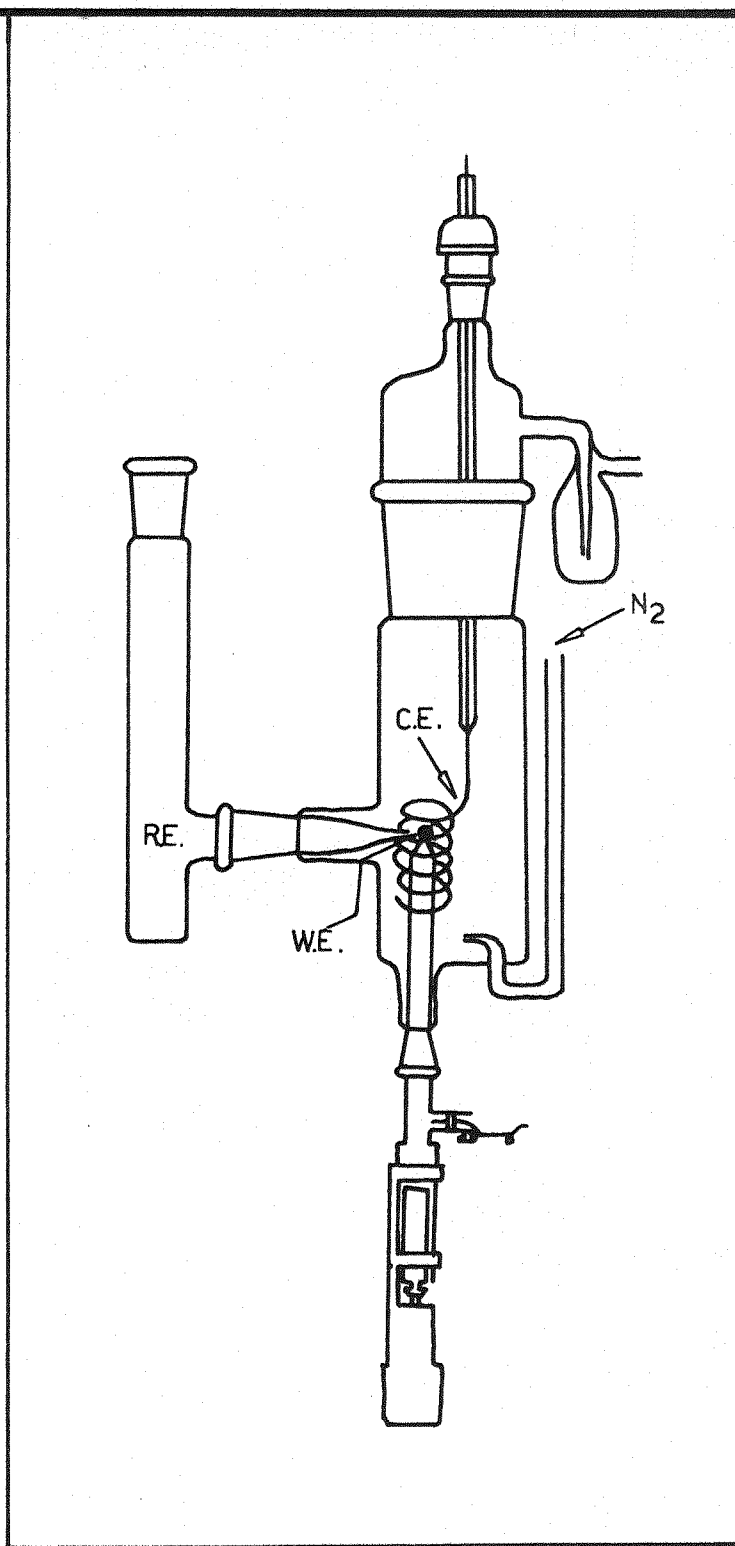
17

Figure 2.3 . Electrochemical cell used for
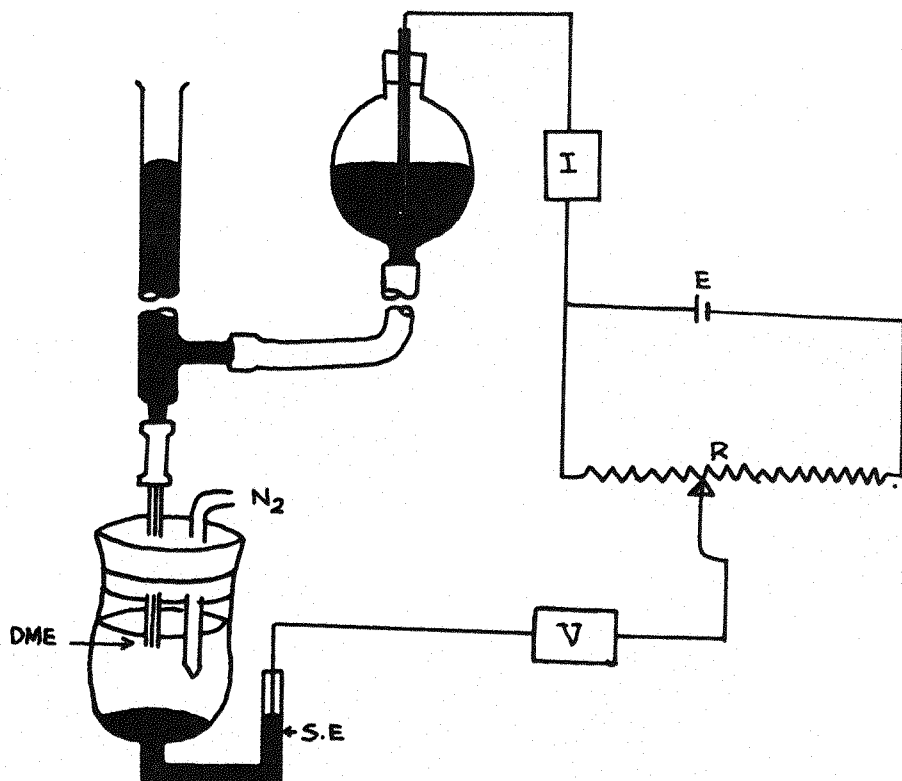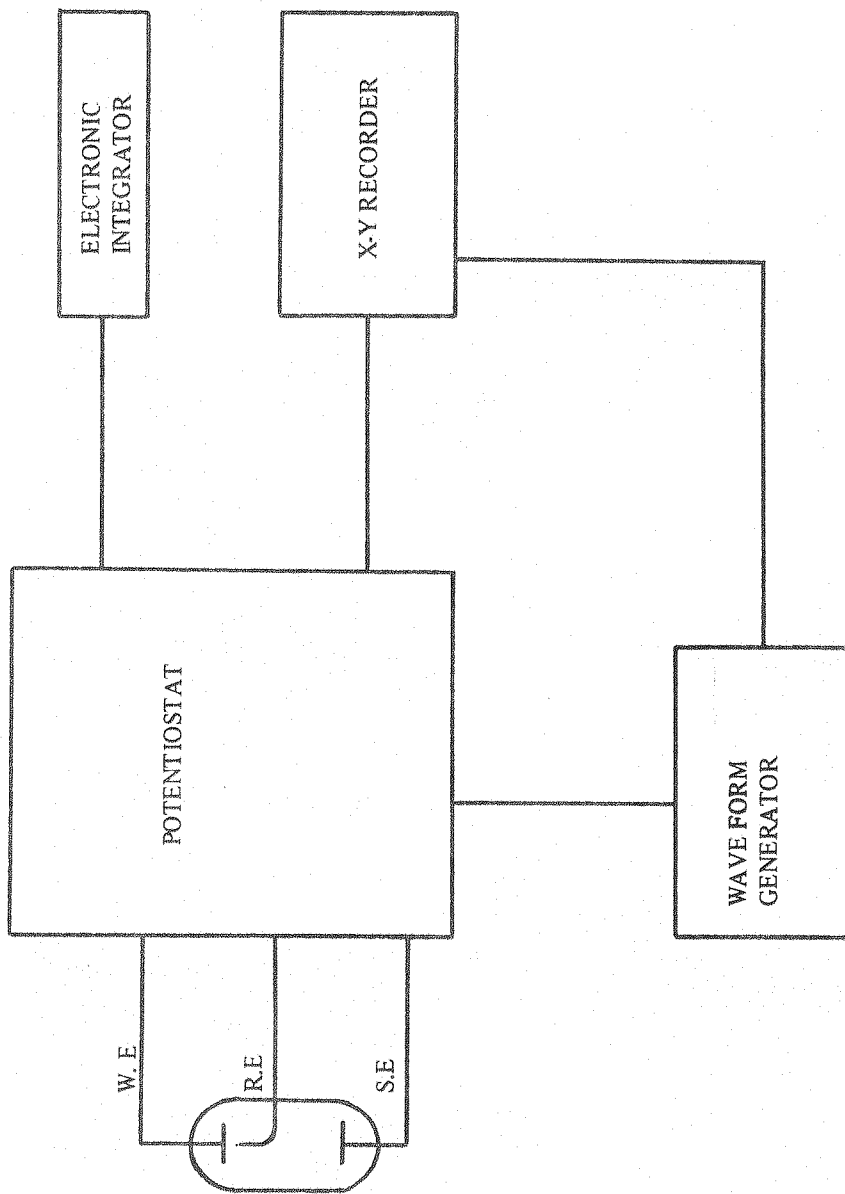experiments with a mercury drop
electrode.

Figure 2.4

Figure 2.5 Apparatus used for electrochemical experiments

was used. The mercury drop was renewed manually in experiments using sitting mercury drop electrode and by a gravitational force in polarography.

2.4 Instrumentation

Most of the electrochemical experiments were carried out using a Chemical Electronics value potentiostat type V150/1.5A and a waveform generator (type RB1S). In some of the disc electrode experiments a Hi-Tek Instruments potentiostat type DT 2101 and a wave-form generator PPR1 were used. In the controlled potential electrolyses an electronic integrator was used for measuring the charge and the current was monitored by using an external ammeter. For rotating disc electrode experiments the electrode is rotated by using a motor controller type MC 43. Cyclic voltammograms and steady state current-potential curves were recorded on an X-Y recorder type Bryans — 26000 A4. Product analysis was carried out using a Unicam SP600 spectrophotometer and comparing the absorbance with those for standards using calibration graphs obtained at the same time. Polarograms were recorded using a Radiometer PO4 polarograph. Solution pH was measured and adjusted with a Radiometer Copenhagen pH meter-26.

2.5 Electrolysis Product Analyses

2.5.1 Analyses for Ammonia

The ammonia yields were determined by the Nessler method[40] and measuring the absorbance at 400 mμ.

Preparation of Nessler's Reagent

This reagent was prepared by dissolving 62.5 g of potassium iodide in 250 cm^3 of distilled water, and a cold saturated solution of mercuric chloride was then added to 245 cm^3 of this solution, until a faint permanent precipitate is formed. About 500 cm^3 would be required. The remaining 5 cm^3 of KI solution was then added, and some more HgCl$_2$ gradually until a slight permanent precipitate was formed. 150g of potassium hydroxide were dissolved in 150 cm^3 of distilled water and then the cooled solution added gradually to the other solution. The whole was made up to 1 litre. After settling, the clear solution, which should have a slight yellow colour, is decanted into a bottle covered with black varnish. The solution which is potassium mercury-iodide containing excess of potassium hydroxide is used as a test for ammonia.

Reagents

(1) Ammonia-free water

(2) Nessler reagent

(3) Standard ammonium chloride solution

21

Procedure

Standard ammonium chloride solutions were prepared as follows:

3.82 g of ammonium chloride was dissolved in ammonia-free water and the solution was made up to 1 litre by adding triple distilled water. From this stock solution the standard solution was prepared by diluting 10 cm³ to 1 litre with ammonia-free water. 1 cm³ of this solution contains 0.01 mg. of nitrogen, equivalent to 0.0129 mg. of NH_4. From this solution a series of sample bottles containing different volumes of standard ammonium chloride solution diluted to 20 ml were prepared. The standards thus prepared were Nesslerized by adding 1 cm³ of Nessler reagent to each sample bottle.

The catholyte was collected from the cell after the completion of the reaction and the solution was made slightly acid or neutral (pH 6-7). A suitable dilution was made so that the colour of the solution after addition of Nessler reagent was more intense than that of the most dilute standard and less intense than that of the most concentrated standard after addition of 1 cm³ of Nessler reagent. (Normally 1−2 cm³ of product was diluted to 20 cm³). The absorbance of the sample from the catholyte and five standards were measured together.

2.5.2   Analyses for Hydroxylamine

Hydroxylamine was estimated by adding benzoyl chloride and ferric chloride[41] and the absorbance was measured at 530 mμ.

Hydroxylamine reacts with benzoyl chloride to give benzoyl hydroxamic acid. With ferric salt in neutral or slightly acid solution this reacts to give a reddish-violet colour.

$$Ph - \overset{\overset{\displaystyle O}{\displaystyle \|}}{C} - Cl + NH_2OH \longrightarrow Ph - \overset{\overset{\displaystyle O}{\displaystyle \|}}{C} - \overset{\overset{\displaystyle H}{\displaystyle |}}{N} - OH + HCl$$

$\Big\downarrow Fe^{3+}$

in neutral or slightly acid solution

reddish-violet colour
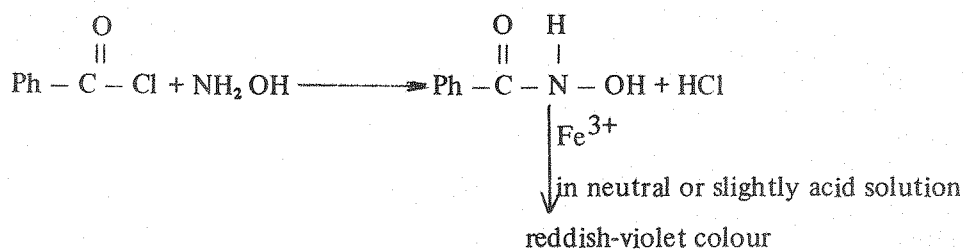
Reagents

(1)   Benzoyl chloride, colourless

(2)   Sodium acetate, 2% solution

(3)   Ferric chloride, 0.5% in 2% hydrochloric acid by volume.

Procedure

A stock solution containing 2g of hydroxylamine per litre was first prepared and then standard solutions were prepared by using different volumes of it (4, 6 and 8 cm³). To the standards thus prepared were added 2 drops of colourless benzoyl chloride followed by

22

4.0 cm^3 of alcohol and 2.0 cm^3 of sodium acetate solution. Then they were shaken for about 30S and the mixture was allowed to stand for a few minutes. 2.0 cm^3 of ferric chloride solution was then added. The solutions were made up to 25 cm^3 in volumetric flasks and after five minutes the absorbance was measured. The catholyte was neutralised and the same treatment followed.

2.6 Chemicals

The following chemicals were used in this study:

1.	Uranyl nitrate	BDH	Reagent grade
2.	Vanadyl sulphate	BDH	Reagent grade
3.	Acetic acid (glacial)	BDH	(Koch-Light)
4.	Sodium perchlorate	(BDH Analar)	
5.	Mercuric chloride	BDH	Reagent grade
6.	Perchloric acid	(BDH Analar)	
7.	Sodium molybdate	(BDH Analar)	
8.	Potassium chloride	(BDH Analar)	
9.	Sodium nitrate	(BDH Analar)	
10.	Sodium nitrite	(BDH Analar)	
11.	Sodium acetate	(BDH Analar)	
12.	Sodium hydroxide	(BDH Analar)	
13.	Potassium iodide	(BDH Analar)	
14.	Ammonium chloride	(BDH Analar)	
15.	Hydroxylamine hydrochloride	BDH	Reagent grade
16.	Benzoyl chloride	BDH	Reagent grade
17.	Alcohol (ethanol)	(BDH Analar)	
18.	Ferric chloride	BDH	Reagent grade
19.	Sodium iodide	BDH	Reagent grade
20.	Sulfuric acid A.R.	(Corfit Lab. Ltd.)	
21.	Potassium sulphate	(BDH Analar)	
22.	Potassium nitrate	(BDH Analar)	
23.	Nitric acid	(Hopkin & Willins Analar)	
24.	Hydrochloric acid A.R.	(Corfit Lab. Ltd.)	
25.	Ammonia	(BDH Analar)	
26.	Sodium chloride	(BDH Analar)	

27.	Soldium bromide	(BDH Analar)
28.	Sodium flouride	(BDH Analar)
29.	Hydroxylammonium sulphate	BDH	Reagent grade
	$(HO. NH_3)_2 SO_4$		

2.7 Solvents

All aqueous solutions were made up with thrice distilled water which was prepared as follows: the distilled water from a commercial still was passed into a distillation flask containing weakly alkaline Analar potassium permanganate. From this flask the water was distilled a second time into another flask containing a trace of Analar ortho-phosphoric acid. Finally, it was distilled for the third time and collected in a glass stoppered bottle and stored.

2.8 Cleaning of Glassware

All the cells and glassware used were left in contact with chromic acid before washing with distilled water. They were then filled with distilled water and left for some time and finally rinsed with thrice distilled water and dried in an oven.

2.9 Techniques

The steady state current potential curves were obtained by manual stepping of the potential. An increment of 10 mV every 30s was applied and the current was measured at the end of the period. The controlled potential electrolysis was carried out by controlling the potential of the working electrode at a value chosen from the data obtained in steady state or potential sweep experiments. The current was monitored as a function of the number of coulombs passed until the electrode reaction was complete. The cyclic voltammograms were obtained by applying appropriate potential sweep rates (usually $0.01 - 0.3$ V s^{-1}) with the help of a waveform generator over the chosen range of potentials and recording the resulting current-potential curves on a X-Y recorder. Rotating disc electrode experiments were carried out by applying very slow potential sweep rate to obtain steady state concentration profile. The electrode was rotated (usually 100–2500 rpm) and the steady state current-potential curves were recorded.

CHAPTER 3

RESULTS

3.1 Nitrate Reduction at a copper disc electrode

3.1.1 Systems without Halides

(I) Cyclic voltammetry

(i) In 0.1 M HClO$_4$ + 0.9 M NaClO$_4$

A series of potential sweep experiments were carried out to study the electrochemical behaviour of nitrate ions at a copper disc electrode using a cell of the type shown in Figure 2.2. Cyclic voltammograms recorded for the supporting electrolyte 0.1 M HClO$_4$ + 0.9 M NaClO$_4$ show no current between 0.0V (Cu dissolution) and − 0.8 V (H$_2$ evolution), whereas when nitrate was added a well formed single reduction peak was observed on sweeping towards negative potentials but on the reverse sweep back to the initial potential no oxidation peak was observed. Hence there was no evidence for electro-oxidisable intermediates. Typical voltammograms for the reduction of 5mM NO$_3^-$ in perchlorate medium pH 1 are presented in Figure 3.1(1); the curves for several potential sweep rates are shown. The plot of peak current (I$_p$) versus the square root of the potential scan rate ($\nu^{1/2}$) is linear passing through the origin as shown in Figure 3.1(2). The value of the diffusion coefficient calculated from the I$_p$−$\nu^{1/2}$ plot using the equation given by Nicholson and Shain[42] and assuming n = 8 (see later) was 1.8 x 10^{-5} cm^2 s^{-1}. It is obvious from the Figure 3.1(1) that the peak potential changes with the potential sweep rate and the variation of E$_p$ with log ν is plotted in Figure 3.1(3). Under all conditions studied no other peak was observed. Cyclic voltammograms for 1 mM nitrate shows one reduction peak as presented in Figure 3.1(5) almost at the same potential as for 5 mM nitrate. The peak current is plotted against square root of the sweep rate for 1mM NO$_3^-$ in perchlorate medium pH1 in Figure 3.1(6). The peak currents were compared and found to be approximately 5 times smaller for 1m M nitrate solution. All the experimental data are presented in tables 3.1 and 3.2.

(ii) Other supporting electrolytes

The effect of pH between 0 − 4 was studied by using different concentrations of perchloric acid, while the perchlorate ion concentration was maintained constant by addition of sodium perchlorate. It is clear from the cyclic voltammograms that as the concentration of proton is increased hydrogen evolution occurs at a less negative potential. On addition of nitrate to the more acidic solutions the cyclic voltammograms showed a single irreversible peak. Peak currents for the nitrate reduction were calculated and plotted against the square
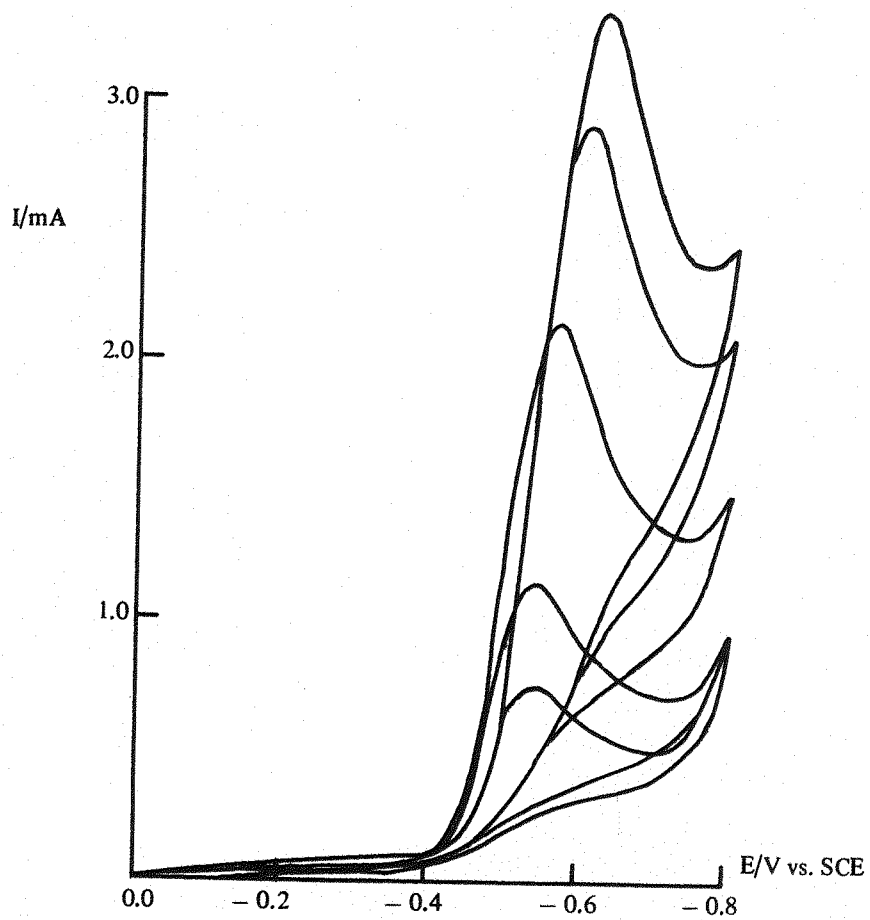
Figure 3.1(1)   Cyclic voltammograms for NO_3^- (5m M) at a copper disc electrode (area 0.16 cm^2) in sodium perchlorate (0.9 M) + perchloric acid (0.1 M). Potential scan rates 0.01, 0.03, 0.1, 0.2 and 0.3 Vs^{-1}
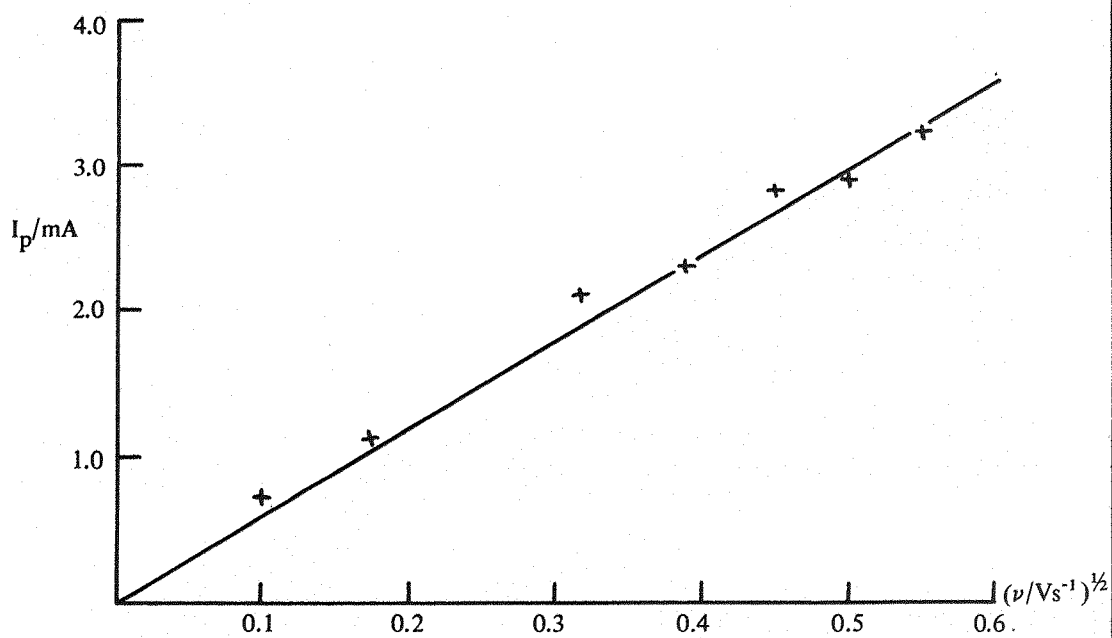
Figure 3.1(2)   Plot of I_p versus $\nu^{1/2}$ for the above cyclic voltammograms

Figure 3.1(3)

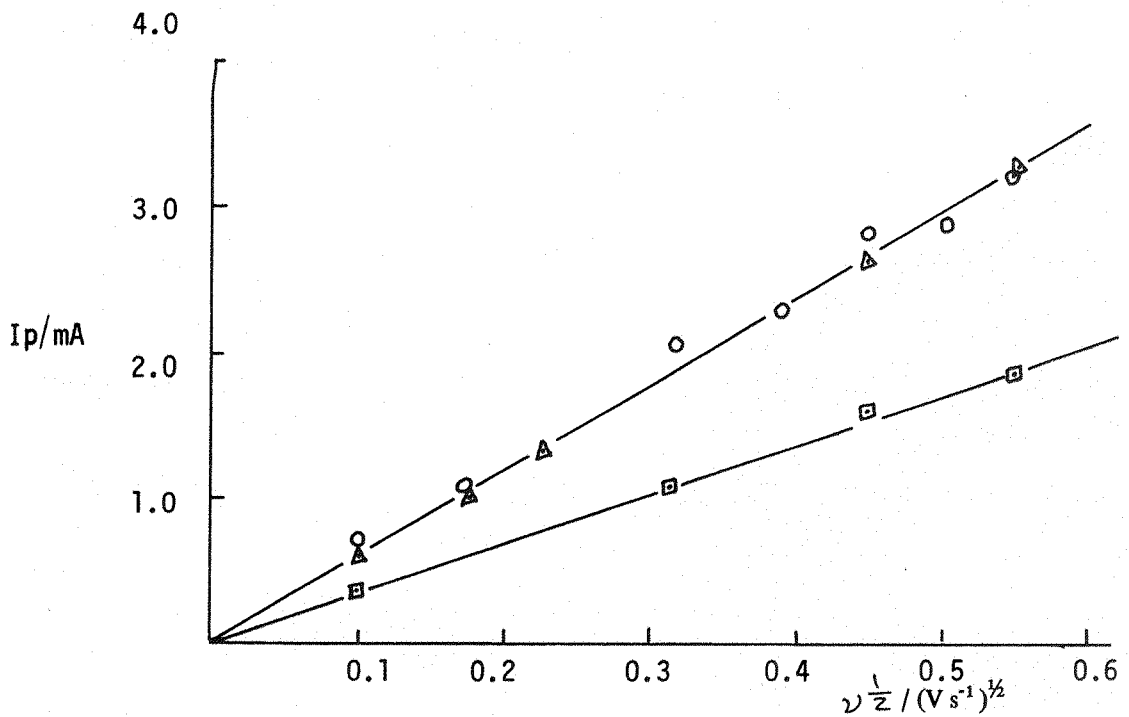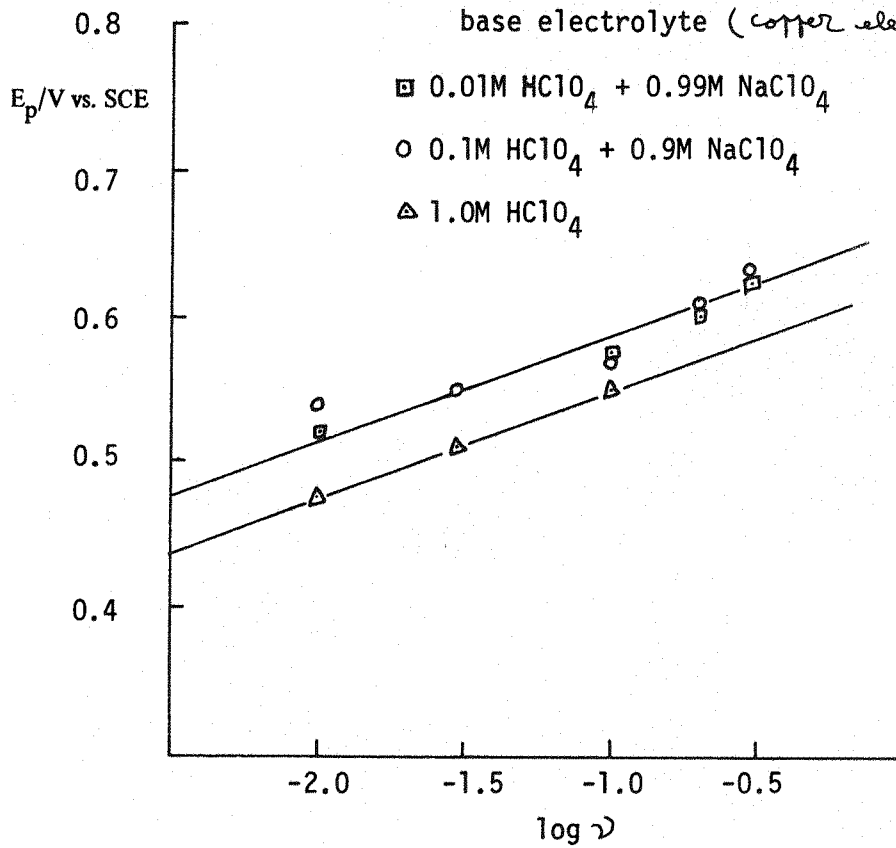### Variation of Ep with log ν for 5mM $NaNO_3$ in different base electrolyte (copper electrode) area (0.16 cm²)

$\square$ 0.01M $HClO_4$ + 0.99M $NaClO_4$

$\circ$ 0.1M $HClO_4$ + 0.9M $NaClO_4$

$\triangle$ 1.0M $HClO_4$

E_p/V vs. SCE

log ν

I_p/mA

$\nu^{\frac{1}{2}} / (V\,s^{-1})^{\frac{1}{2}}$

Figure 3.1(4)

I_p vs. $\nu^{\frac{1}{2}}$ FOR 5mM $NaNO_3$ IN DIFFERENT BASE ELECTROLYTES WITH

COPPER ELECTRODE (area 0.16 cm²)

$\square$ 0.01 M $HClO_4$ + 0.99M $NaClO_4$

$\circ$ 0.1 M $HClO_4$+ 0.9M $NaClO_4$

$\triangle$ 1.0 M $HClO_4$

28
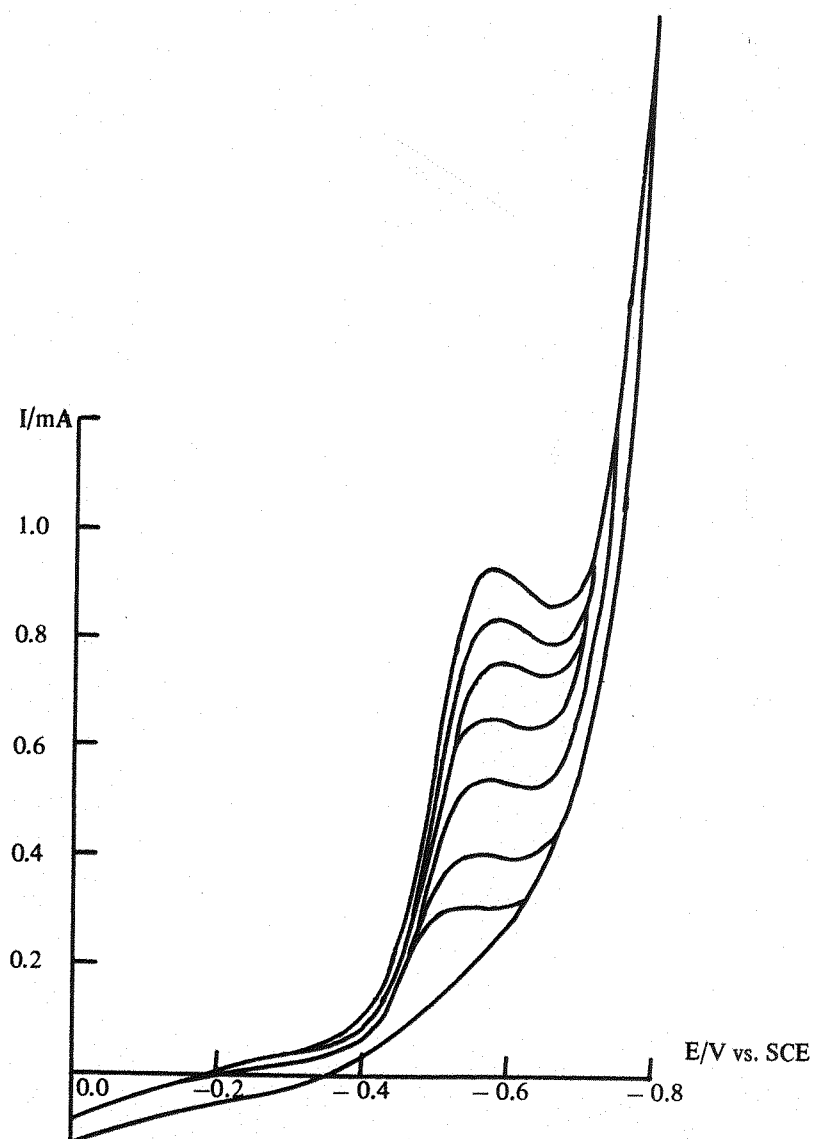
Figure 3.1(5) The effect of changing the potential sweep rate on the cyclic voltammogram for the reduction of $1m$ M NO_3^- in 0.1 M $HClO_4$ + 0.9 M $NaClO_4$ on a copper disc electrode (area 0.16 cm^2). Potential sweep rates 0.03, 0.05, 0.1, 0.15, 0.2, 0.25, and 0.3 V s^{-1}.
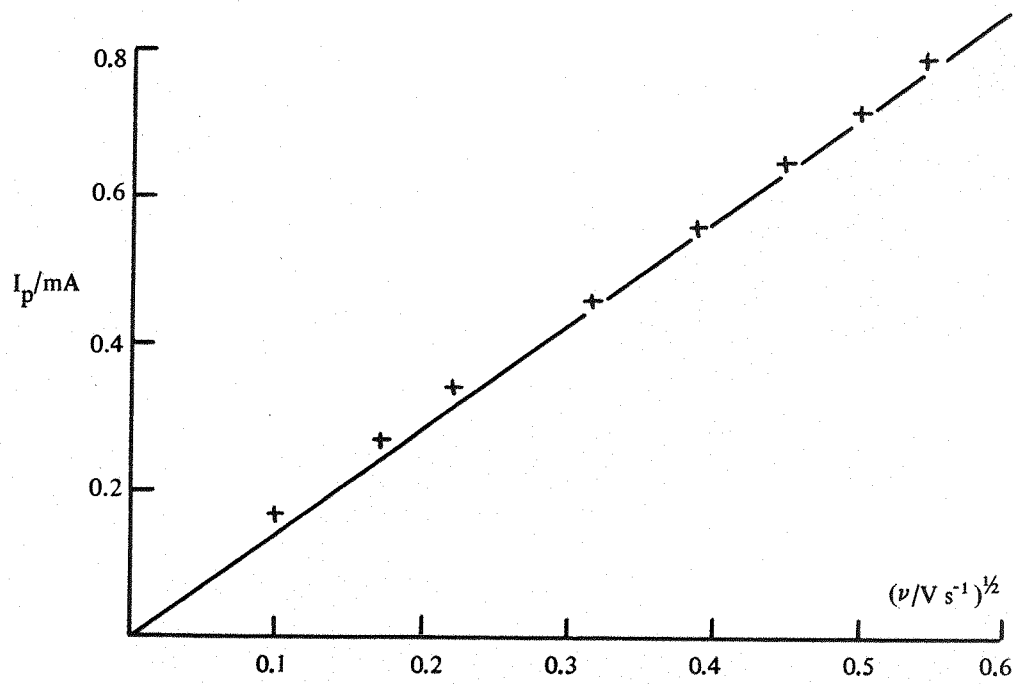
Figure 3.1(6) Plot of I_p versus $\nu^{\frac{1}{2}}$ for cyclic voltammograms presented in figure 3.1(5)

TABLE 3.1

Results of potential sweep experiments for the reduction of 5m M $NaNO_3$ in different pH
(Potential sweep rate 0.1V s^{-1})

$c_{H^+}/mol\,dm^{-3}$	E_p / V	$(E_{P/2} - E_P)/(mV)$	$\dfrac{I_p}{v^{1/2}\,AC} \bigg/ \dfrac{mA}{V^{1/2}\,s^{-1/2}\,cm^2\,mM}$
0.01	-0.58	70	4.37
0.10	-0.56	80	7.50
1.00	-0.46	90	7.50

$W \cdot E$ = copper disc electrode (area 0.16 cm^2)

Supporting electrolytes   1.0 M $HClO_4$

                                    0.1 M $HClO_4$ + 0.9 M $NaClO_4$

                                    0.01 M $HClO_4$ + 0.99M $NaClO_4$

TABLE 3.2

Results of potential sweep experiments for the reduction of 1m M $NaNO_3$ in different pH
(Potential sweep rate $0.1V\ s^{-1}$)

$C_{H^+}/mol\ dm^{-3}$	$Ep\ /\ V$	$(E_{\frac{p}{2}} - E_P)/(mV)$	$\dfrac{Ip}{\nu^{\frac{1}{2}}A\ C}\quad\dfrac{mA}{V^{\frac{1}{2}}\ s^{-\frac{1}{2}}cm^2\ mM}$
0.01	-0.58	80	7.8
0.10	-0.56	80	8.4
1.00	-0.54	90	7.5

W.E = copper disc electrode (area $0.16\ cm^2$)

Supporting electrolytes   1.0 M $HClO_4$

                                         0.1 M $HClO_4$ + 0.9 M $NaClO_4$

                                         0.01 M $HClO_4$ + 0.99M $NaClO_4$

root of the sweep rates for solutions of several pH. All the graphs were linear passing through the origin as shown in Figure 3.1(4). The peak currents for the reduction of 5 mM nitrate in different pH were compared; the results clearly show that when 1 and 0.1M perchloric acid were used as supporting electrolytes the peak currents are almost the same. Whereas on further reducing the proton concentration i.e. pH2, the peak current was less, while at pH3 no reduction peak was observed, although a more extensive cathodic potential range was available. It appears that at the higher pH the amount of proton available is not sufficient for complete reduction of the electroactive species. With 1 mM nitrate at pH2, the peak current obtained is almost the same value as that for lesser pH. The peak potentials, peak shape factors and current functions for 5 mM and 1 mM nitrate obtained at different pH are collected in tables 3.1 and 3.2.

Experiments with other supporting electrolytes showed that nitrate reduction also occurs in sulfate media, pH 0 –2 and cyclic voltammograms showed a well formed reduction peak very similar to those obtained previously. A typical result for the blank solution and in the presence of nitrate is shown in Figure 3.1(7). The variation of the peak current with the square root of the sweep rate shows a good linear relation plotted in Figure 3.1(8). On the other hand no reduction was observed when hydrochloric acid (pH 0 − 2) was used as the supporting electrolyte. The cyclic voltammograms obtained were all completely reproducible.

(II) Rotating disc experiments

(i)   In 0.1M HClO$_4$ + 0.9 M NaClO$_4$

The electrochemical reduction of nitrate ion (5 mM and 1 mM) was studied at a polished copper electrode and a series of current-potential curves were recorded at various rotation rates and using a very slow potential sweep rate ($\nu = 0.005$ V s^{-1}). A current-potential curve was first recorded for the perchlorate medium only between 0.0V (copper oxidation) and − 0.8V (hydrogen reduction), and no current was observed. When the same experiment was carried out in the presence of nitrate ion, well formed reduction waves were obtained. In the limiting current region of the curves, the current is proportional to the nitrate ion concentration and to the square root of the rotation rate of the disc electrode. A series of current-potential curves for 5m M NO$_3^-$ in this electrolyte (pH 1) and at a rotating copper disc electrode is shown in Figure 3.1(9) for several rotation rates. Figure 3.1(10) contains a plot for the limiting current (I_L) versus the square root of the rotation rate ($\omega^{1/2}$), which shows a linear relationship and the graph passes through the origin. Hence the current is determined by the rate of mass transport of nitrate ion to the electrode surface and assuming
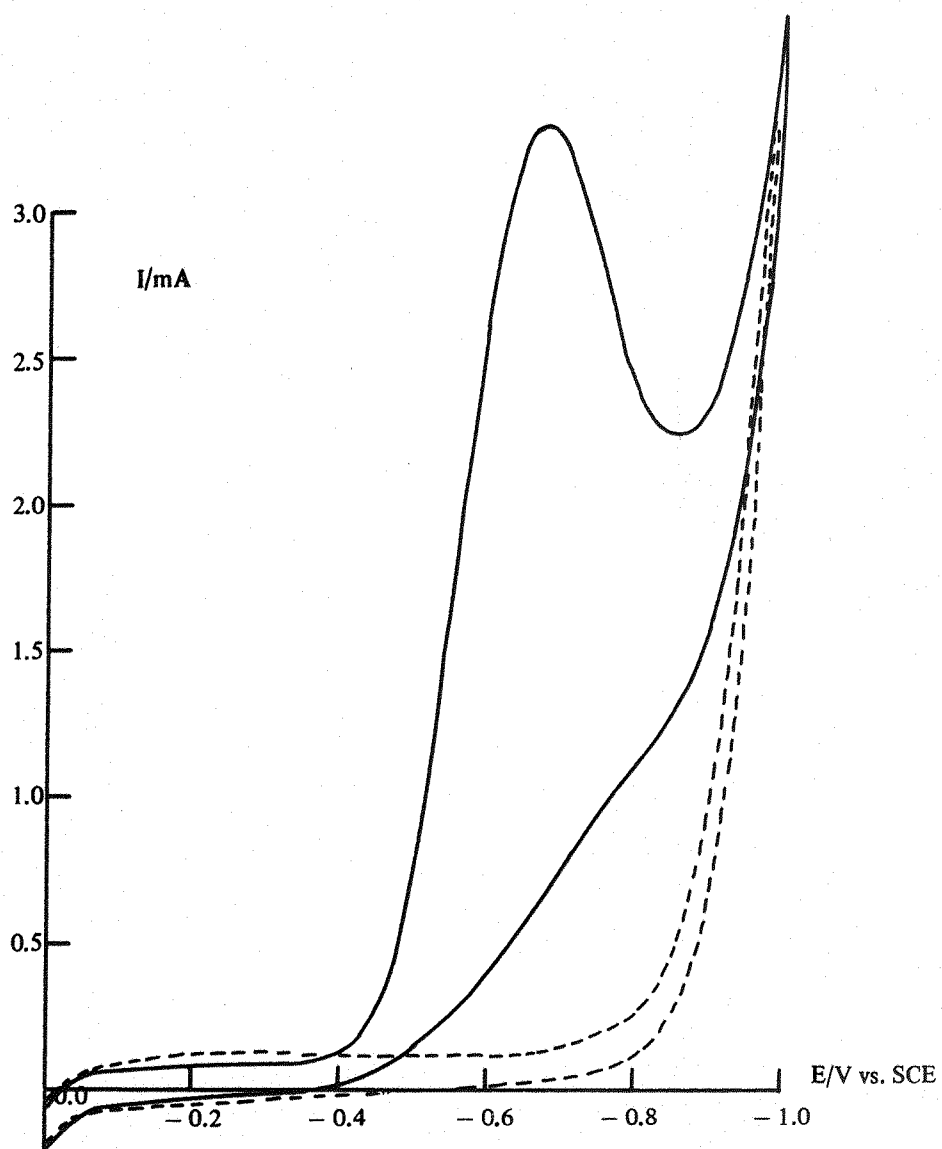
33

Figure 3.1(7) Cyclic voltammograms obtained for

--------- H₂SO₄ (0.05 M) + Na₂SO₄ (0.45 M)

——— H₂SO₄ (0.05 M) + Na₂SO₄ (0.45 M) + 5m M NaNO₃

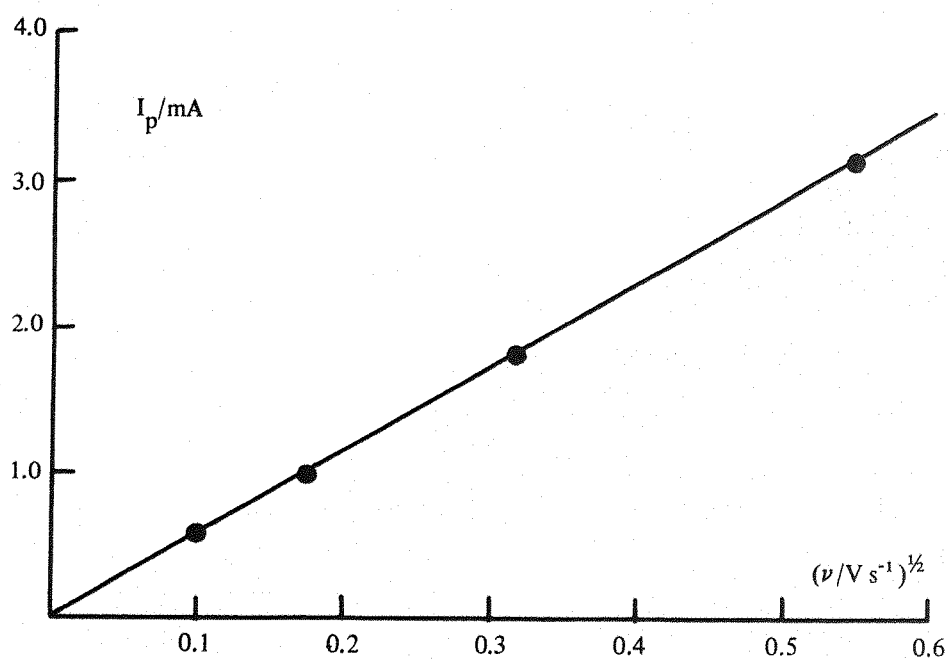on a copper disc electrode (area 0.16 cm²). Potential scan rate 0.3 V s⁻¹

34

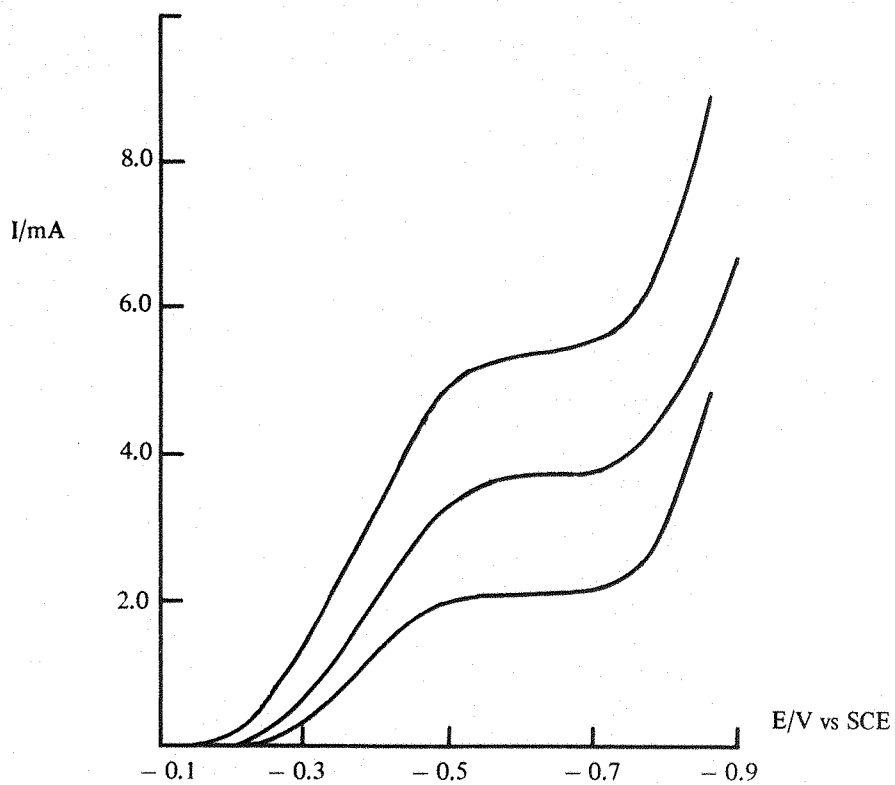Figure 3.1(8) Plot of I_p versus $\nu^{1/2}$ for cyclic voltammograms obtained for the solutions in Figure 3.1(7)

Figure 3.1(9) Polarization curves obtained for the reduction of NO_3^- (5m M) in $HClO_4$ (0.1 M) + $NaClO_4$ (0.9 M) at a polished copper disc electrode (area 0.16 cm^2). Potential sweep rate 0.005 V s^{-1}. Rotation rates 100, 400 and 900 rpm
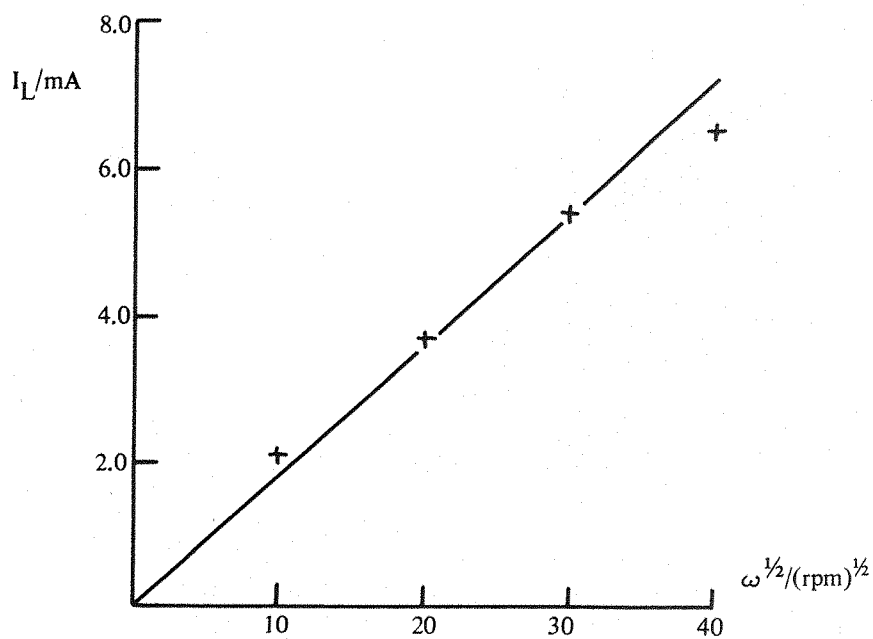
Figure 3.1(10) Plot of limiting current versus $\omega^{1/2}$ for above curves

n = 8, the Levich equation[43] was used to estimate a value for the diffusion coefficient for nitrate ion, and it was found to be 1.6×10^{-5} cm^2 s^{-1}. All the data obtained are reported in tables 3.3 and 3.4 for 5 mM and 1 mM nitrate ion.

(ii) Other supporting electrolytes

Rotating disc experiments were carried out in a perchlorate medium for two concentrations of nitrate ion (1 mM and 5 mM) at several pH between 0 – 3. It was found that when the solution pH was 0 or 2, the current-potential curves were similar to those observed at pH 1, except for a shift in the half wave potential. Also the limiting current for 5mM nitrate at pH 2 was lower than with the other acid concentrations although with 1mM nitrate the limiting current had the same values as at lower pH. In each case the limiting current was proportional to the square root of the rotation rate as shown in Figure 3.1(12). When the acid concentration is increased, the half wave potential shifts to less negative potentials and in the case of the 1.0M $HClO_4$ as supporting electrolyte $E_{1/2}$ is –0.30V. At pH 2, the half wave potential was – 0.51V. At pH 3 no reduction wave was observed and when the acid concentration was above 1.0M, the current for the hydrogen evolution reaction was found to overlap the nitrate reduction wave. A series of steady state current-potential curves for the reduction of 5 mM NO_3^- in 1.0M $HClO_4$ at the rotating copper disc electrode is presented in Figure 3.1(11). The data taken from these experiments are reported in tables 3.3 and 3.4 for 5 mM and 1 mM nitrate ion solution at different pH.

Very similar current-potential curves were obtained for nitrate reduction in sulfate medium, while no reduction wave was seen when hydrochloric acid was used as supporting electrolyte.

The cyclic voltammograms and current-potential curves recorded with potassium nitrate were exactly the same as those for the sodium nitrate solution in perchlorate medium.

(III) Controlled potential electrolysis and spectrophotometric experiments

A series of controlled potential electrolyses were carried out to determine the products and the number of electrons involved in the reduction of nitrate ion at a copper electrode in perchlorate medium (pH 0–1). The potential of the working electrode was controlled at a value chosen from the data obtained in steady state or potential sweep experiments. The current was monitored as a function of the charge consumed during the electrolysis and the catholytes were also analysed for NH_2OH and NH_3 when the current had dropped to a low value. Several different potentials were used and it was found that when a more negative potential was used, the reaction proceeded much faster than when the electrolysis was
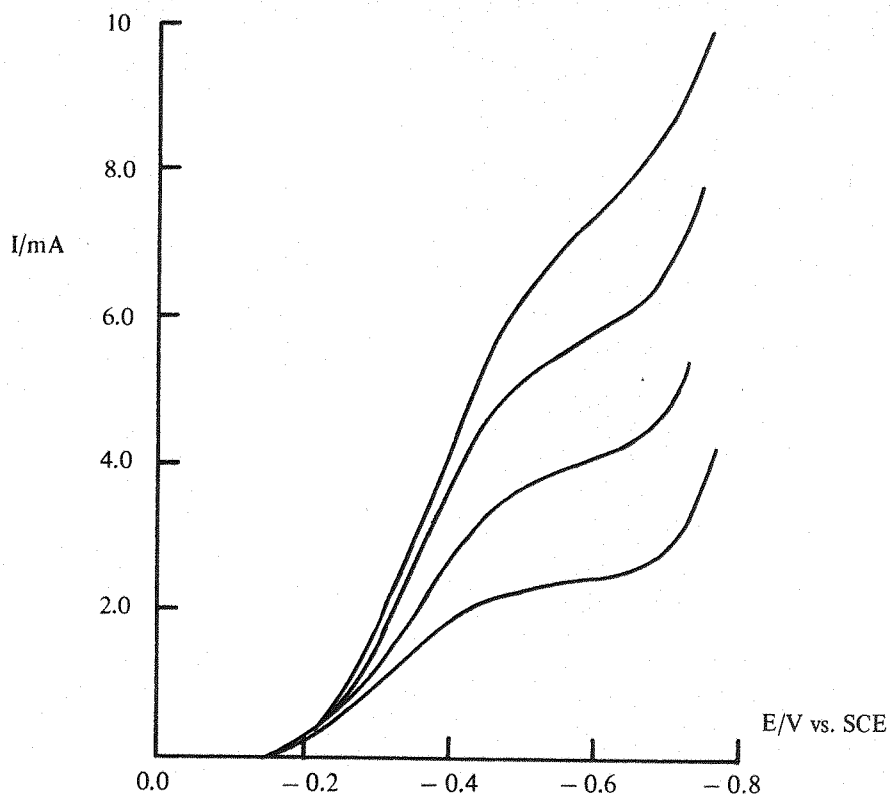
Figure 3.1(11) I-E curves at a rotating Cu disc electrode (area 0.16 cm^2) for NO$_3^-$ (5m M) in 1.0 M HClO$_4$.
Rotation rates 100, 400, 900 and 1600 rpm.
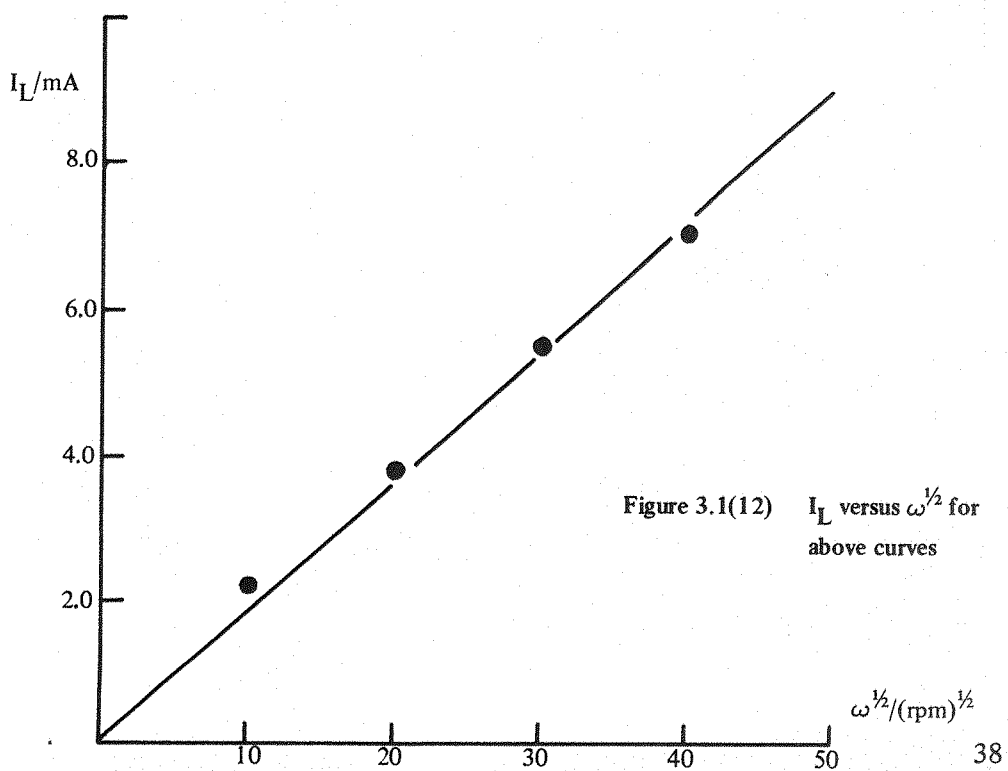Potential scan rate 0.005 V s^{-1}

Figure 3.1(12) I$_L$ versus $\omega^{1/2}$ for above curves

38

TABLE 3.3

Results of rotating disc electrode experiments for the reduction of 5.0m M $NaNO_3$ in different pH

$C_{H^+}/mol\ dm^{-3}$	$E_{1/2}$ at ω = 100 rpm (mV)	$E_{1/4} - E_{3/4}$ (mV)	Slope $\dfrac{I_L}{C\omega^{1/2}A}$ $\dfrac{mA}{mM \times (rpm)^{1/2} \times cm^2}$
0.01	− 500	91	0.12
0.1	− 485	106	0.18
1.0	− 300	111	0.20

W.E. = copper disc electrode (area 0.16 cm²)

TABLE 3.4

Results of rotating disc electrode experiments for reduction of 1.0m M $NaNO_3$ in different pH

$C_{H^+}/mol\ dm^{-3}$	$E_{1/2}$ at ω= 100 rpm (mV)	$E_{1/4} - E_{3/4}$ (mV)	Slope $\dfrac{I_L}{C\omega^{1/2}A}$
0.01	− 515	102	0.16
0.1	− 500	80	0.16
1.0	− 300	112	0.15

W.E. = copper disc electrode (area 0.16 cm²)

carried out at a potential on the rising part of the current-potential curve. In most of the electrolyses the current-charge plots were linear and these lines were extrapolated to $I = 0$ to obtain the n value for nitrate ion reduction. A typical set of current versus charge data is presented in Figure 3.1(13). The n value and yields of ammonia from nitrate reduction in various conditions is reported in table 3.5 and the conversion of nitrate to ammonia during the electrolysis of 5 mM NO_3^- in 0.1M $HClO_4$ + 0.9M $NaClO_4$ is reported in table 3.6. Some hydrogen gas evolution could be observed and in some cases a low current was observed even after the passage of much more than 8F mol^{-1}.

The study of the effect of pH showed that pH1 is optimal for complete reduction of nitrate since at lesser pH the rate of hydrogen evolution was relatively fast and at higher pH range the reaction was very slow and the amount of ammonia obtained was low. For example the electrolysis of 5 mM NO_3^- in 0.025M $HClO_4$ was carried out and the yield of ammonia formed was only 27.6 percent. The ammonia formed was detected spectrophotometrically and the data is presented in table 3.5. In none of the experiments could hydroxylamine be identified in the catholyte during or after the electrolysis.

3.1.2 Effect of Halides

Because no nitrate reduction wave was observed when hydrochloric acid was used as the supporting electrolyte, it was decided to study the effect of addition of halides to the perchlorate media.

(I) Cyclic voltammetry

Cyclic voltammograms were recorded for 5mM NO_3^- solution in perchlorate media (pH 1) during stepwise addition of the halides. It was found that addition of fluoride up to 1M had no effect on the voltammograms but even low concentrations of chloride, bromide or iodide were sufficient to cause a shift of the nitrate reduction peak to more negative potentials and further addition led to the nitrate reduction peak being obscured by the hydrogen evolution current. It was found that 10^{-5} M iodide was sufficient to shift the peak beyond the negative potential limit. The effect of bromide ion is shown in Figure 3.1(14) and it is clear from the figure that the peak current always remained the same. The shift in peak potential as adding bromide ion is presented graphically in Figure 3.1(16).

(II) Rotating disc experiments

The steady state current-potential curves for 5mM NO_3^- in 0.1M $HClO_4$ + 0.9M $NaClO_4$ were recorded and the effect of halides was studied. It was noticed that addition of halides causes the half wave potential for nitrate reduction to shift to more negative potentials.
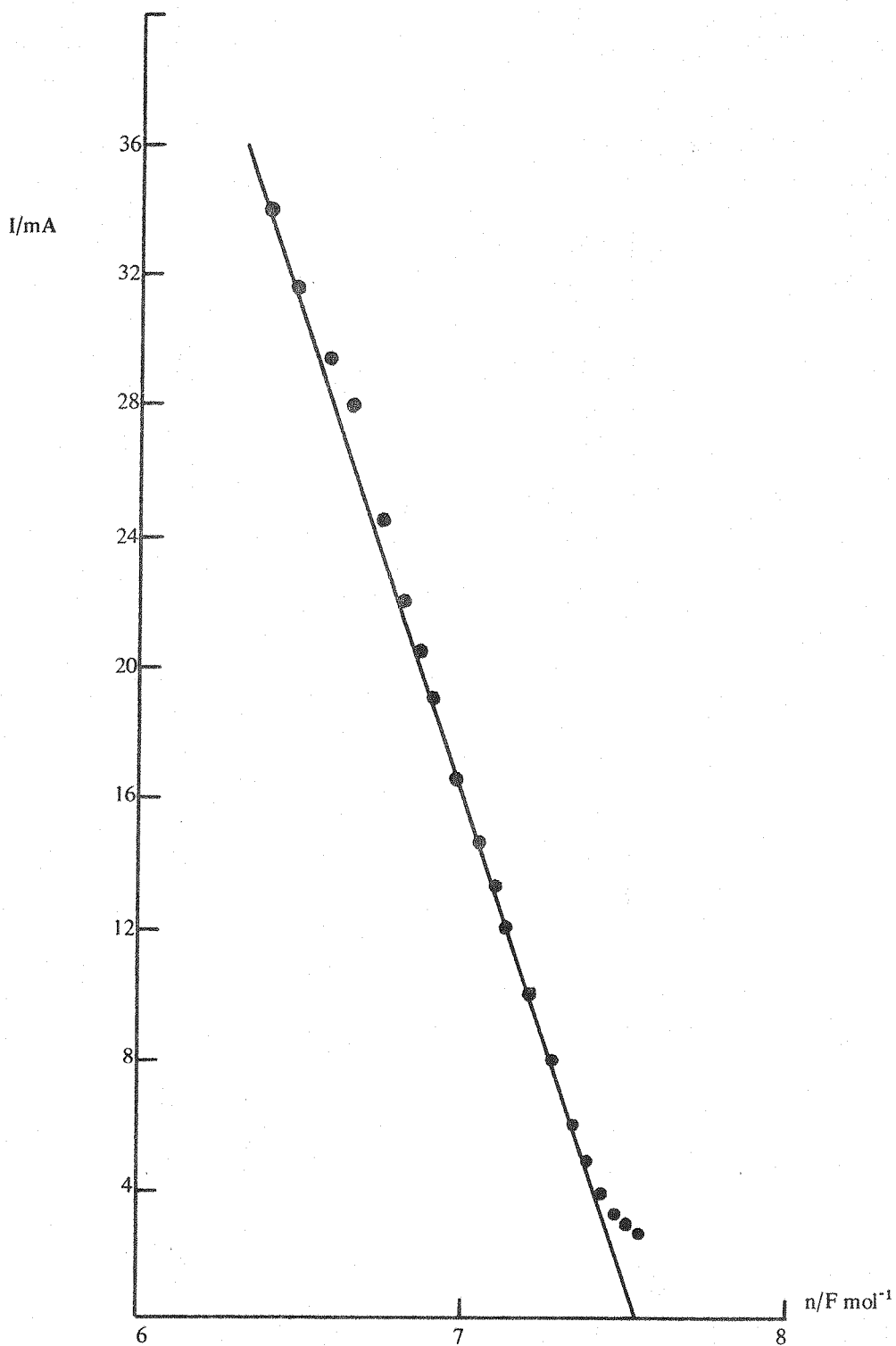
Figure 3.1(13)   I-Q plot from a controlled potential electrolysis of 5 mM NO_3^- at a Cu gauze electrode (area 8.58 cm^2) in 0.1 M $HClO_4$. Potential – 0.62 V.
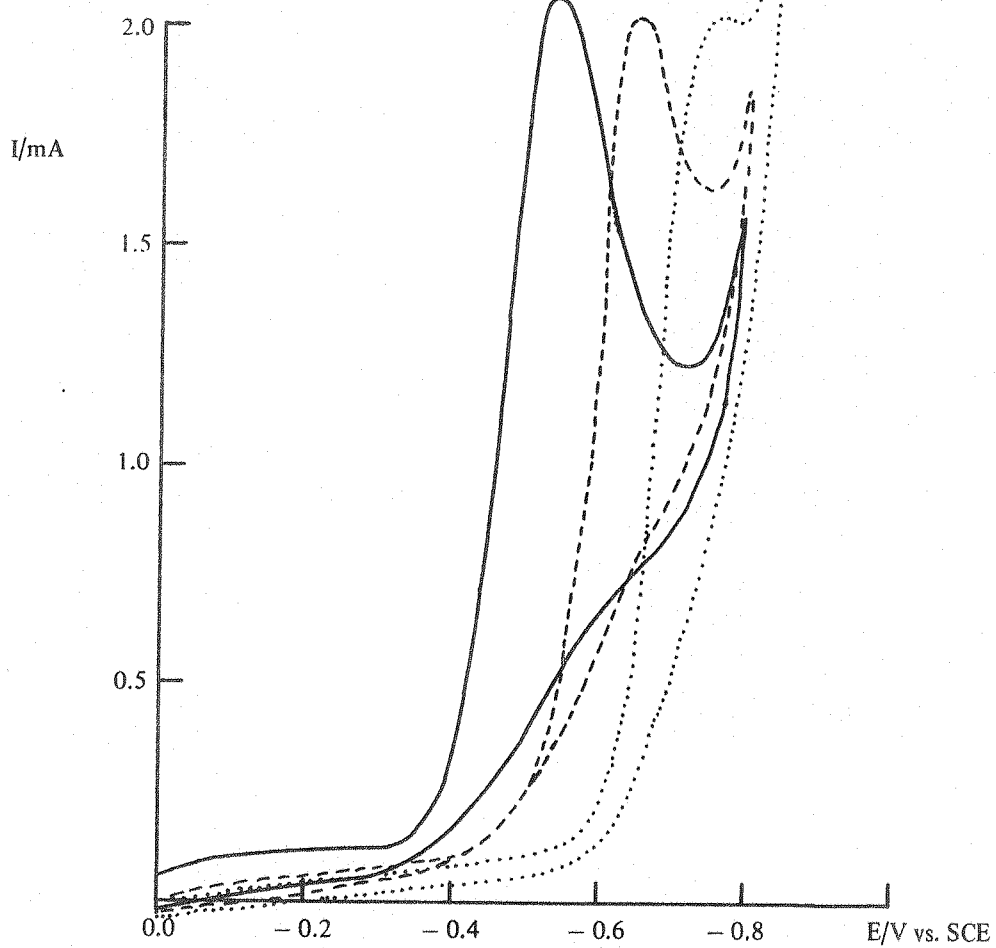
Figure 3.1(14)   The effect of bromide ion on the peak potential of the cyclic voltammogram
                 obtained for the reduction of NO_3^- (5m M) in $HClO_4$ (0.1 M) + $NaClO_4$ (0.9 M)
                 on a copper disc electrode (area 0.16 cm^2). Potential sweep rate 0.1 V s^{-1}.
                 Potential range 0.0 V to $-$ 0.8 V.

——— NO_3^- (5 mM) in $HClO_4$ (0.1M) + $NaClO_4$ (0.9 M)

- - - - - NO_3^- (5 mM) in $HClO_4$ (0.1 M) + $NaClO_4$ (0.9 M) + 5 x 10^{-5} M Br^-

.... NO_3^- (5 mM) in $HClO_4$ (0.1 M) + $NaClO_4$ (0.9 M) + 5 x 10^{-4} M Br^-
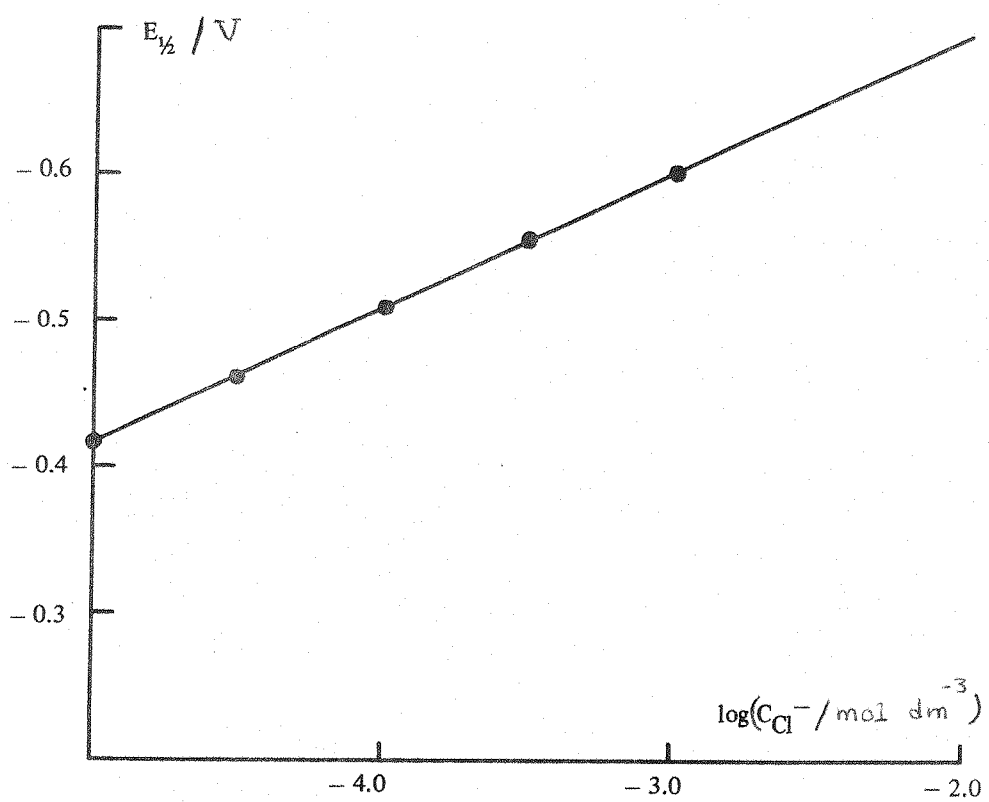
Figure 3.1(15) $E_{1/2}$ versus concentration of Cl^- for NO_3^- reduction at a rotating Cu disc electrode (area 0.16 cm^2). Electrolyte 0.1M HClO$_4$ + 0.9 M NaClO$_4$
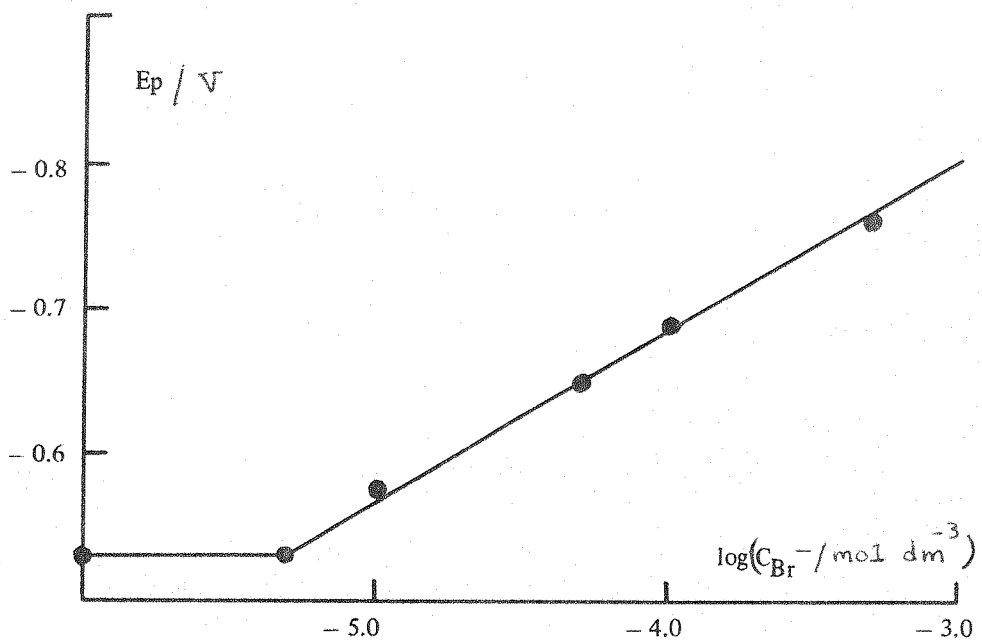
Figure 3.1(16)　Ep from cyclic voltammograms for NO_3^- reduction versus concentration of Br^- at a Cu disc electrode (area 0.16 cm^2). Electrolyte 0.1 M $HClO_4$ + 0.9 M $NaClO_4$

TABLE 3.5

	Electrolyte	$-E$ V vs. SCE	Initial n-value F mole^{-1}	Yield of NH$_3$[a] %
(a) NO$_3^-$	HClO$_4$ (1.0 M)	0.55	9	68
	HClO$_4$ (0.1M) + NaClO$_4$ (0.9 M)	0.45	7	88
		0.55	7	88
		0.62	9	88
	HClO$_4$ (0.1M) + NaClO$_4$ (0.9M) + NaCl (0.01M)	0.60	8	68
		0.65	8	69
		0.70	8	70
	HClO$_4$ (0.025 M) + NaClO$_4$ (0.9M) + NaCl (0.01 M)	0.67	4	53*
	H$_2$SO$_4$ (0.05M) + Na$_2$SO$_4$ (0.45 M)	0.60	7	78
(b) NO$_2^-$	HClO$_4$ (0.1M) + NaClO$_4$ (0.9M)	0.67	6	64

Electrolyses of NO$_3^-$ and NO$_2^-$ (5m M) at a copper cathode in various electrolytes.

a. current yield after the passage of 8F mol^{-1} except * where electrolysis was stopped when the current reached a low value.

The effect of addition of chloride ion on the half wave potential ($E_{1/2}$) is illustrated in Figure 3.1(15). Fluoride up to 1M had almost no effect on the current-potential curves. It can be concluded that the effectiveness of the halides in poisoning the copper electrode used for nitrate reduction decreases along the series $\bar{I} > \bar{Br} > \bar{Cl} > \bar{F}$. It was also noted that with the higher concentrations of halides (except $\bar{F}$), the limiting current was not entirely mass transfer controlled and plots of I_L against $\omega^{1/2}$ were only linear at low rates of mass transport.

(III)   Controlled Potential Coulometry

Several electrolyses were carried out for 5mM nitrate solution in perchlorate media (pH 1) in the presence of 0.01M sodium chloride. In almost all the experiments, plots of current against charge were linear and the n value was found by extrapolation of the current charge line to I = 0. A typical current-charge plot is shown in Figure 3.1(17), when the potential of the working electrode (copper gauze) was maintained constant at -0.60V. The n value in this case found to be 8 and the percentage yield of ammonia was 68. The yield of ammonia from the electrolysis of this solution (pH 1) at several working potentials is reported in table 3.5. For some of the experiments the yield of ammonia was determined during the electrolysis and the results of one of these series of experiments is reported in table 3.6. The current efficiency was calculated and is plotted against charge for the electrolysis of 5 mM $\bar{NO_3}$ in 0.1M $HClO_4$ and 0.9M $NaClO_4$ in the presence of 10^{-2} M $\bar{Cl}$ in Figure 3.1(18).

3.2 Steady State Experiments for Reduction of Nitrate at a Copper Wire Electrode

Steady state current-potential curves were obtained by using a point by point potentiostatic technique for nitrate and nitrite solution at several pH. It is found that well formed reduction waves were observed both for nitrate and nitrite when the solution pH was 1, but with increasing pH, the limiting currents decreased and above pH 3 no reduction could be observed up to the potential for hydrogen evolution. The limiting current showed a strong dependence on the concentration of nitrate and nitrite ion and was found to be much smaller for nitrite than that of nitrate. Typical plots are shown in Figure 3.2(1). Hydroxylamine is not reduced in these systems.

3.3 Reduction of Nitrite at a Copper Disc Electrode

(I) Cyclic voltammetry

Potential sweep experiments were carried out for the study of electrochemical behaviour of 5 and 1 mM nitrite. As in the case of nitrate a single irreversible reduction peak
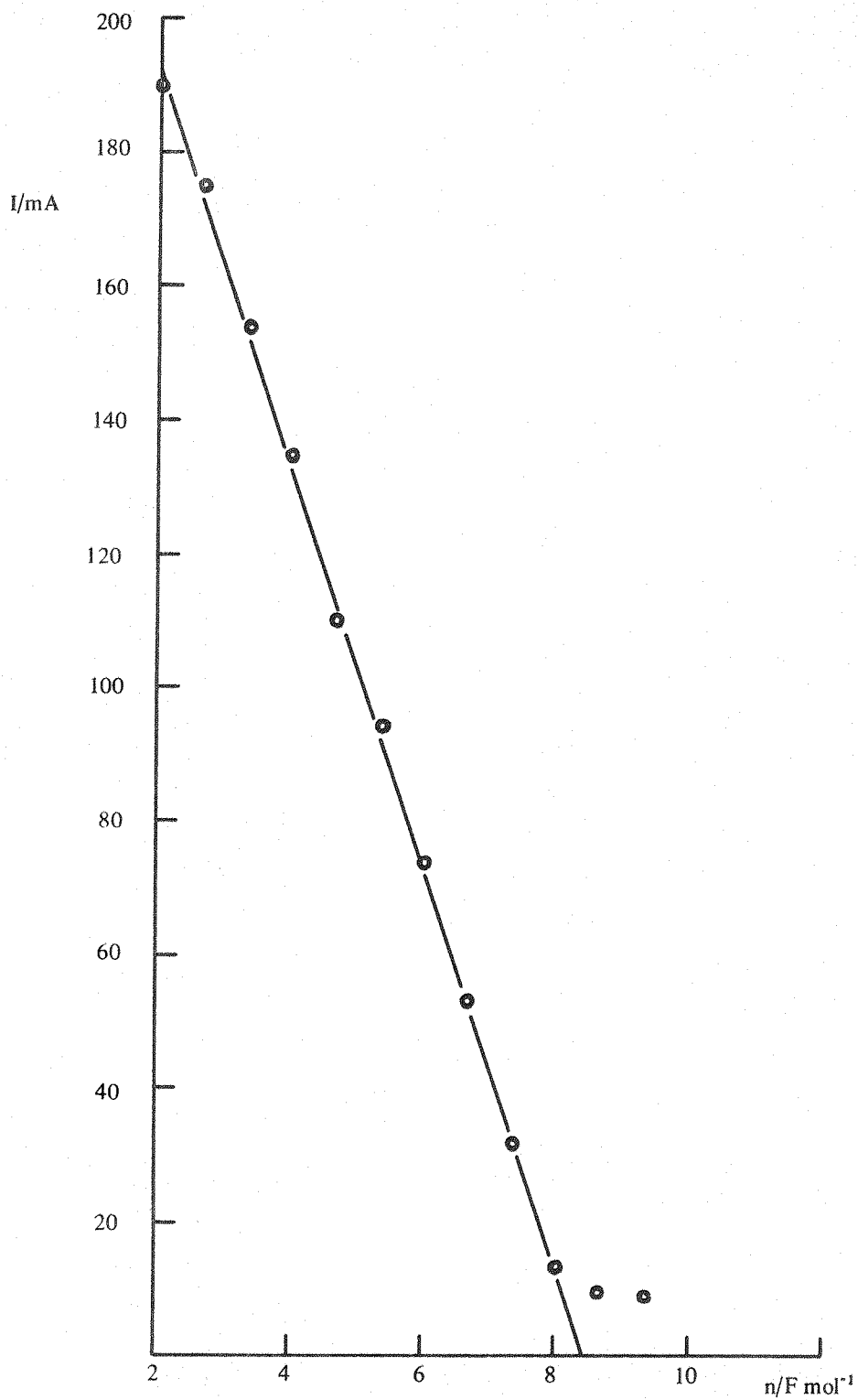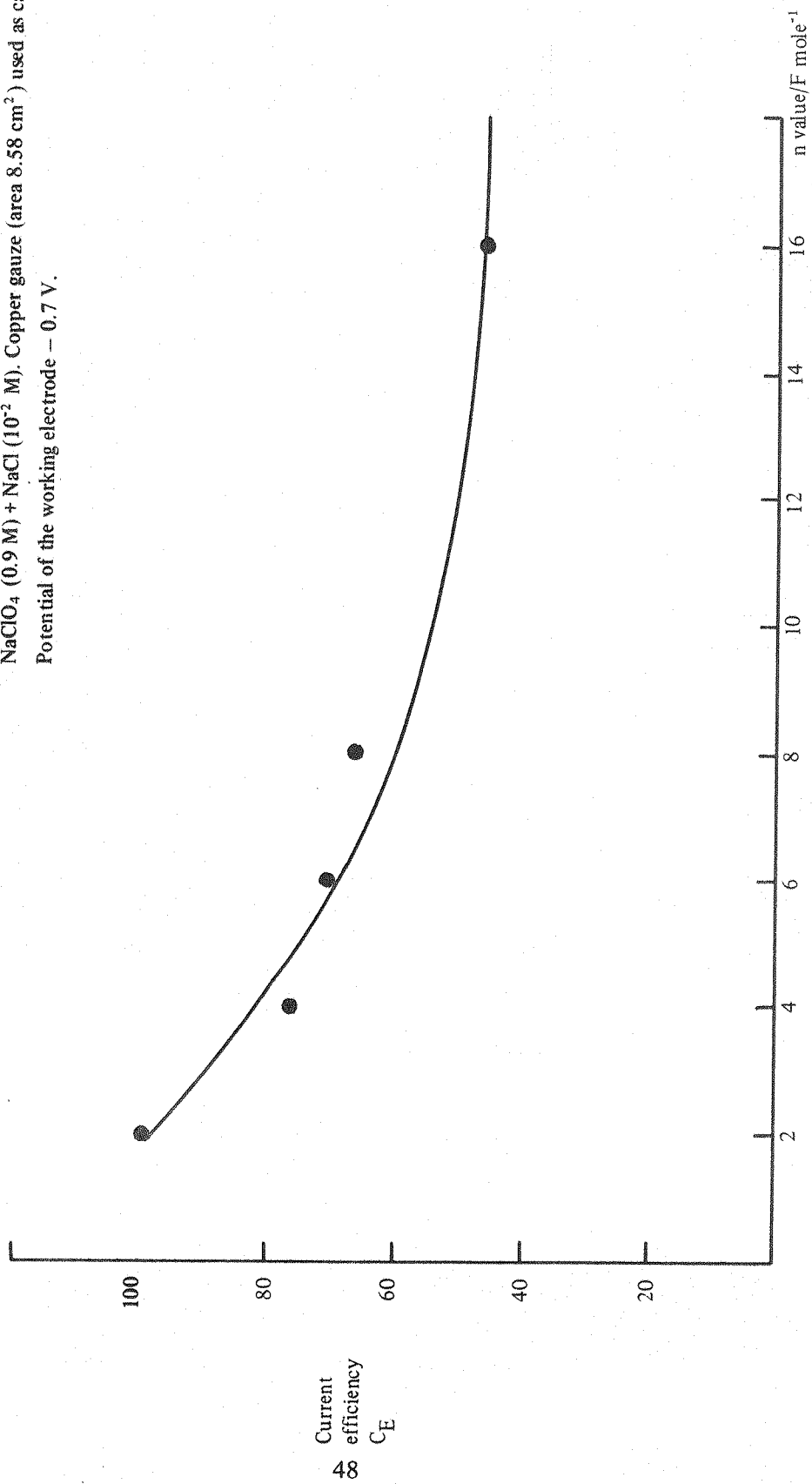
Figure 3.1(17)   I-Q plot from a controlled potential electrolysis at a Cu gauze electrode (area 8.58 cm^2). Potential $-$ 0.6V, solution contains NO_3^- (5 mM), $HClO_4$ (0.1 M) $NaClO_4$ (0.9 M) and Cl^- (10^{-2} M).

Figure 3.1(18)   Plot of C_E versus n value for electrolysis of NO_3^- (5m M) in $HClO_4$ (0.1 M) + $NaClO_4$ (0.9 M) + NaCl (10^{-2} M). Copper gauze (area 8.58 cm^2) used as cathode. Potential of the working electrode – 0.7 V.

48

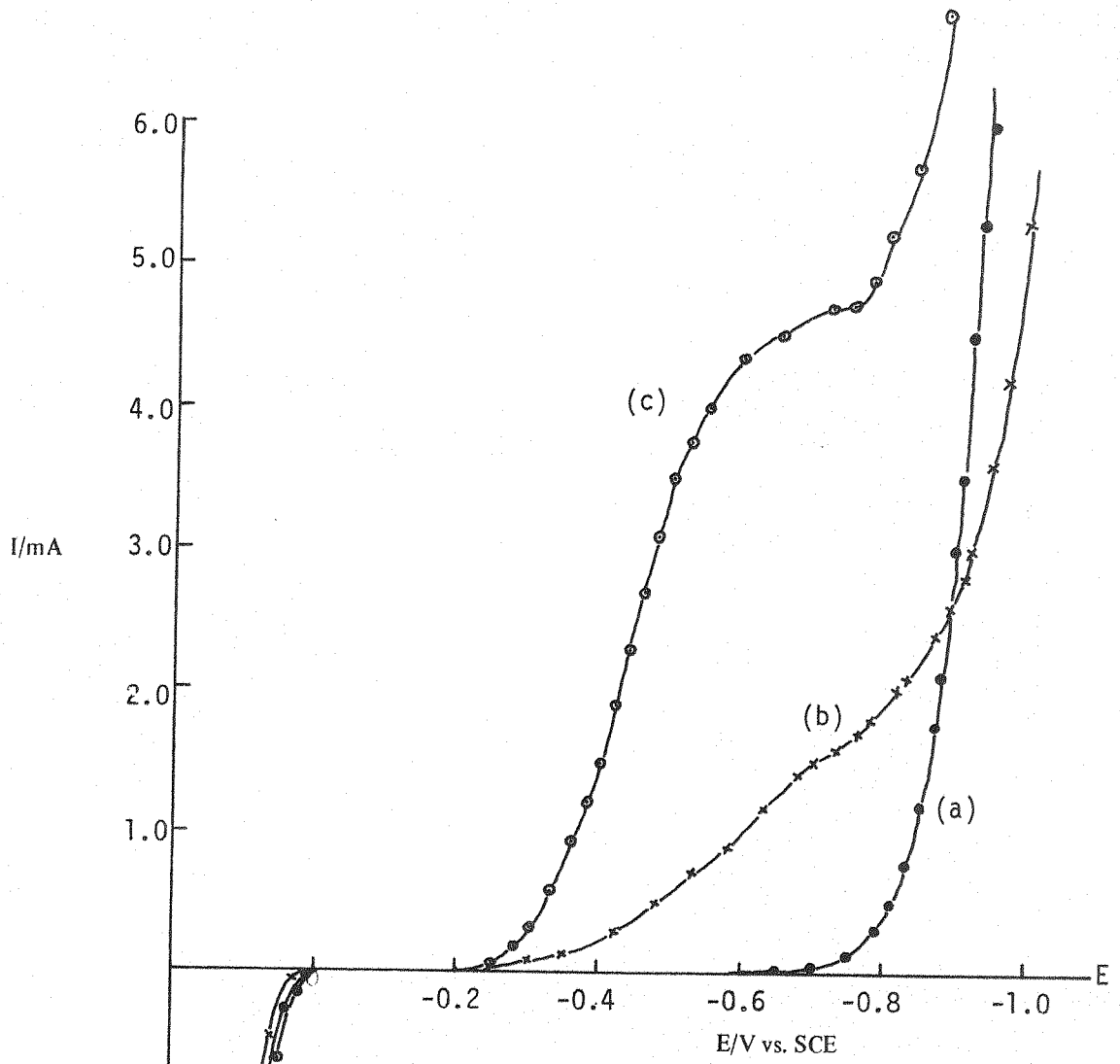**Figure 3.2(1)**

Polarisation curves for the solutions of

(a)   0.1M HClO₄

(b)   0.1M HClO₄ + 5mM NaNO₂

(c)   0.1M HClO₄ + 5mM NaNO₃

W.E. = Copper wire (length 2.5cm)

TABLE 3.6

F mol^{-1}	Conversion of NO$_3^-$ to NH$_3$	
	(a)	(b)
2	25	25
4	46	38
6	67	54
8	88	67
16	—	90
26	—	100

(a) -0.62 V. 0.9 M NaClO$_4$ + 0.1 M HClO$_4$

(b) -0.70 V. 0.9 M NaClO$_4$ + 0.1 M HClO$_4$ + 0.01 M NaCl

was observed on sweeping towards negative potential. It may be noted that the reduction of nitrite occurs at a potential very similar to that for nitrate reduction. A typical cyclic voltammogram is presented in Figure 3.3(1) and the corresponding dependence of peak current (I_p) against square root of the sweep rate ($v^{1/2}$) is plotted in Figure 3.3(2), which shows a linear relation passing through the origin. The results are summarised in table 3.7.

(II) Rotating disc experiments

A series of current-potential curves for nitrite reduction at a rotating copper disc electrode in perchlorate media were recorded. In perchlorate medium (pH 1) nitrite showed a well formed wave with $E_{1/2} = -0.43V$ and $E_{3/4} - E_{1/4} = 110\,mV$. The limiting current was proportional to the square root of the rotation rate of the disc, but, however it was lower than the corresponding value for nitrate ion. It is concluded that the nitrate and nitrite reduction processes overlap completely. The rotating disc data is summarized in table 3.8.

(III)   Controlled potential electrolysis

Several electrolyses at constant potential were carried out to determine n, the number of electrons transferred in the overall electrode reaction and the product of the electrode reaction. The current was monitored and plotted as a function of the charge consumed and the n value was found to be 6, while spectrophotometric analysis confirmed the formation of ammonia.

The study of the effect of halides on the nitrite reduction at a copper disc electrode showed very similar results to those obtained for nitrate ion solutions. The peak potential for nitrite reduction was found to shift to more negative potential when bromide ion was added to the solution and when 10^{-4} M bromide ion was present in the solution, the reduction peak for nitrite ion was obscured by the hydrogen evolution current. The effect of bromide ion on nitrite reduction is shown graphically in Figure 3.3(3). The variation of peak potential with concentration of bromide ion is presented in Figure 3.3(4).

3.4 Nitrate Reduction at a Rotating Cadmium Disc Electrode

Steady state current-potential curves were recorded for a solution of 5 mM and 1 mM nitrate at a rotating cadmium disc electrode in several supporting electrolytes to investigate the electrochemical behaviour of nitrate ion. It should be mentioned, however, that the current-potential curve first was recorded for each of the supporting electrolytes in the absence of nitrate ion and no reduction current was observed between the cadmium oxidation and hydrogen evolution potential. Then the current-potential curves were recorded for
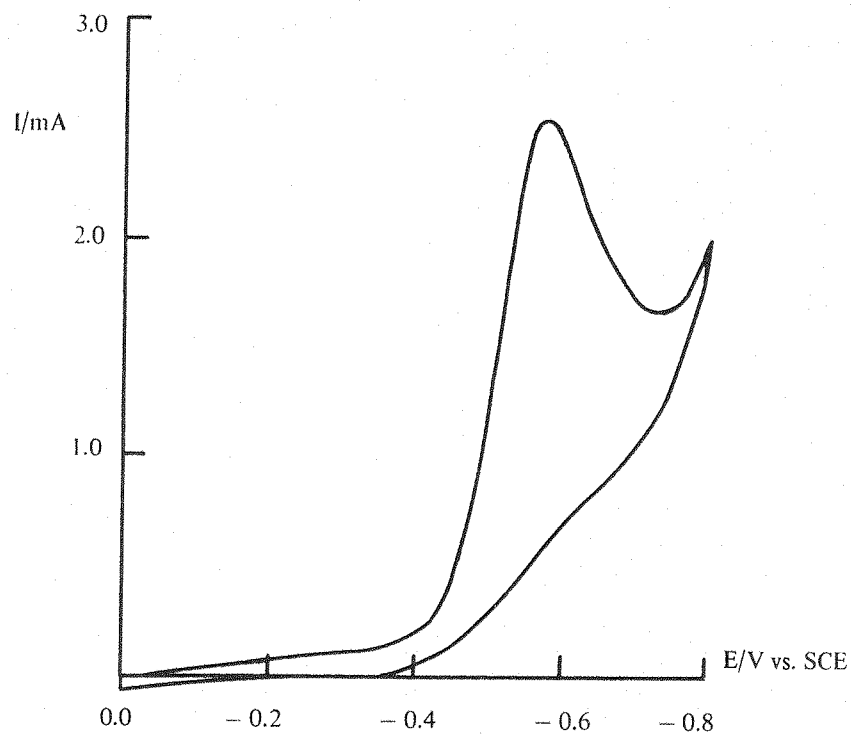
Figure 3.3(1) Cyclic voltammogram for 5m M $NaNO_2$ in $HClO_4$ (0.1 M) + $NaClO_4$ (0.9 M) at 0.3 V s^{-1} on a copper disc electrode (area 0.16 cm^2). Potential range 0.0 V to − 0.8 V.
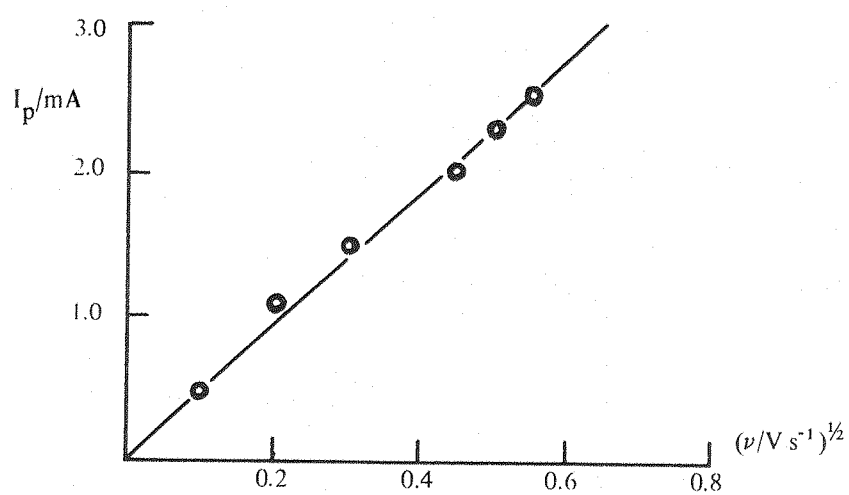

Figure 3.3(2) A plot of I_p versus $v^{1/2}$ for a set of cyclic voltammograms for 5m M $NaNO_2$ in 0.1 M $HClO_4$ + 0.9 M $NaClO_4$ run on a copper disc electrode
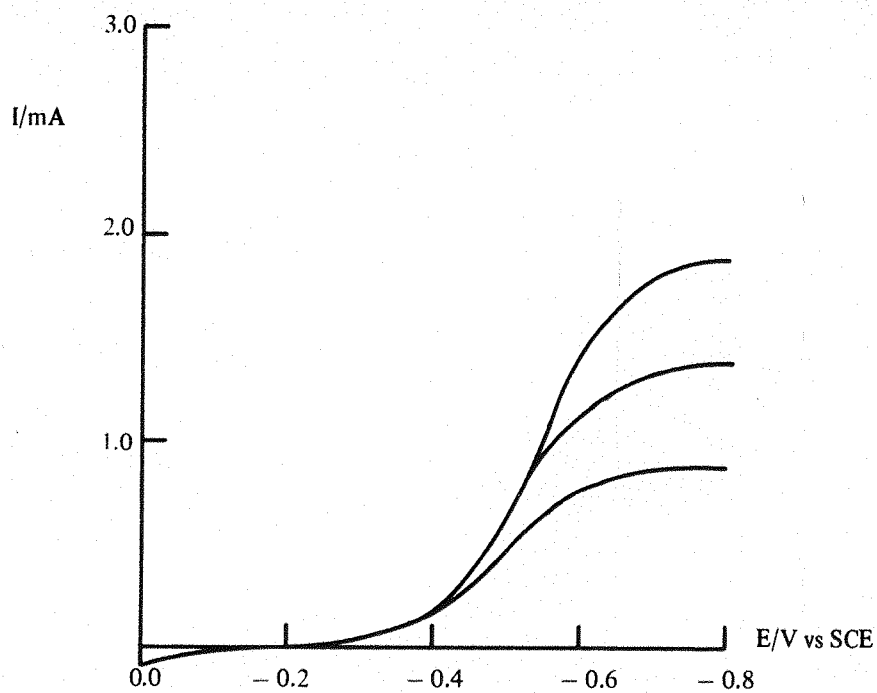
Figure 3.3(3)   Polarization curves for the reduction of NO_2^- (5m M) in $HClO_4$ (0.01M) + $NaClO_4$ (0.99M) at a polished copper disc electrode (area 0.16 cm^2). Potential sweep rate 0.005 V s^{-1}. Rotation rates 100, 400 and 900 rpm
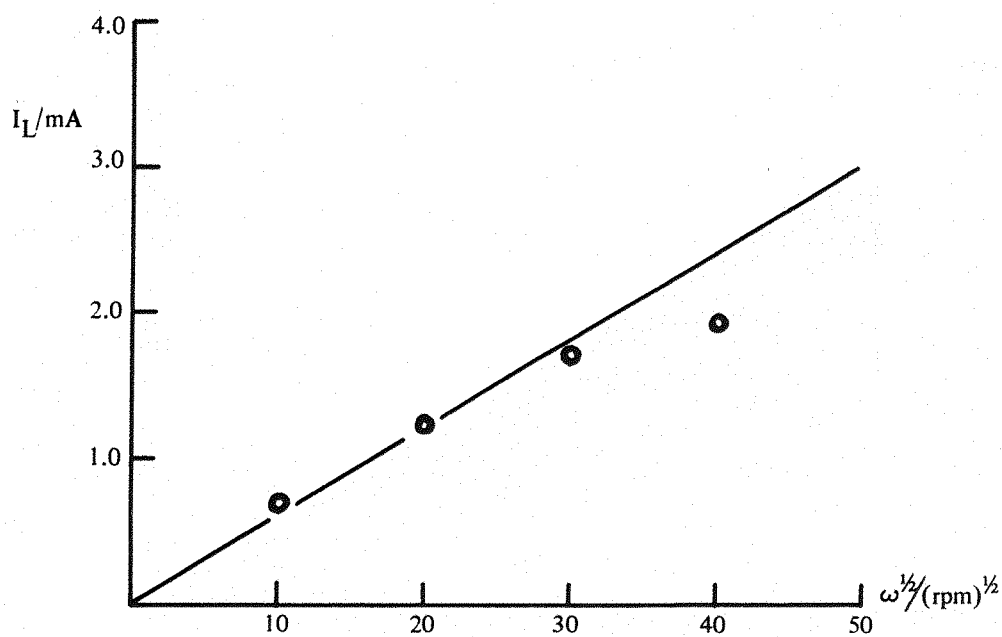

Figure 3.3(4)   Plot of limiting current against $\omega^{1/2}$ for NO_2^- (5m M) in $HClO_4$ (0.01M) + $NaClO_4$ (0.99M) using a copper disc electrode (area 0.16 cm^2). Potential sweep rate 0.005 V s^{-1}
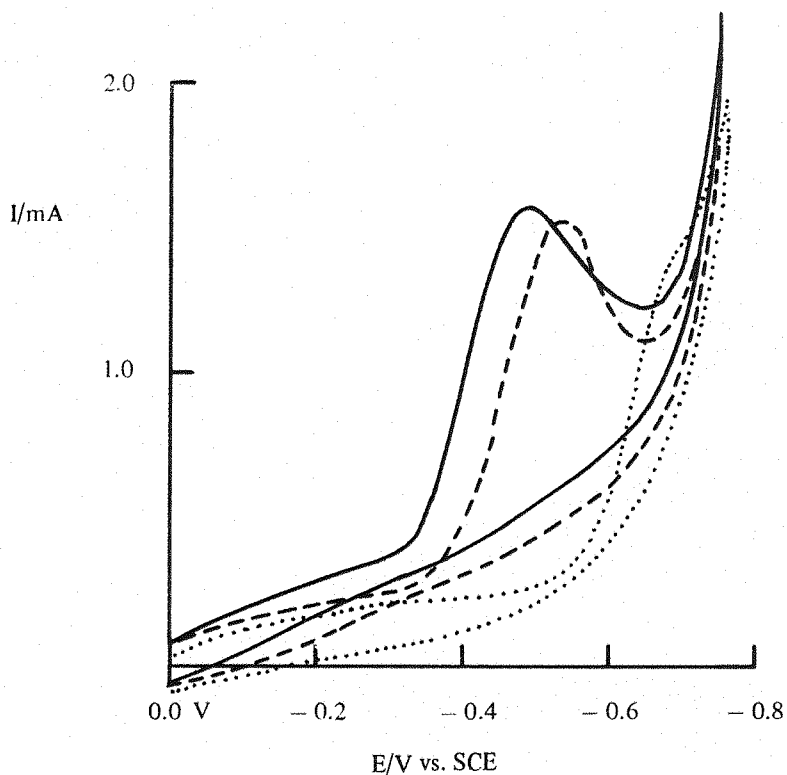
Figure 3.3(5)   The effect of bromide ion on the peak potential of the cyclic voltammogram for the reduction of NO_2^- (5m M) in $HClO_4$ (0.1 M) + $NaClO_4$ (0.9 M) on a copper disc electrode (area 0.16 cm^2). Potential sweep rate 0.1 V s^{-1}

—————— NO_2^- (5 mM) in $HClO_4$ (0.1 M) + $NaClO_4$ (0.9 M)

------------ NO_2^- (5 mM) in $HClO_4$ (0.1 M) + $NaClO_4$ (0.9 M) + 5 x 10^{-6} M Br$^-$

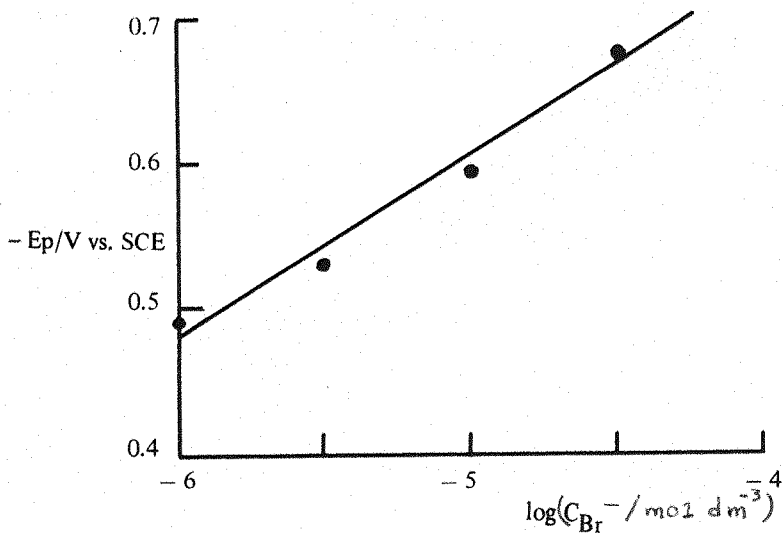·············· NO_2^- (5 mM) in $HClO_4$ (0.1 M) + $NaClO_4$ (0.9 M) + 5 x 10^{-5} M Br$^-$

Figure 3.3(6)   Ep for NO_2^- reduction versus concentration of bromide ion at a Cu disc electrode

54

TABLE 3.7

TABLE 3.7

Results of potential sweep experiments for the reduction of 5m M $NaNO_2$ in different pH

(Potential sweep rate 0.1 V s^{-1})

$C_{H^+}/\text{mol dm}^{-3}$	E_p / V	$(E_{P/2} - E_P)/(mV)$	$\dfrac{I_p}{\nu^{1/2} A C} \Big/ \dfrac{mA}{V^{1/2} s^{1/2} cm^2\, mM}$
0.01	− 0.58	80	2.38
0.10	− 0.56	70	5.75
1.00	− 0.49	90	5.81

W.E. = copper disc electrode (area 0.16 cm^2)

Supporting electrolytes   1.0   M $HClO_4$

                                    0.1   M $HClO_4$ + 0.9 M $NaClO_4$

                                    0.01 M $HClO_4$ + 0.99M $NaClO_4$

TABLE 3.8

Results of rotating disc electrode experiments for reduction of 5.0 mM $NaNO_2$ in different pH

$C_{H^+}/mol\ dm^{-3}$	$E_{1/2}$ at $\omega = 100$ rpm (mV)	$E_{1/4} - E_{3/4}$ (mV)	Slope $\dfrac{I_L}{C\omega^{1/2}A}$ $\dfrac{mA}{(mM) \times (rpm)^{1/2} \times cm^2}$
0.01	-495	117	0.066
0.1	-475	100	0.080
1.0	-400	105	0.070

W.E. = Copper disc electrode (area 0.16 cm^2)

Supporting electrolytes   1.0 M HClO$_4$

0.1 M HClO$_4$ + 0.9 M NaClO$_4$

0.01 M HClO$_4$ + 0.99M NaClO$_4$

nitrate ion in each electrolyte and they were found to depend strongly on the conditions. In all of them the curves crossed the zero current axis, going directly from cadmium dissolution to the reduction of nitrate and a well formed plateau was observed in each case. The steady state current-potential curves for 5 mM NO_3^- in perchlorate and chloride medium are shown in Figures 3.4(1) and 3.4(3), while several rotation rates were used. The plots of limiting current (I_L) versus the square root of the rotation rates ($\omega^{1/2}$) were always linear and passed through the origin, the slopes of such plots were lower in perchlorate than in chloride medium as reported in table 3.9. The limiting current (I_L) against the square root of the rotation rates ($\omega^{1/2}$) is plotted in Figures 3.4(2) and 3.4(4) for 5 mM NO_3^- in perchlorate and chloride media respectively. The steady state current-potential curves were found to depend on the pH of the solution, since at very high concentrations of acid the hydrogen evolution occurred at less negative potentials and interfered with the nitrate reduction wave while with a pH > 3 no reduction wave was observed. Furthermore in perchlorate media the curve shape and number of reduction processes at a cadmiun electrode is different than those obtained for the reduction of nitrate at a copper disc cathode and one more reduction wave was obtained near the positive end of the potential range when the reduction was done at a cadmium disc electrode (Figure 3.4(5)). Controlled potential electrolyses were carried out to determine the number of electrons involved in the reduction of nitrate and the products when a cadmium wire formed onto a flat spiral was used as the working electrode. Both hydrochloric acid and perchloric acid were used as supporting electrolytes. It was found that in the case of hydrochloric acid the amount of ammonia formed was greater than when using perchloric acid but, however, the yield of ammonia is not very high. The results of two electrolyses is shown in Table 3.10.

3.5 Steady State Experiments for Reduction of Nitrate and Nitrite at a Cadmium Wire Electrode

Steady state polarization curves were constructed using a point by point procedure for both nitrate and nitrite solution at a cadmium wire electrode. The reduction of these anions occurred at a potential very close to the cadmium dissolution, and well formed limiting currents region were observed as shown in Figure 3.5(1). The reduction occurred only in acid solutions pH < 3. The limiting currents showed a strong dependency on the concentration of electroactive species and on the concentration of proton and the current for nitrate found to be more than that of nitrite ion.
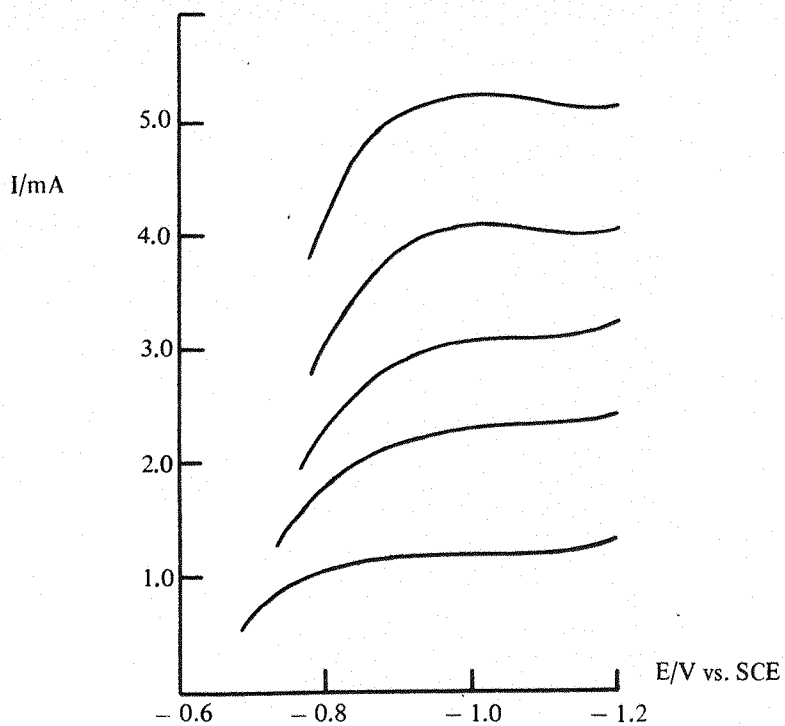
Figure 3.4(1) Typical polarization curves for the reduction of 5 mM NO_3^- on a polished rotating cadmium disc electrode (area 0.33 cm^2) in HClO$_4$ (0.01 M) + NaClO$_4$ (0.99 M). Potential sweep rate 0.005 V s^{-1}
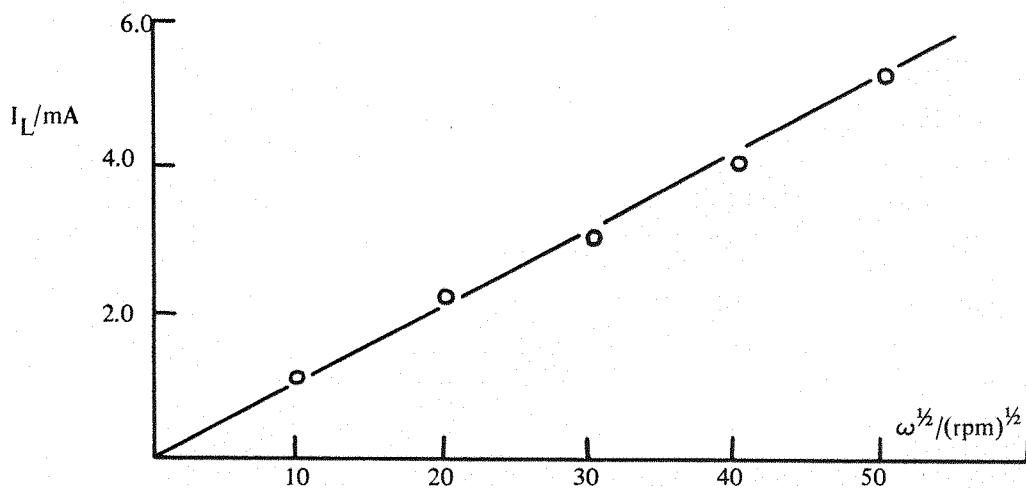

Figure 3.4(2) I_L versus $\omega^{1/2}$ for above curves
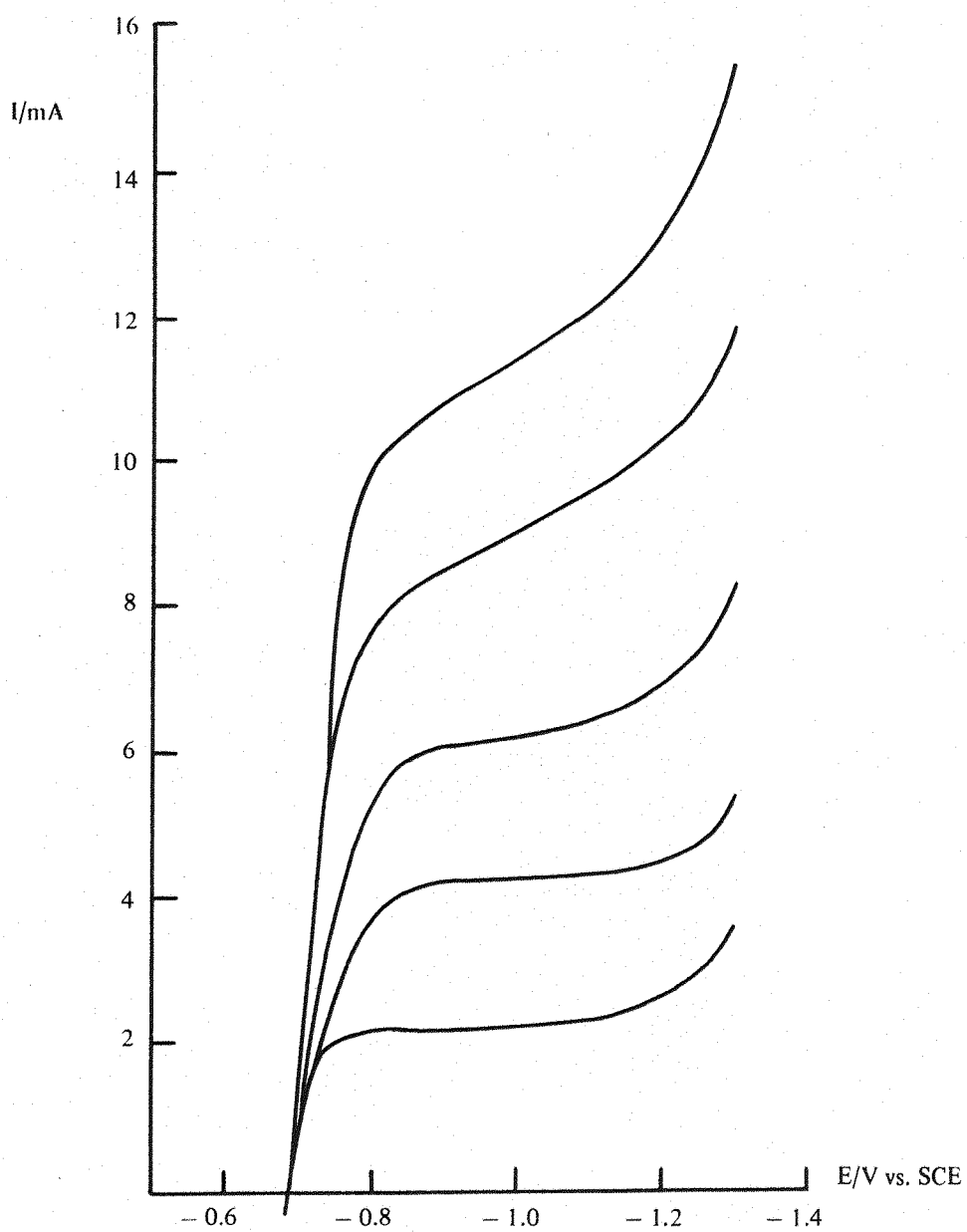
Figure 3.4(3) I-E curves obtained for the reduction of NO_3^- (5m M) in 0.01 M HCl at a rotating cadmium disc electrode (area 0.33 cm^2). Rotation rates 100, 400, 900, 1600 and 2500 rpm. Potential scan rate 0.0166 V s^{-1}
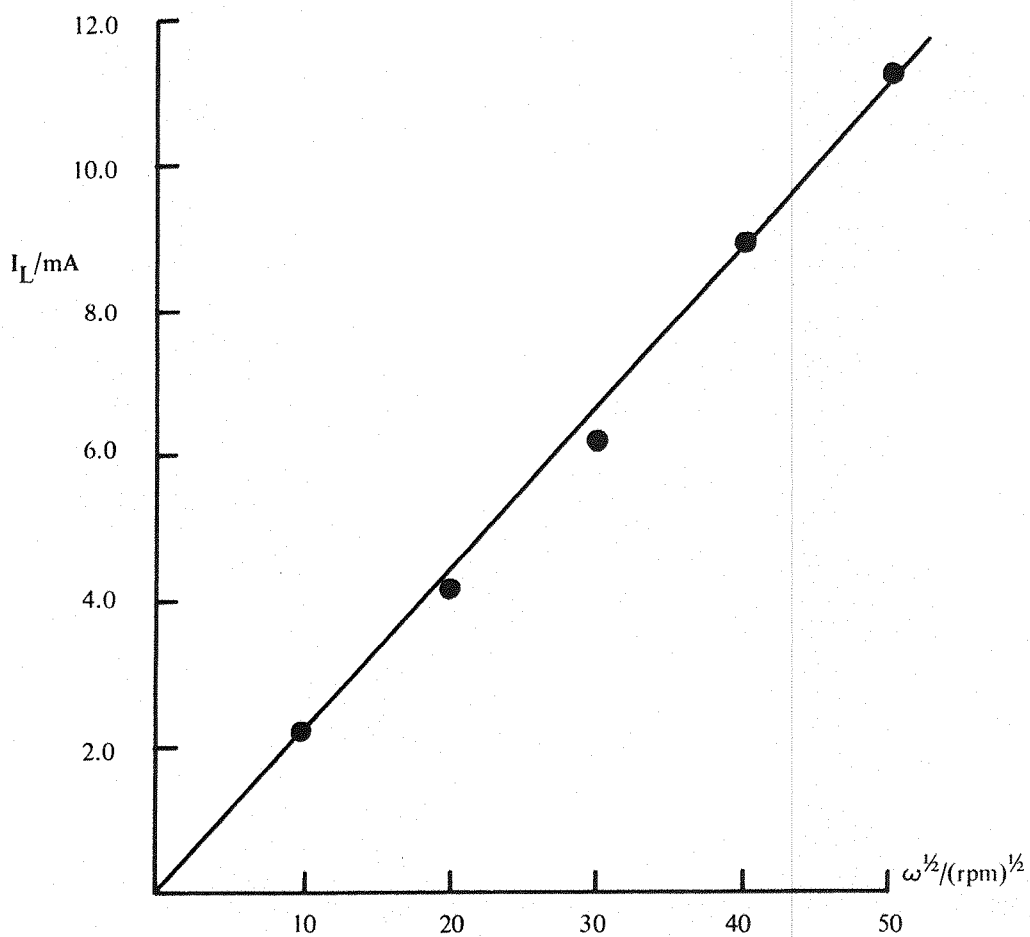
Figure 3.4(4) Plot of limiting current (I_L) versus square root of rotation rates for the reduction of 5m M NO_3^- in 0.01M HCl using a polished rotating cadmium disc electrode (area 0.33 cm^2).   Potential sweep rate 0.0166 V s^{-1}

Figure 3.4(5) Results for Cd rotating disc experiment with 5m M NaNO₃ in 0.1 M HClO₄
Rotation rate = 900 rpm

(a) sweeping towards anodic potential

(b) sweeping towards cathodic potential
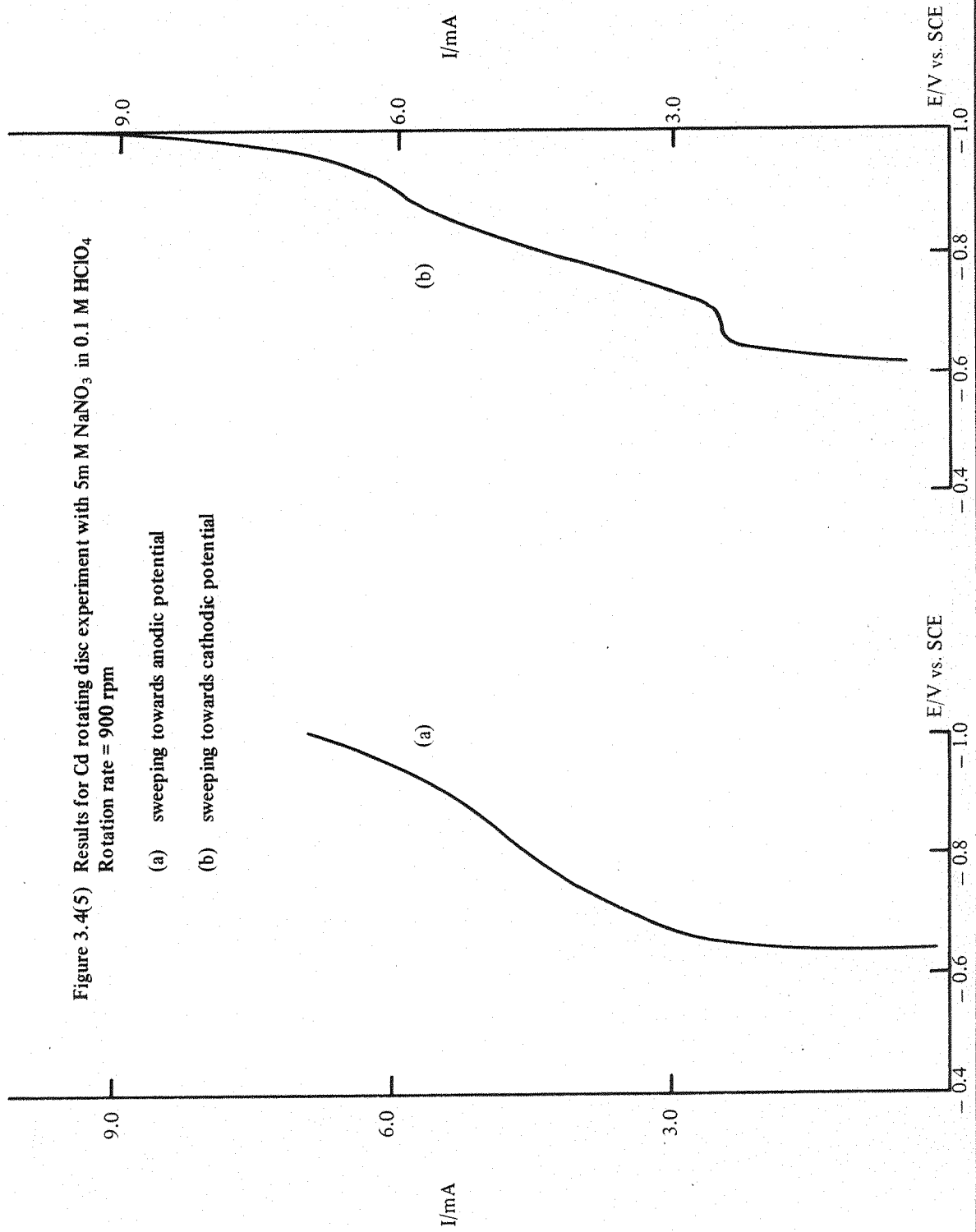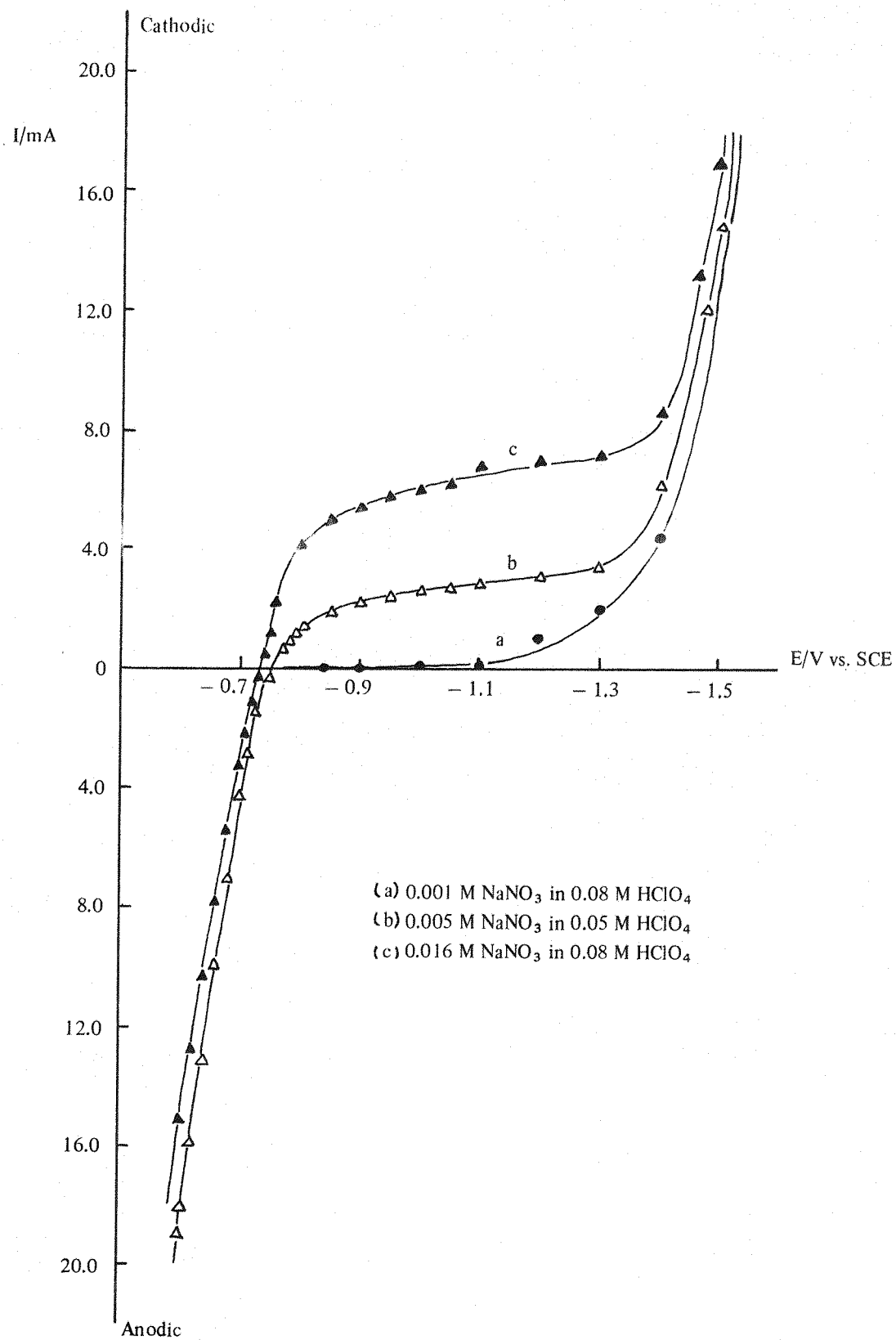
Figure 3.5(1)   Polarization curves for Cd-electrode (length 2.7 cm)

Cathodic

I/mA

20.0

16.0

12.0

8.0

4.0

c

b

a

0

E/V vs. SCE

−0.7   −0.9   −1.1   −1.3   −1.5

4.0

8.0

(a) 0.001 M NaNO₃ in 0.08 M HClO₄
(b) 0.005 M NaNO₃ in 0.05 M HClO₄
(c) 0.016 M NaNO₃ in 0.08 M HClO₄

12.0

16.0

20.0

Anodic

TABLE 3.9

Results of rotating disc electrode experiments for reduction of 5.0 mM $NaNO_3$ in different pH

Supporting Electrolyte	Slope $\dfrac{I_L}{\omega^{1/2}AC}$ $\dfrac{mA}{(rpm)^{1/2} \times (cm^2) \times (mM)}$
0.01 M $HClO_4$ + 0.99 M $NaClO_4$	0.06
0.1 M $HClO_4$ + 0.9 M $NaClO_4$	0.10
1.0 M $HClO_4$	0.08
1.0 M $HClO_4$ + 0.1 M HCl	0.12
0.01 M HCl	0.14
1.0 M HCl	0.14

5.0 mM $NaNO_2$

0.01 M $HClO_4$ + 0.99 M $NaClO_4$	0.05

63

TABLE 3.10

Electrolyte	E	Initial n-value	Yield of NH$_3$
	V vs SCE	F mole^{-1}	%
1.0 M HCl	− 0.9	6.1	67
1.0 M HClO$_4$	− 0.9	9.0	29.3

Electrolyses of NO$_3^-$ (5 mM) at a cadmium cathode

64

3.6 Other Electrodes

Certain other metals have also been tried to determine their ability to act as a cathode for reducing nitrate in perchlorate medium (pH 1). A point by point method was used for each of them and the current was measured after 30 s at each applied potential. No reduction was observed when mercury, nickel and lead cathodes were used but it was found that zinc and tin electrodes are also suitable for reducing nitrate. In the case of a zinc electrode the current-potential curves cross the zero current axis, going directly from zinc dissolution to nitrate reduction, which shows that the chemical reaction between nitrate and zinc is spontaneous. Similar results were also obtained when nitrate is reduced at a cadmium electrode. Cyclic voltammograms for nitrate reduction at a zinc cathode confirm that the oxidation of zinc occurs in a potential very close to the nitrate reduction. The steady state current-potential curve for nitrate reduction at a zinc and tin electrode are presented in Figures 3.6(1) and 3.6(2). Electrochemical reduction of nitrate ion at mercury cathode in the presence of concentrated acid i.e. 15N H_2SO_4 was studied. Steady state polarization curves were recorded and the result of one experiment is presented in Figure 3.6(3), where 0.1M NO_3^- was used. Several controlled potential electrolyses were carried out when different potentials (i.e. -0.7, -0.62, -0.1 V) were applied to the cathode (mercury pool electrode), for the reduction of 0.1M and 1.0M nitrate iron. Although previous workers[22-23] found hydroxylamine as the major product, but we analysed the product of the electrolyses which showed neither ammonia nor hydroxylamine present in the catholytes. Gas formation was observed during all the electrolyses at the working electrode. The plots of current against charge showed n value between 1 and 2 F mole^{-1}, suggesting the formation of NO_2. In one experiment the gases formed were collected in a test tube and visually brown gas (NO_2) was observed. It is concluded that nitrate in the presence of concentrated acid at mercury electrode is converted to gaseous products.
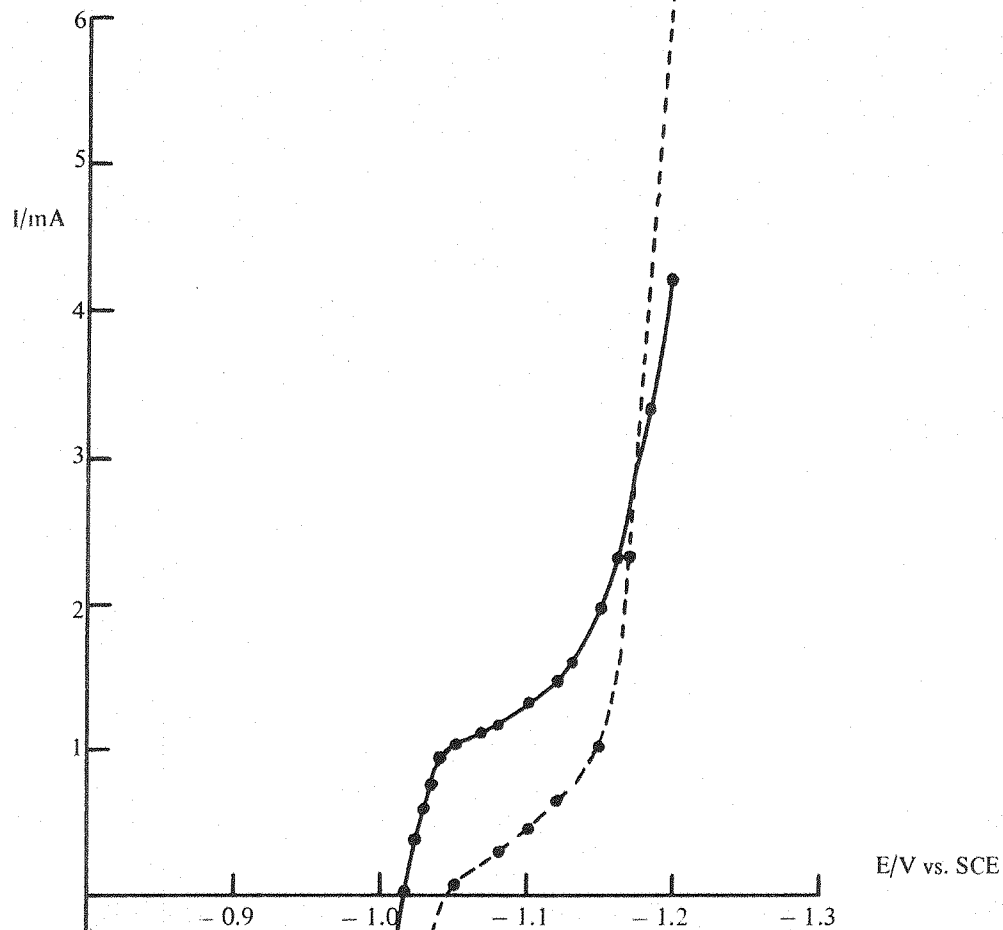
Figure 3.6(1) Polarization curves for zinc disc electrode (area 0.38 cm^2)

-------- 0.1 M HCl

———— 5m M NaNO$_3$ in 0.1 M HCl

Figure 3.6(2) Polarization curves for the solutions of

    — . —   0.1 M HCl

    — + —   5m M NaNO$_3$ in 0.1 M HCl

on a tin electrode (area 1.47 cm^2)

Figure 3.6(3) Steady state I-E curves for

. — .   15 N H$_2$SO$_4$

$^\circ$ — $^\circ$ 0.1 M NaNO$_3$ in 15 N H$_2$SO$_4$

using mercury drop electrode

68

CHAPTER 4

DISCUSSION

4.1 Chemical Reduction of Nitrate

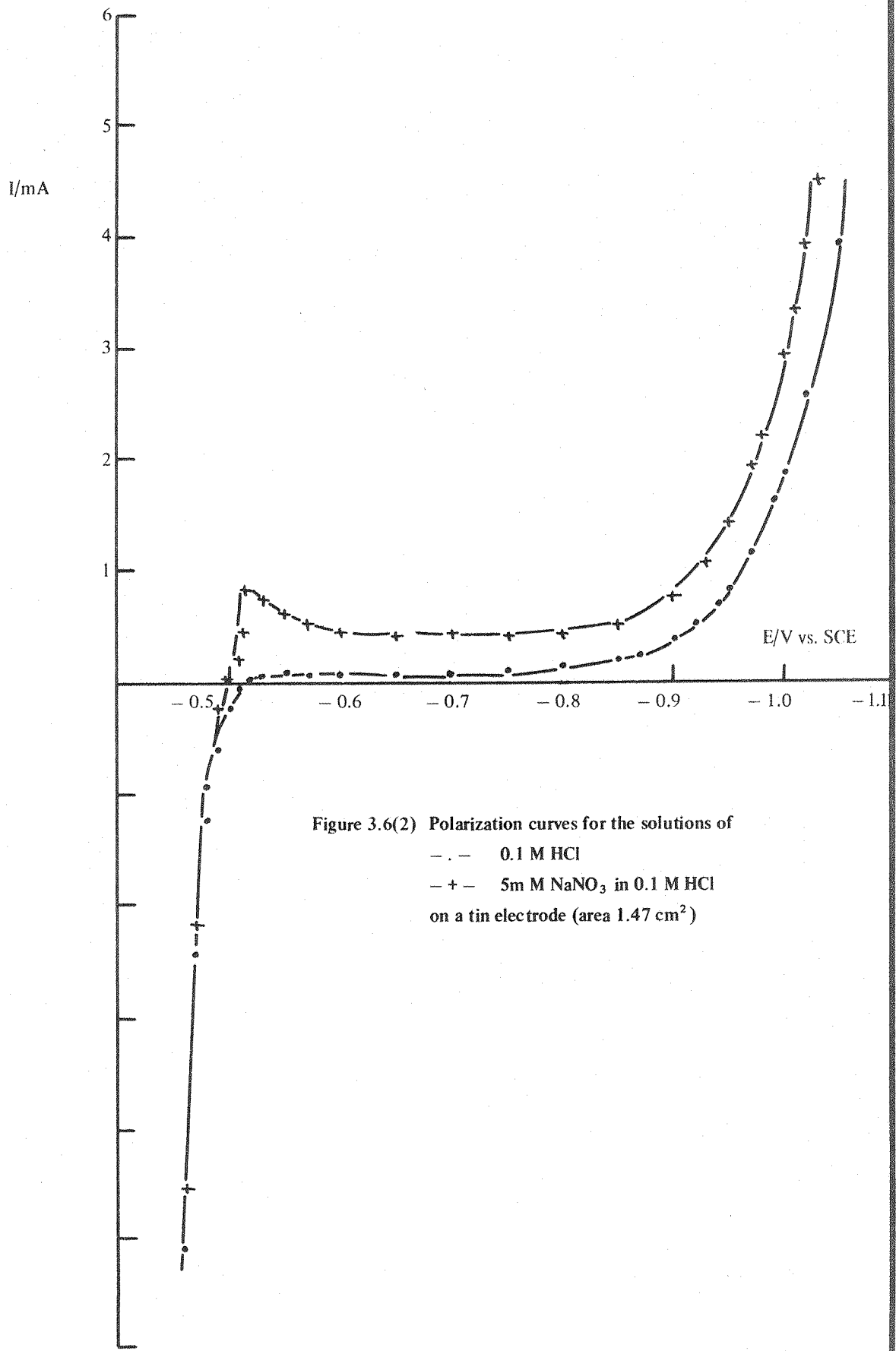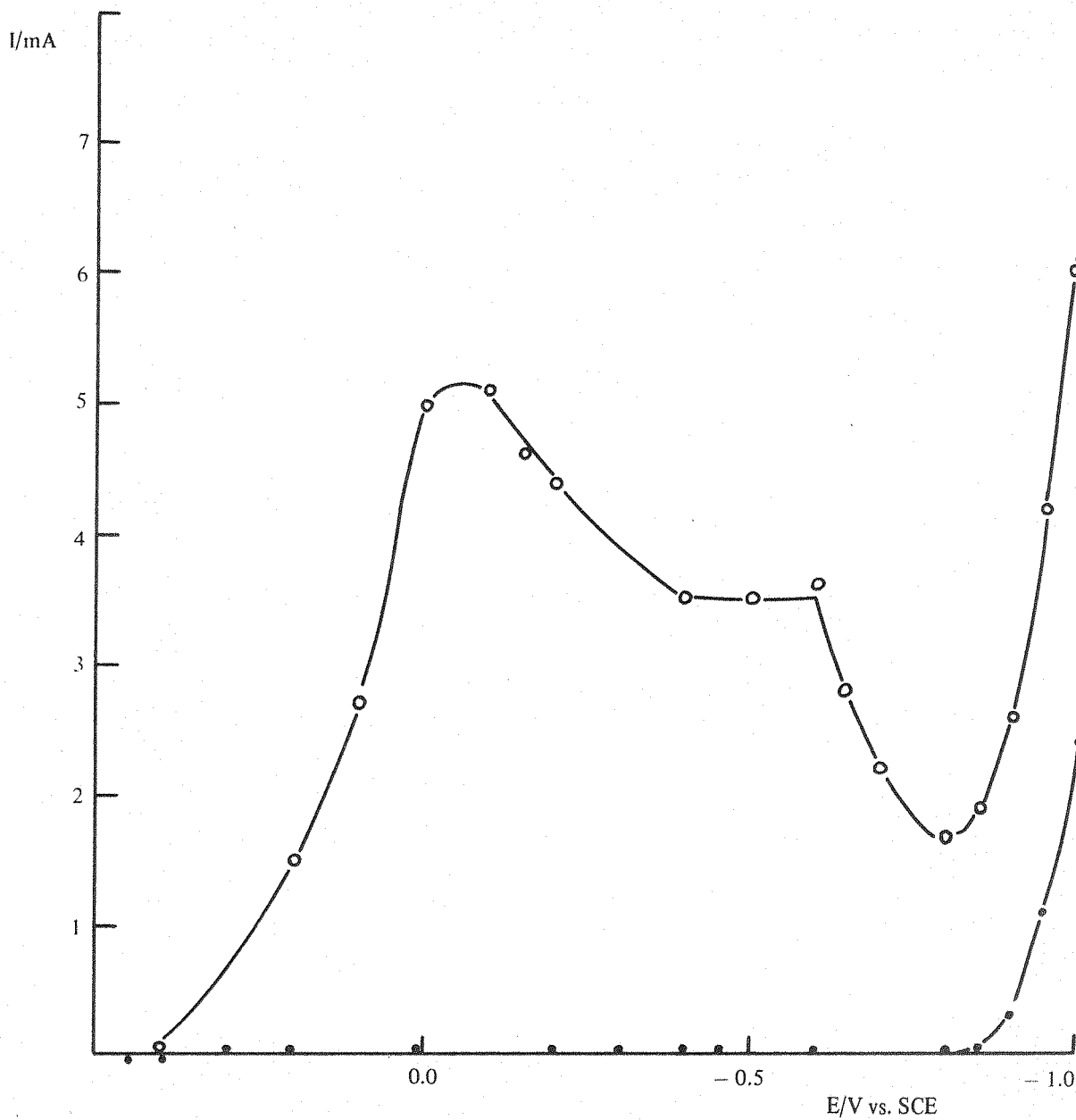Concentrated nitric acid has been widely used both as an oxidising agent in organic chemistry and for the dissolution of metals. The nitrogen containing products can be one or a mixture of NO_2^-, NO_2, N_2O, NO, N_2 and NH_3 depending on the concentration of the acid and the nature and concentration of the reducing agent. Many of these reactions require forcing conditions, however, and there is little evidence that nitrate in neutral or mildly acidic media is an effective oxidising agent and this suggests some kinetic limitation since at pH 1 the standard potential of for example the NO_3^-/NO_2^- couple is + 0.94V.

The acidity of the medium is of prime importance in determining the kinetics of the reactions of anions in aqueous solution. With nitrate ion two equilibria may be important:

$$NO_3^- + H^+ \rightleftharpoons HNO_3$$
$$HNO_3 + H^+ \rightleftharpoons H_2NO_3^+ \rightleftharpoons H_2O + NO_2^+$$
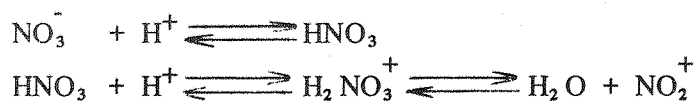
and the role of the proton is presumably to weaken the strong bond between the negative oxygen atom and the positive nitrogen central atom. Also, in general, the oxidation state of the central atoms affects markedly the rate of the reactions of oxyanions and usually when more than one oxidation state is stable the lower oxidation state is reduced more rapidly i.e. at the same pH nitrite is reduced more rapidly than nitrate.

The reactions of nitrate ion with metals ions in solution are often very slow or they do not occur even when thermodynamics would predict reaction e.g. Fe^{2+}, Cr^{2+}. The reduction of nitrate by stannous ion catalysed by molybdate is well known. Haight and Coworkers[39] studied this system in both hydrochloric acid and sulphuric acid solutions and proposed that the role of the molybdate was to render the nitrate reducible while stannous ions acted as oxygen transfer agents. In view of the catalytic nitrate waves observed on polarograms of molybdenum(VI) it seems more likely that it is a reduced molybdenum species which acts as the oxygen transfer agent and the role of the stannous ion is to maintain the catalyst in the active reduced state.

In general, three different mechanisms may be considered for the reduction of nitrate.

(i) Oxygen transfer:

$$NO_3^- + ML_n \longrightarrow NO_2^- + MOL_n$$
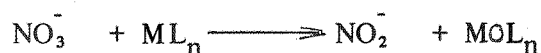
and the rate of such reactions will depend on the ability of the metal species to form a M-O bond and this will depend on the ligands around the metal.

TABLE 4.1

IMPORTANT COMPOUNDS OF NITROGEN

Oxidation state (Average) of N	Compounds and Names
− 3	NH_3, ammonia NH_4Cl, ammonium chloride $NaNH_2$, sodium amide
0	N_2
+ 1	N_2O, dinitrogen oxide
+ 2	NO, nitrogen oxide
+ 3	N_2O_3, dinitrogen trioxide; HNO_2, nitrous acid
+ 4	NO_2, nitrogen dioxide N_2O_4, dinitrogen tetroxide
+ 5	N_2O_5, dinitrogen pentoxide HNO_3, nitric acid

The only metals ions which reduce nitrate ion readily in aqueous media are from elements which form strong bonds with oxygen[44] e.g. Mo, U, W and this leads to the proposal that this is the most probable route for homogeneous reactions. Certainly the rates of the reactions of metals ions which do react are very sensitive to the presence of potential ligands e.g. the reactions of monomeric molybdenum(V) complexes with nitrate in dimethylformamide[38].

(ii) Electron transfer:

$$NO_3^- + e \longrightarrow NO_3^{2-} \qquad (I)$$

$$HNO_3 + e \longrightarrow HNO_3^- \qquad (II)$$
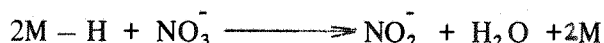
$$NO_2^+ + e \longrightarrow NO_2 \qquad (III)$$
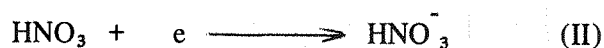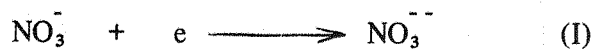
Reaction (I) seems unlikely although reaction (III) would be expected to be facile. Hence the extent of electron transfer initiated reduction would be expected to depend strongly on pH.

(iii) Adsorbed Hydrogen Intermediates: In heterogeneous systems, reactions of the type

$$2M - H + NO_3^- \longrightarrow NO_2^- + H_2O + 2M$$

must also be considered.

The complexity of the possible reaction pathways, for the reduction of nitrate can be seen from an early scheme given by E.J. Joss[45]:
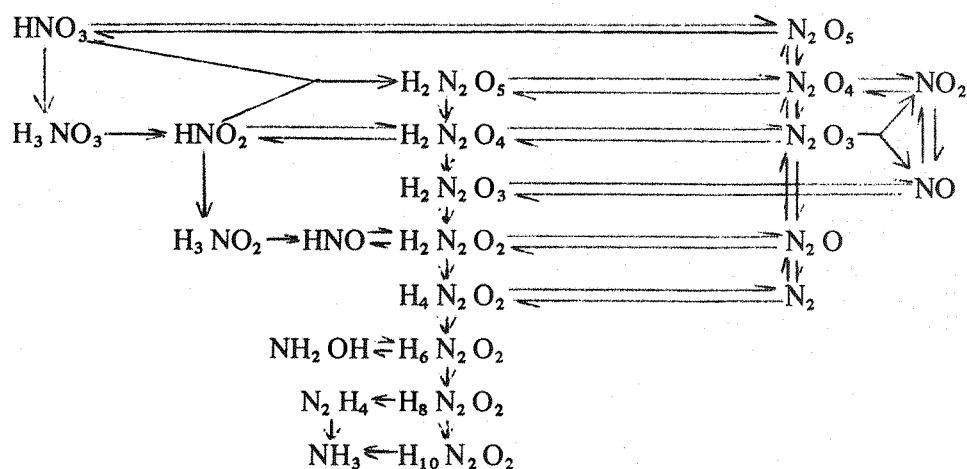
The vertical lines represent changes in oxidation state and the horizontal lines gain or loss of water. In this author's view the reductions were due to hydrogen. In addition it should be recognised that subsequent reactions of primary products are also possible, for example,

$$HNO_3 + HNO_2 \longrightarrow 2NO_2 + H_2O$$

and $\qquad HNO_2 + NH_2OH \longrightarrow N_2O + 2H_2O$
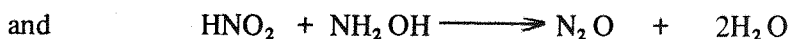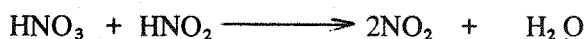
Reactions of metals with nitric acid are often autocatalytic[46] because the rate of dissolution by nitrous acid is faster than nitric acid and the nitrous acid is continuously formed by reaction of nitric acid with other nitrogen intermediates.

4.2 Electrochemical reduction of nitrate and nitrite at a copper cathode

The coulometry and product analysis show that the overall reactions occurring at a copper cathode in acidic nitrate or nitrite solution are

$$NO_3^- + 8e + 9H^+ \longrightarrow NH_3 + 3H_2O$$
$$NO_2^- + 6e + 7H^+ \longrightarrow NH_3 + 2H_2O$$

respectively. The yield of ammonia based on the starting material consumed is always almost 100% and the current yield is always high. Under some conditions some charge is wasted in competing side reactions, for example hydrogen evolution which is most important at more negative potentials and in highly acidic solutions. It should also be noted that at the pH used during this study, no spontaneous chemical reaction occurs between the copper and the catholytes.
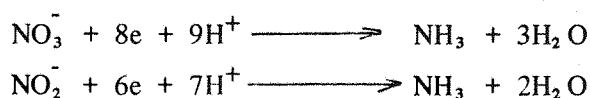
In perchlorate and sulphate media the cyclic voltammetry and rotating disc experiments show that nitrate and nitrite ions are reduced in single step processes well separated from the potentials for copper dissolution and hydrogen evolution. The processes are totally irreversible but at suitable pH, the I—E curves can show well formed mass transfer controlled peaks or plateaux. The variation of peak current with potential sweep rate and of limiting current with rotation rate show the diffusion coefficient of nitrate to be approximately 1.7×10^{-5} cm^2 s^{-1}.

From the viewpoint of analysis, the best I—E curves are obtained at pH 1. At lower pH, current for proton reduction deforms the limiting current plateau while at higher pH the limiting current decreases. Unfortunately, the reduction of nitrate and nitrite occur at very similar potentials and the dependences of the half wave potentials on pH and halide ion concentration are the same, so that no analytical procedure based on this system could discriminate the two ions.

The I-E curves allow little to be deduced concerning the reaction mechanism. The cyclic voltammograms even at fast sweep rates show no evidence for reactive intermediates, and, moreover, electrolyses carried out at potentials at the foot of the wave in the I-E curve give only ammonia as product. It can be shown that hydroxylamine is not an intermediate since it is not electroreducible at copper. Moreover, it is clear that proton has an important role in the reaction. Firstly, the shifts in the half wave potentials towards positive potential

72

on increasing the acidity probably indicates a pre-protonation equilibrium and that it is the acids which are reduced. Secondly, no reduction was observed above pH 3 and in the intermediate pH range the limiting currents and peak currents depended on the ratio of proton to nitrate or nitrite ions. The cyclic voltammetry at pH 2 showed the process of nitrate reduction to be diffusion controlled although the peak currents were smaller than at pH 0 or 1 and this may reflect the large number of protons consumed during chemical steps subsequent to the initial electron transfer.

The effect of halide ion on the reduction of nitrate and nitrite ions at copper is unusual. The experiments with bromide and chloride ion showed that the reduction processes shifted to more negative potentials with increasing halide ion concentration but the limiting current did not decrease and the product of the reduction of nitrate ion was still ammonia although the yield is decreased because of the higher hydrogen evolution current at the more negative potential. Hence the essential nature of the process is unchanged and the role of the halide ion is solely to inhibit the rate of the reaction. The effectiveness of the halide ion in shifting the nitrate reduction potential decreases along the series $I^- > Br^- > Cl^- > F^-$. Two effects could cause this shift in reduction potential with halide ion concentration :

(i)   complex formation between the halide ion and the electroactive species or its precursors.

(ii) adsorption of the halide ion at the copper surface leading to changes in the double
      layer structure and/or changes in the detailed nature of the reduction process.

(i) seems unlikely in this system; there seems little likelihood of chemical interaction between halides ions and nitrate ions or nitric acid. On the other hand, although it was not possible to obtain evidence for the adsorption of halide ions at copper, the effect could well be a double layer effect i.e. simply the reverse of the catalysis of nitrate ions by lanthanum ions at mercury[36]. The highly positively charged cations are believed to adsorb on mercury and reduce the electrostatic repulsion between the cathode and the nitrate ion. Certainly relative effects of the different halides reflects the likely extent of adsorption and it is also interesting to note that the magnitudes of the shifts, although not the signs, are similar to those observed for the reduction of chromium(III) at mercury when the same halides were added[47 48].

4.3 Electrochemical reduction of nitrate and nitrite at a cadmium cathode

At a cadmium electrode the I-E curves for solutions of nitrate and nitrite ions in dilute acid media cross the I = 0 axis at about − 0.6V, going directly from cadmium oxidation to nitrate reduction. It is clear that nitrate and nitrite reduce at a potential more positive

73

than — 0.6V and hence that the chemical reaction between cadmium metal and the two oxyanions should occur spontaneously. Indeed there is evidence that such a reaction does occur (i) when current-potential curves are run by sweeping from positive to negative potentials, a break is observed in the I-E curve, see Fig. 3.4(5), which suggests that there are two processes occurring, i.e. the reduction of Cd^{2+} as well as NO_3^- or NO_2^- (ii) during a controlled potential reduction, the surface of the cadmium changes from a bright finish to a matt, black appearance which would be compatible with deposition of metal during the electrolysis. The I-E curves for nitrate reduction at a cadmium cathode show well formed mass transfer controlled limiting currents at more negative potentials and these limiting currents are proportional to the nitrate concentrations. The limiting current density does, however, depend on the anions present in solution. In chloride media, the value of $I_L/\omega^{1/2}CA$ at cadmium is close to that for a copper electrode in perchlorate or sulphate media and the yield of ammonia is high (see tables 3.9 and 3.10). In perchlorate media the limiting currents at a cadmium disc are smaller and the yield of ammonia is lower although it was not possible to find significant deviations from linear I_L vs. $\omega^{1/2}$ plots. This suggests the n-value is lower although it was not possible to identify intermediate reduction products.

The results found during this study concerning the variation of the limiting current density with base electrolyte do not agree with those reported by some earlier workers[9]. They report that the limiting current densities were highest in a perchlorate medium although in a later paper they chose chloride pH 2 as the best medium for analysis.

There is also evidence that nitrite ion is not completely reduced at cadmium. The limiting currents for nitrite were always less than expected based on a comparison with the limiting currents for nitrate reduction. Thus it may be that less than 6F/mol of nitrite is consumed in the electrolysis.

4.4 Reduction of nitrate at other metals

In this study six metals were used as cathodes in dilute acid media. The results at zinc resembles those at a cadmium cathode except for a shift on the potential axis but it was noted that at mercury, lead and nickel no reduction could be observed. The result at mercury is to be expected since nitrate is a common non-complexing base electrolyte for polarographic studies.

The few experiments in a strong sulphuric acid medium (IOM) confirmed earlier reports[22][23] that nitrate does reduce at mercury in such conditions although in the preparative experiments it was not possible to identify hydroxylamine as the product. It seems likely that in

74

strong acid the reduction is initiated by the steps

$$NO_3^- + 2H^+ \rightleftharpoons NO_2^+ + H_2O$$

$$NO_2^+ + e \longrightarrow NO_2$$
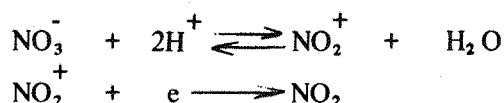
4.5 Further comments on the reduction mechanism

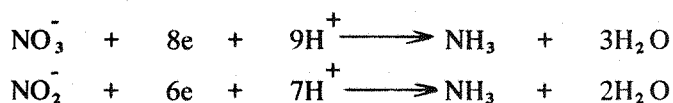While the overall reactions can be defined and certainly at a copper cathode and pH 0–2 these are given by the equations

$$NO_3^- + 8e + 9H^+ \longrightarrow NH_3 + 3H_2O$$

$$NO_2^- + 6e + 7H^+ \longrightarrow NH_3 + 2H_2O$$

the electrochemical data gives relatively little information concerning the mechanism or, indeed, the reaction pathway. The following comments can be made concerning possible reaction intermediates (i) nitrite may be an intermediate in the reduction of nitrate since it is reduced at the same potential and the product of both nitrite and nitrate reduction is ammonia, at least on copper (ii) hydroxylamine, nitrogen and nitrous oxide are not electro-reducible and therefore cannot be intermediates (iii) most of the other obvious intermediates, e.g. NO_2, NO, cannot be studied because they undergo complex reactions including disproportionation on dissolution in aqueous acid.

Moreover the specificity for the oxyanion reductions to particular cathode metals helps little in deducing the type of mechanisms. The following types of reactions should be considered:

(i) Electron transfer

$$HNO_3 + e \longrightarrow HNO_3^-$$

although such a reaction would be expected to occur at all the metals tried unless the product of electron transfer is adsorbed and the free energy of adsorption of the intermediate varies strongly with the metal.

(ii) Reduction via adsorbed hydrogen

$$H^+ + e + M \longrightarrow M\text{-}H$$

$$M\text{-}H + HNO_3 \longrightarrow product$$
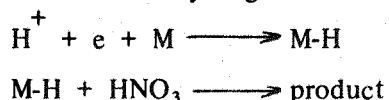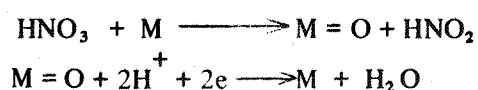
Such a mechanism has been proposed for a platinum cathode but seems unlikely here since nickel would be expected to be a better substrate than copper for such a sequence. Moreover, cadmium and zinc would be expected to be poor cathodes.

(iii) Oxygen transfer

$$HNO_3 + M \longrightarrow M = O + HNO_2$$

$$M = O + 2H^+ + 2e \longrightarrow M + H_2O$$

the only "evidence" for such a mechanism would be the analogy with homogeneous reductions. There is no obvious reason why copper, cadmium and zinc would allow oxygen transfer but not mercury, lead and nickel.

Hence it must be a conclusion of this study that further experimental investigations are necessary before the mechanism will become clear. This study has, however, shown conclusively that (i) the reduction of nitrate and nitrite is possible at copper, cadmium and zinc cathodes in dilute aqueous acid; (ii) at copper the reactions are mass transfer limited at high overpotentials in perchlorate and sulphate media; (iii) the reductions at copper are inhibited by halides; (iv) the electrode process involves complete reduction to ammonia; and (v) in strong acid the reaction occurs at all cathodes.

APPENDIX

Polarography

A method for the determination of nitrate, based on the catalytic polarographic reduction of nitrate ion by molybdenum(VI) and uranium (VI), has been investigated. It was also hoped that the experiments would give some insight into the factors determining the rate of reaction between transition metal species and nitrate.

(I) Polarography of Molybdenum and Uranium in the Absence of Nitrate

The polarographic reduction of Mo(VI) and U(VI) was studied in both sulphate and chloride supporting electrolytes. The data obtained for several concentrations of each ion is reported in tables I and II. A polarogram was also run for Cd^{2+} in chloride media, a system chosen because it is known to give a reversible and diffusion controlled 2-electron reduction wave; the half wave potential was $-0.66V$ and the limiting current for a 2×10^{-4} M solution of Cd^{2+} in 0.1M HCl was 1.25 μA.

The polarographic behaviour of both Mo(VI) and U(VI) is not straight forward and depends strangely on the supporting electrolyte.

(i) Molybdenum (VI)

In chloride media, Mo(VI) shows a single reduction wave but the limiting current is not proportional to the concentration of the ion in solution. Hence the process is clearly not diffusion controlled and a comparison of the limiting current with that of cadmium cannot be used to estimate a value for the number of electrons transferred. In sulphate medium two reduction waves are observed but again the limiting current does not depend linearly on the concentration of Mo(VI) in solution. Indeed the ratio of the limiting currents for the two waves varies with concentration. The total limiting currents for the two waves obtained for molybdenum ion in sulphate media is twice that for molybdenum ion in chloride ion solution.

Controlled potential electrolyses data of a solution of 2×10^{-5} M Mo(VI) in 0.1M sulphuric acid at E= $-0.4V$ and E= $-0.8V$ indicates each wave to be a 1e process. While in the presence of nitrate controlled potential coulometry was carried out at $E = -0.8V$ and the extrapolation of the current-charge plot indicates four electrons transferred per mole of nitrate ion.

(ii) Uranium (VI)

In sulphate media U(VI) shows one reduction wave. The limiting current versus the concentration of uranium ion is plotted in figure 1 and a good relationship is observed showing a diffusion controlled process. The height of the wave was compared with that

obtained for Cd^{2+} and the n value was found to be 2. Polarograms of U(VI) in chloride medium indicate two reduction waves, the first one ($E_{1/2} = - 0.27$ V) clearly shows a diffusion controlled process and the comparison of the limiting current with that of cadmium would suggest n = 1. The second wave is obviously a hydrogen catalytic current because the limiting current for that is much higher than the diffusion controlled current for cadmium.

Further polarograms were run for U(VI) in acetate media and again at all pH two waves were observed. The first wave was compatible with n = 1 but the second wave is clearly a catalytic hydrogen wave i.e. $I_L >> I_D^{Cd^{2+}}$. The experimental results (half wave potential, shape factor and limiting current) for U(VI) in acetate medium are reported in table III.

(II) Polarography in the Presence of Nitrate Ion

Polarograms of molybdenum (VI) and uranium (VI) were run before and after the stepwise addition of nitrate in chloride and sulphate media. In many cases a catalytic nitrate wave is observed but the limiting current shows a strong dependence on the nature of the supporting electrolyte.

(i) Reduction of nitrate in the presence of Mo(VI)

The polarograms obtained with nitrate and molybdenum (VI) in sulphuric acid solution showed two reduction waves in which the height of the wave obtained at more negative potential was changed on increasing the nitrate ion concentration. Hence the reduction of nitrate involves the species produced at this potential. Polarograms for nitrate and molybdenum in chloride medium showed only one reduction wave. Typical polarograms for solutions of 2×10^{-4} M Mo(VI) and 2×10^{-4} M Mo(VI) + 4×10^{-4} M NO_3^- in 0.1M KCl + 0.01M HCl are shown in figure 2. The limiting current is plotted against concentration of nitrate ion in figure 3. The results are reported in table IV.

### (ii) Nitrate reduction in the presence of U(VI)

The polarographic behaviour of nitrate ion in the presence of uranium was also studied and in sulphuric acid the polarograms showed a single reduction wave with $E_{1/2} = - 0.5$V. In chloride media always two reduction waves were observed. All the results are summarised in table V. The slopes of the limiting current versus the concentration plots is an indication of the rate of the reaction between the lower oxidation state of the transition metal and nitrate. The intercept is the limiting current in the absence of nitrate. The variation of the limiting current versus concentration of nitrate in one case is shown graphically in figure 4.

The complexity of the system is again seen since the slopes do not show a single dependence on the concentration of the uranium(VI); this, however, is to be expected from the polarograms in the absence of nitrate. It should be noted that the intercepts for the experiment with uranium (VI) are large, because the reduction waves, even when nitrate is not present in the solution are catalytic hydrogen waves. It was not possible to find conditions where the lower oxidation states of these cations reacted rapidly with nitrate but not with hydrogen ions.

The conclusions from this polarographic study concerning the reduction of nitrate ions are listed below:

(i) Nitrate reduction occurs chemically only when a suitable oxidation state of molybdenum or uranium ions is generated electrochemically, at the dropping mercury electrode and the nitrate reoxidises these ions, which are then reduced again at the cathode.hence resulting in a higher current when nitrate is present. It is clear that the reduction currents for nitrate solution in the presence of molybdenum or uranium are limited by the rate of chemical interaction between the nitrate and these cations.

(ii) A high concentration of proton or a proton donor (e.g. acetic acid) is essential (see figure 5).

(iii) With both molybdenum and uranium, the catalytic current is markedly increased by the presence of a supporting electrolyte capable of being a ligand for the transition metal e.g. Cl^- or CH_3COO^- (see table V).

(iv) The catalytic current increases with increasing the concentration of molybdenum or uranium, but it is not directly proportional to their concentrations.

The results obtained in this study are similar to those reported in earlier publications[33] and are certainly compatible with a mechanism such as

$$Mo(VI) \ + \ e \longrightarrow Mo(V)$$

$$Mo(V) \ + \ 2e \longrightarrow Mo(III)$$

$$Mo(III) \ + \ NO_3^- \longrightarrow Mo(V) \ + \ product$$
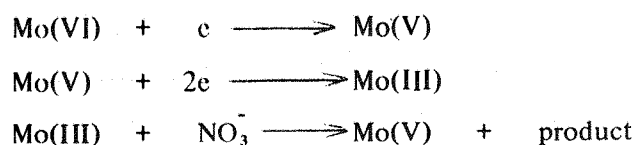
It seems likely that the success of molybdenum and uranium species in reducing nitrate ions is due to the ability of such ions to form metal-oxygen bonds[44] since many other reducing agents with similar redox potentials are quite unreactive towards nitrate. Moreover, it is confirmed that the exact nature of the metal species in solution is critical (c.f. SO_4^{--} vs. Cl^- media) and that proton and ligands can strongly affect the activity of the ions. We would conclude that the optimum condition for the analysis of nitrate using these systems involves uranium in an acetate buffer or acidic chloride medium.

TABLE A1

POLAROGRAPHIC REDUCTION OF Mo^{VI} IN DIFFERENT BASE ELECTROLYTES

Base Electrolyte	$E_{1/2}$ (v)	$E_{1/4}-E_{3/4}$ (mV)	2x10^{-5}M	6x10^{-5}M	I_L(μA) 18x10^{-5}M	54x10^{-5}M
0.1M HCl	-0.32	30	0.19	0.35	0.67	1.08
0.1M H$_2$SO$_4$	-0.13 -0.48	60 50	0.435 0.19	0.30 0.28	0.69 0.52	1.75 1.20
0.1M KCl + 0.01M HCl	-0.46	50	0.18	0.30	0.55	1.97

TABLE A2

POLAROGRAPHIC REDUCTION OF U^{VI} IN DIFFERENT BASE ELECTROLYTES

Base Electrolyte	$E_{1/2}$ (V)	$E_{1/4}-E_{3/4}$ (mV)	2x10^{-5}M	6x10^{-5}M	18x10^{-5}M I_L(μA)	54x10^{-5}M
0.1M HCl	-0.27 -0.99	55 60	0.18 2.30	0.32 4.87	0.68 13.90	1.90 38.50
0.1M H$_2$SO$_4$	-0.57	60	0.11	0.31	0.88	2.72
0.1M KCl + 0.01M HCl	-1.08	60	0.72	2.24	7.05	18.5

TABLE A3

THE EFFECT OF pH IN THE REDUCTION OF 2×10^{-4} M U^{VI}

IN 0.1M KCl + 0.1M Na-ACETATE + 1.0M ACETIC ACID

pH	$E_{1/2}$ (V)		$E_{1/4}-E_{3/4}$ (mV)		limiting current (μA)	
	first wave	second wave	first wave	second wave	first wave	second wave
3.95	-0.43	-1.32	50	60	0.69	12.45
4.86	-0.43	-1.38	50	70	0.74	13.35
5.90	-0.42	-1.57	50	60	0.78	17.10

81

TABLE A4

Results of polarographic reduction of nitrate in the presence of Mo^{VI} ion.

Base Electrolyte	C_{Mo}^{VI} (M)	$E_{\frac{1}{2}}$ (V)	$I\alpha = M\ CNO_3^- + K$	
			$M\ \dfrac{mA}{mole/lit}$	$K\ (\mu A)$
* 0.1M HCl	2×10^{-5}	-0.32	0.37	0.17
* 0.1M KCl + 0.01M HCl	2×10^{-5}	-0.45	0.26	0.19
* 0.1M H_2SO_4	2×10^{-5}	-0.33 -0.61	0.0	0.14
− 0.1M HCl	2×10^{-4}	-0.33	0.62	0.7
+ 0.1M KCl + 0.01M HCl	2×10^{-4}	-0.47	1.27	0.67
+ 0.1M H_2SO_4	2×10^{-4}	-0.28 -0.63	0.36	0.64

* range of nitrate concentration $4 \times 10^{-5} - 4 \times 10^{-4}$ M
+ range of nitrate concentration $4 \times 10^{-4} - 4 \times 10^{-3}$ M
− range of nitrate concentration $4 \times 10^{-5} - 8 \times 10^{-4}$ M

TABLE A5

Results of polarographic reduction of nitrate in the presence of U^{VI} ion

Base Electrolyte	$C_U{}^{VI}$ (M)	$E_{\frac{1}{2}}$ (V)	$I\alpha = M\ CNO_3^- + K$	
			$M\ \dfrac{mA}{mole/lit}$	$K\ (\mu A)$
0.1 M HCl	2×10^{-5}	-0.26 -1.03	16.42	2.0
0.1M KCl + 0.01M HCl	2×10^{-5}	-0.26 -1.12	10.71	1.2
0.1M H_2SO_4	2×10^{-5}	-0.57	0.00	0.28
0.1M HCl	2×10^{-4}	-0.27 -1.04	28.57	14.0
0.1M KCl + 0.01M HCl	2×10^{-4}	-0.26 -1.10	24.64	12.5
0.1M H_2SO_4	2×10^{-4}	-0.51	0.00	1.0
0.1M KCl 0.1 Na-Acetate 1.0 acetic acid	2×10^{-4}	-0.43 -1.34	30.10	10.0
0.1M KCl 0.1 Na-acetate 1.0 acetic acid	2×10^{-5}	-0.43 -1.36	29.71	2.33
0.1M Na-acetate 1.0M acetic acid	2×10^{-5}	-0.56 -1.49	28.39	2.5
10^{-4}M HCl + 0.1M KCl	2×10^{-4}	-0.27 -1.16	0.00	2.2

* range of nitrate concentration $4 \times 10^{-5} - 4 \times 10^{-4}$M

\+ " " " $4 \times 10^{-4} - 4 \times 10^{-3}$M
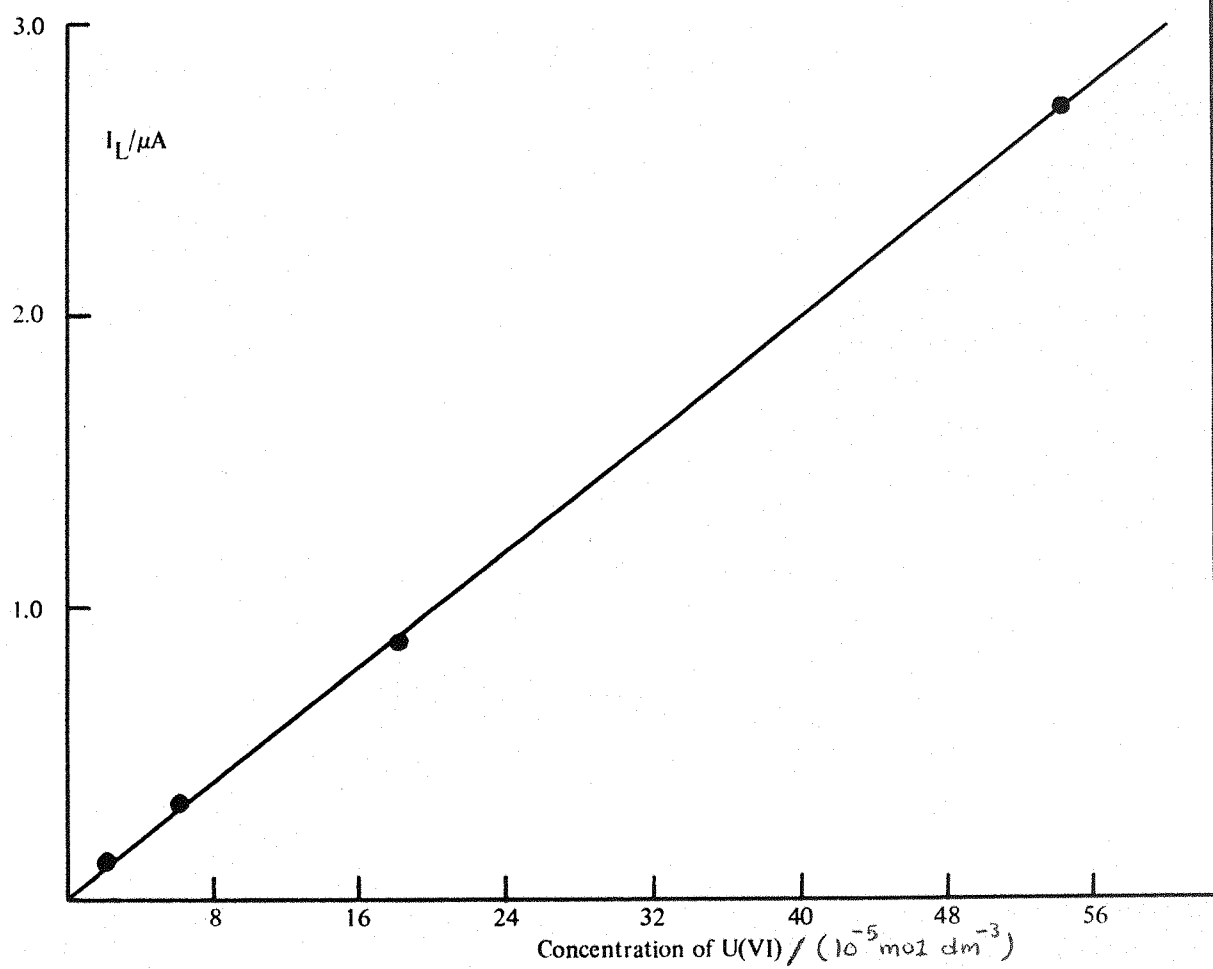
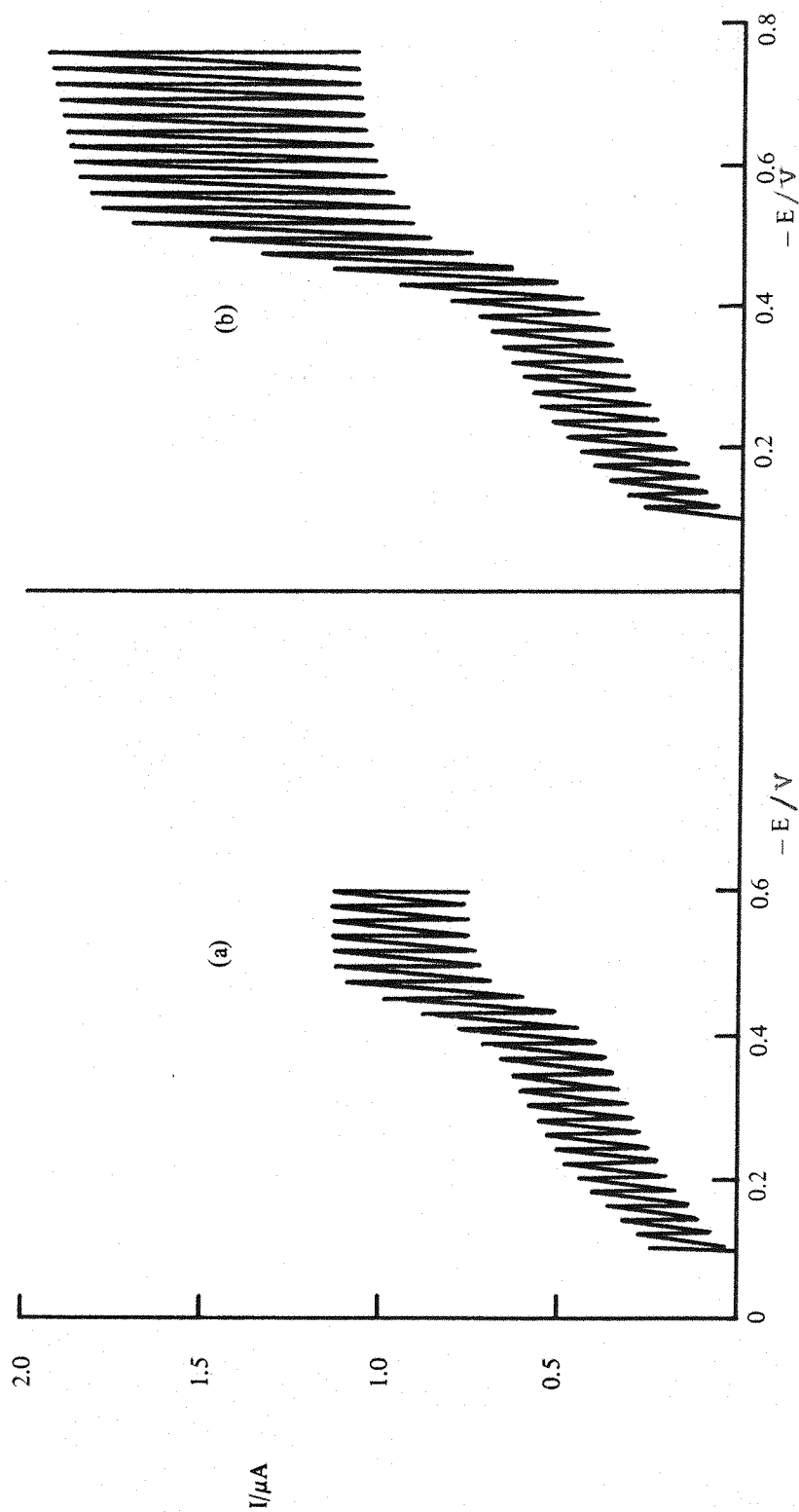Figure A1 Plot of the limiting current versus concentration of uranium (VI) ion in 0.1 M sulfuric acid

Figure A2 Polarograms for

a) 2×10^{-4} M   Mo(VI) in 0.1 M KCl + 0.01 M HCl

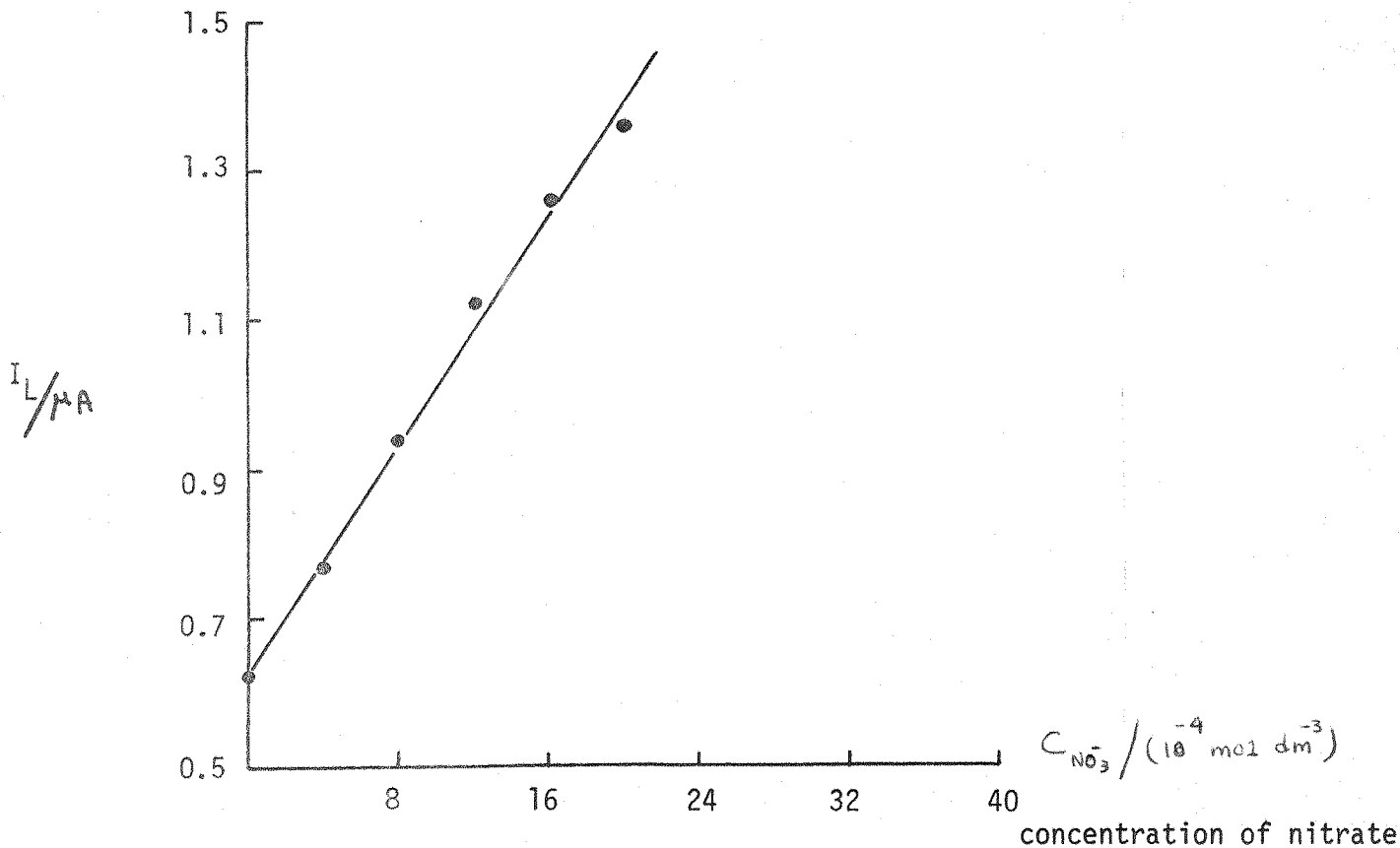b) 2×10^{-4} M   Mo(VI) + 4×10^{-4} M NO_3^- in 0.1 M KCl + 0.01 M HCl

Figure A3

I_L vs $C_{NO_3^-}$ For solution of 2×10^{-4}M Mo^{VI} in 0.1 M H_2SO_4
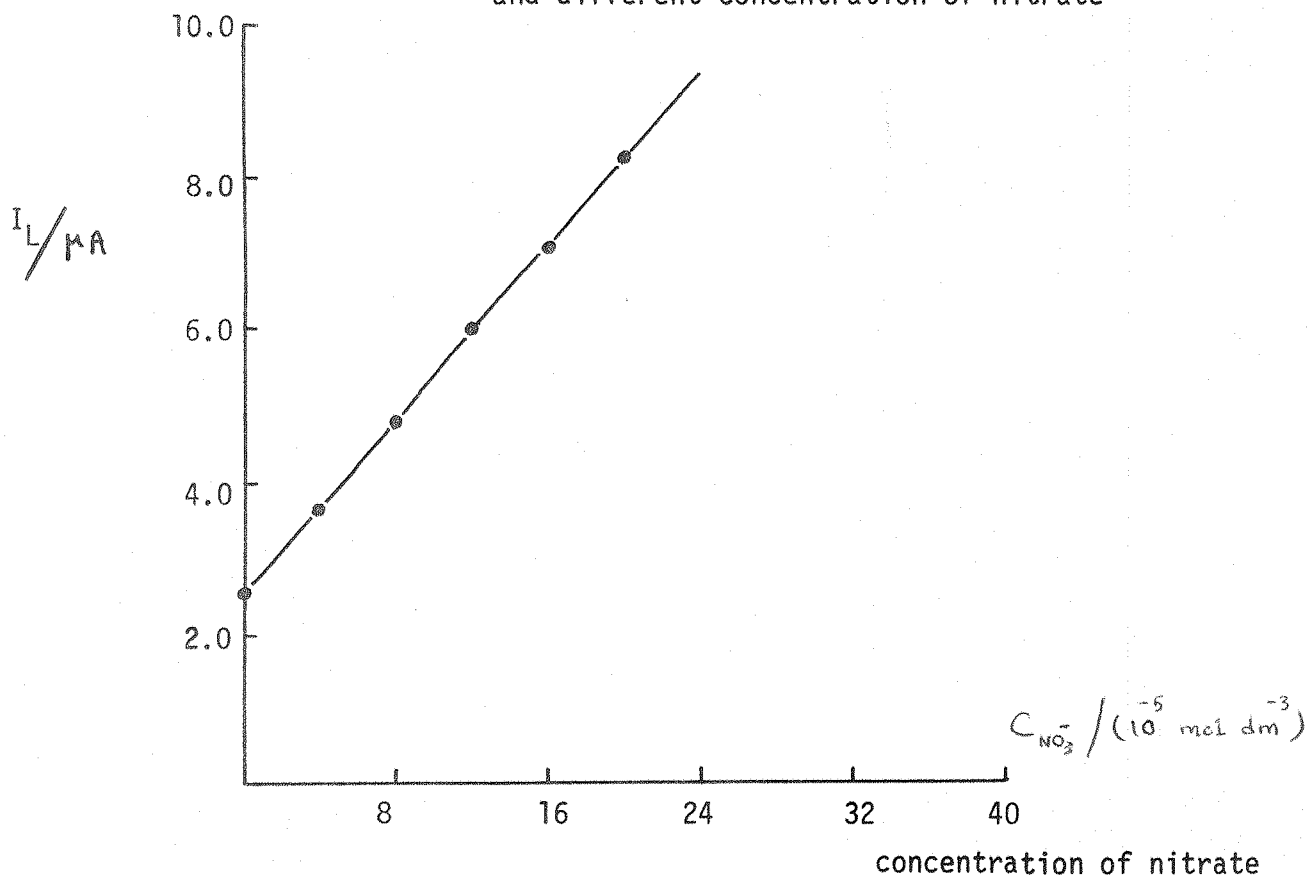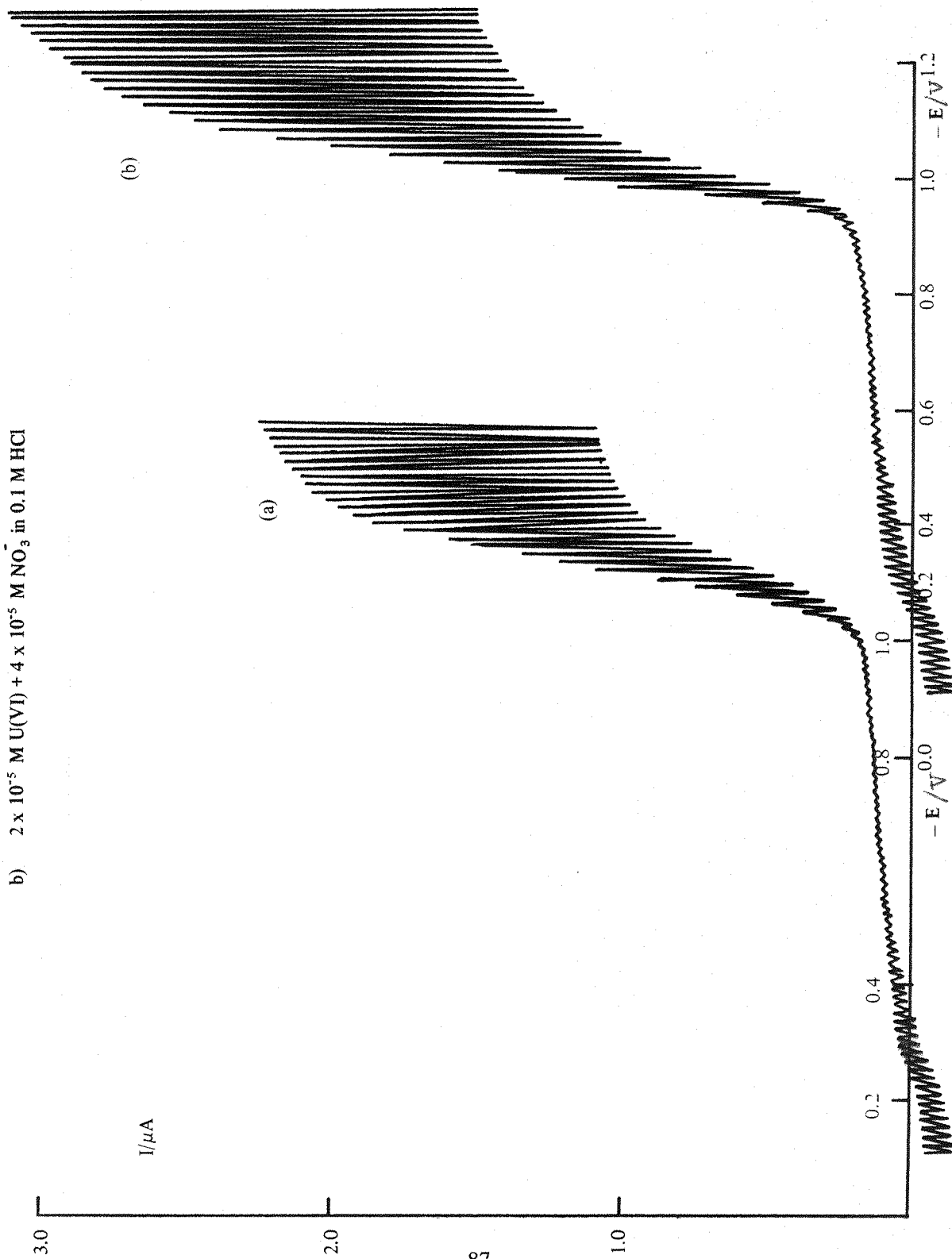and different concentration of nitrate

Figure A4

I_L vs $C_{NO_3^-}$

For a solution of 2×10^{-5}M U^{VI} in 0.1M Na - acetate and
and 1.0M acetic acid and different concentration of nitrate

Figure A5   Effect of pH on the polarographic reduction of nitrate

a) 2×10^{-5} M U(VI) + 4×10^{-5} M NO_3^- in 0.01 M HCl + 0.1 M KCl

b) 2×10^{-5} M U(VI) + 4×10^{-5} M NO_3^- in 0.1 M HCl

LITERATURE CITED

1. J.W. Turrentine, Trans. Amer. Electrochem. Soc. 10, (1906), 49.

2. J.W. Mellor, Comprehensive Treatise on inorganic and theoretical chemistry, Vol. III, P. 94.

3. Chem. Abs. 70, (1968), 63421d.

4. Chem. Abs. 73, (1971), 150277n.

5. Chem. Abs. 71, (1969), 118954h.

6. Chem. Abs. 69, (1968), 64100q.

7. J. Tafel, Z. Anorg. Allgem. Chem. 31, (1902), 289.

8. R.J. Davenport and D.C. Johnson, Anal. Chem., 45, (1973), 1979.

9. R.J. Davenport and D.C. Johnson, Anal. Chem., 46, (13), (1974), 1971.

10. V.A. Panin and K.V. Rybalka, Elektrokhimiya, 8, (1972), 1202.

11. J. Knoeck, Anal. Chem. 41, (1969), 2069.

12. E.D. Wood, F.A.J. Armstrong, and F.A. Richards, J. Mar. Biol. Assoc. U.K., 47, (1967), 23.

13. M.E. Bodini and D.T. Sawyer, Anal. Chem., 49, (3), (1977), 485.

14. Faraday, Phil. Trans., 124, (1834), 96.

15. I. Oknin, Zh, Prikl. Khim. 24, (1951), 61.

16. I. Oknin, Zh. Prikl. Khim. 27, (1954), 873.

17. I.Owe-Berg, Z. Anorg. Chem. 265, (1951), 336.

18. N.M. Trepak, L.K. Il'ina, A.L. L'vov, and V.N. Rodnikova, Chem. Abs. 77, (1972), 82945p.

19. K.J. Vetter, Z. Phys. Chem. 194, (1950), 199; Chem. Abs. 44, (1950), 8263g.

20. K.J. Vetter, Z. Elektrochem. 55, (1951), 121; Chem. Abs. 45, (1951), 9394c.

21. J.A. Epstein, I. Levin and S. Raviv, Electrochimica Acta, 9, (1964), 1665.

22. J.G. Stscherbakow and D.M. Libina, Z. Elektrochem, 35, (2), (1929), 70; Chem. Abs. 23, (1929), 2372p.

23. Lazzari, G., Proc. Intern. Congr. pure and appl. chem., 11, (1947), 177; Chem. Abs. 44, (1947), 6751e.

24. Sekine, T., J. Electrochem. Soc. Japan. 20, (1952), 390; Chem. Abs. 47, (1952), 2065d.

25. N.I. Alekseeva, YA. D. Zytner, and V.A. Nikol'skii, Chem. Abs. 74, (1971), 70866p; and Chem. Abs., 74, (1971), 70868r.

26. W. Davis, and H.J. Bruin, J. Inorg. Nucl. Chem., 26, (1964), 1069.

27. E.N. Mirolyubov, Zh. Prikl. Khim. 35, (1962), 132; Chem. Abs. 56, (1962), 12658g.

28. W.M. Latimer, Oxidation Potentials. Prentice-Hall, New York (1952).

29. Sihvonen, V., Ann. Acad. Sci. Fennincae, 24A, (16), (1925), 3; Chem. Abs. 20, (1925), 3270.

30. Purush Chalilpoyil and Fred C. Anson, Inorg. Chem, 17, (9), (1978), 2418.

31. I.M. Kolthoff and I. Hodara, J. Electroanal. Chem. 4, (1962), 369.

32. G.P. Haight, Jr., J. Inorg. Nucl. Chem., 24, (1963), 673.

33. Johnson and Robinson, Anal. Chem. 24, (2), (1952), 366.

34. I.M. Kolthoff, W.E. Harris and G. Matsuyama, J. Am. Chem. Soc. 66, (1944), 1782.

35. Paul Delahay and George L. Stiehl, J. Am. Chem. Soc. 74, (1952), 3500.

36. H. Whitney Wharton, J. Electroanal. Chem. 9, (1965), 134.

37. E. Park Guymon and Jack T. Spence, J. Phys. Chem., 70, (6), (1966), 1964.

38. R.D. Taylor and J.T. Spence, Inorg. Chem. 14, (11), (1975), 2815.

39. G.P. Haight, Jr. Patricia Mohiner and Alfred Katz. Acta. Chem. Scan., 16, (1962), 221.

40. I.M. Kolthoff and E.B. Sandell, "Quantitative Inorganic Analysis", Macmillan Co., (1959), 634.

41. G.W. Pucher and H.A. Day, J. Am. Chem. Soc., 48, (1426), 672.

42. P. Delahay, J.Am. Chem. Soc., 75, (1953), 1190.

43. Lecture notes for the course, "Advance Instrumental Methods in Electrode Kinetics". The Department of Chemistry, Southampton University.

44. P.C.H. Mitchell, Quarterly Reviews, Vol. XX. No. 1, (1966). 103.

45. J.W. Mellor "Comprehensive Treatise on Inorganic and Theoretical Chemistry" Vol. VIII, P. 582.

46. Ibid. p. 591.

47. M.J. Weaver and F.C. Anson, J. Electroanal. Chem. 65, (1975), 737.

48. K. Alias, W.R. Fawcett and R. Parsons, J. Chem. Soc. Faraday I, (1974), 1046.

49. P. Delahay, "Double Layer and Electrode Kinetics", Inter Science, New York, 1965.