A STUDY OF THE ELECTROCHEMICAL REDUCTION OF NITROBENZENE AND o-HALONITROBENZENES IN ACIDIC MEDIA

by

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ABSTRACT

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A STUDY OF THE ELECTROCHEMICAL REDUCTION OF NITROBENZENE AND o-HALONITROBENZENES IN ACIDIC MEDIA

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The electrochemical reduction of nitrobenzene and o-halonitrobenzenes has been studied in aqueous organic solvents containing sulphuric acid. The reaction products and their maximum rate of production depend upon the solvent, cathode metal, electrode potential, concentration of acid and the rate of stirring of the catholyte.

From studies in a glass batch reactor it was possible to find conditions (i.e. using 1:1 1-propanol/water, a copper cathode, a 3M sulphuric acid and rapid stirring at low electrode potentials) where the yield of p-aminophenol was over 75% at a current density of 150 $mA.cm^{-2}$.

Conditions for the complete $6e^-$ reduction to the corresponding anilines were also defined. The highest yield was obtained with a mercury electrode, 0.1M H_2SO_4, slow stirring and a higher negative electrode potential. With nitrobenzene, o-fluoronitrobenzene and the o-chlorocompound, the anilines were formed in yields exceeding 75% and current densities above 100 $mA.cm^{-2}$. With o-bromonitrobenzene the yield was lower because of competing cleavage of the C-Br bond.

The reactions were also investigated in a parallel plate reactor with recycled electrolyte flow and conditions closer to those in an industrial electrochemical cell. The study revealed that p-aminophenol could be produced with a 76% material yield and 5.7 Kwh Kg^{-1} energy consumption, and anilines at 95% material yield and 10 Kwh Kg^{-1} energy consumption. The results compare very favourably with other attempts to produce these compounds.

To

Keyla

Kira

Olga

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CONTENTS

CHAPTER II.- EXPERIMENTAL

CHAPTER I

CHAPTER I

INTRODUCTION

I.1.- General Organic Electrochemistry

The history of electrochemistry goes back to the eighteenth century when the fundamental principles were established (1). The first electrochemical investigations were those by A. Volta in 1796, who constructed the first primary battery used for the production of electricity. Associated with the other early investigations are names such as L. Galvani (studies on electrical nerve impulses, 1791), M. Faraday (the laws of electrolysis, 1834), J. W. Gibbs and W. H. Nernst (studies of the relationship between the chemical affinity of reactants and the cell potential, 1875 and 1889 respectively), and Sir W. Grove (designed a fuel cell, 1839). It was about 1950 when studies of electrode processes increased explosively, and this fact resulted in the development of electrochemistry as an interdisciplinary area in the search of solutions to a variety of different problems. Now, at the present stage in the development of electrochemistry, it covers an area as wide as that of chemistry itself, and sub-areas of specialization have become necessary. It is frequent now to talk about electroanalytical chemistry, electroorganic chemistry, electroinorganic chemistry, etc. It is now clear that electrochemistry has much to offer organic chemistry both from the viewpoint of synthesis and investigation of kinetics and reaction mechanism.

Electrosynthetic routes have several possible advantages. Among the most important are:

1. Energy can be introduced selectively into a molecule to produce specific reactions by controlling the electrode potential.

It is possible to supply by electrochemical means up to 3.5 eV (2) and within this range of energy, almost any electron transfer reaction is possible.

2. Reactions involving electrode processes are often cleaner than those using conventional redox reagents. The presence of unwanted and polluting compounds is avoided.

3. The reactive intermediates are generally similar to those postulated for homogeneous chemical reactions (table 1.1). It is often possible also to control their reactions to give a good yield of final products.

4. A great deal of scientific research nowadays is concerned with energy. There is a great need to look for new and cheaper sources of energy and for methods to change from one form to another. While it cannot be claimed that electroorganic processes are presently energy efficient, certainly electricity is an energy form which is likely to be around for a very long time.

On the other hand, there are some problems that presently prevent the widespread commercial exploitation of organic electrosynthesis (3), among these, it can be mentioned that:

1. We must recognise that organic-electrosynthetic processes are complex. Usually the overall electrode reaction is not simple electron transfer, but a sequence of electron transfers and coupled chemical processes. The organic intermediates (table 1.1) too frequently have competing reactions available to them. It is for this reason that electrochemists have often failed to produce the promised selectivity in organic products.

Table 1.1

Electrochemical Synthesis of Organic Compounds

1. Direct electron transfer to generate:

At anode:	At cathode:
Cation radicals	Anion radicals
Dications	Dianions
Carbonium ions	Carbanions
Radicals	Radicals

2. Indirect electrolyses

   a. to regenerate redox couples - metal ions (unusual valence state)

   - halogens

   b. to generate reactive inorganic species:

   $O_2^{\cdot -}$, $OH^{\cdot}$, $CO_2^{\cdot -}$, ClO_2, $NO_3^{\cdot}$, etc.

3. Generation of acid (at anode) or base (at cathode).

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2. The reaction variables in electrochemical processes are complex and still poorly understood. In addition to the usual variables considered in chemical processes, an understanding of the role of current density, electrode potential, nature of the electrode material, nature of the solvent-supporting electrolyte system, electric field at the electrode-solution interface, adsorption on the electrode, membrane or separator material and cell design are required.

3. Organic electrosynthetic processes have also suffered from a failure to develop the cell components and the technology essential for successful operation. Indeed, the reason has been essentially an economic one.

In electrolytic systems many variables must be controlled (table 1.2), but although this can be a disadvantage it also opens the opportunity of a better control over the process studied. For instance, by controlling the electrode potential, what may appear to be a single process can be split into several steps, with the chance to stop the process at one of these intermediate steps or even to alter the normal reaction course. In this way other products can be obtained and also mechanistic hypothesis can be confirmed. A good example of this principle is provided by the study of the electrochemical reduction of nitrobenzene, the subject of this work. The effects of the electrode material, adsorption phenomena and electrolytic medium are not yet completely understood, but it is clear that they affect the electrode processes (table 1.3) and a great amount of work

Table 1.2

Variables to consider in electrochemical reactions

Usual Variables	Electrochemical Variables
Concentrations of:	Electrode Potential
1. Solvent/supporting electrolyte	Electrode Material
2. Substrate	Current density
3. Other components	Electric field
Temperature	Adsorption
Pressure	Cell design
pH	1. Compartmented
Time	2. Membrane or porous separator
	3. Static or flow cell
	Solution conductivity

has been reported to this end. The cell design is also an important variable to consider, and we must keep in mind that each particular process has its own requirements of cell construction. The general requirements of electrode materials, electrolytic media and cell design are described in the works of Goodridge (4,5) and Fleischmann (6).

The progress made in the development of electroanalytical methods has vastly increased our ability to investigate reaction mechanisms and hence to improve synthetic procedures. An enormous number of papers on organic electrochemistry are now to be found in the literature, and extensive reviews have been published on both oxidation and reduction of organic molecules by electrochemical means (7-10). Several organic electrochemical processes are receiving active interest for commercial development and some other industrial processes are in current operation (table 1.4). Considerable interest has been shown in electrochemical routes to pharmaceutical compounds and fine chemicals, and a number of small scale processes are being used in several countries.

In summary it could be said that a great deal of opportunities are still available in electroorganic processing for the development of existent and entirely new reactions, many of these of possible industrial interest.

Table 1.3

Examples of the effect of the a) medium and b) electrode material on electroorganic processes

Compound	Electrode	Medium	Product	Ref.
a) Nitrobenzene	Zn	Aq. acid	Phenylhydroxylamine	3
	Zn	basic, C_2H_5OH	hydrazobenzene	4
b) Iodobenzene	PbO_2	H_2O, H_2SO_4	Hydroquinone	5
	Pt	H_2O, H_2SO_4	Quinone	5

Table 1.4

Some electroorganic processes

Starting material	Product	Oxid/Redn.	Status
Acrylonitrile	Adiponitrile	Redn.	Commercial
Ethylmagnesium chloride	Tetraethyllead	Oxid.	Commercial
Octanoic acid	Perfluoroderivative	Fluorination	Commercial

I.2.- Electroanalytical Techniques

Electroanalytical techniques can be used to determine mechanisms, to follow the progress of a reaction and for analysis. There are numerous electroanalytical techniques (11,12) for the elucidation of electrochemical reactions, and by increasing the mechanistic knowledge of electrochemistry we are also increasing the fund of basic organic mechanistic understanding. The versatility of these techniques allows an unambiguous identification of intermediates, their half lives, and hence the mechanism of the reaction. A short description of the electroanalytical techniques used in this study is given below.

Voltammetry.- Voltammetry is an electrochemical technique in which the electrode potential is swept with time through the region of interest and the I-E curve directly recorded. The electrode potential therefore varies linearly with time

$$E = E_i + \nu t$$

where E_i is the initial potential and ν is the sweep rate. If the electrode reaction is of the type

$$O + ne \rightleftharpoons R$$

and the electron transfer is sufficiently rapid, the Nernst equation may be used to calculate surface concentrations

$$E(t) = E_i - \nu t = E^o + \frac{RT}{nF} \ln \frac{C_o(o,t)}{C_R(o,t)}$$

which can be rewritten as

$$f(t) = \frac{C_o(o,t)}{C_R(o,t)} = \exp\left[\frac{nF}{RT}(E_i - \nu t - E^o)\right] = \theta e^{-Jt} = \theta S(t) \qquad (1)$$

where

$$S(t) = e^{-Jt} \;,\; J = \frac{nF}{RT}\nu \;,\; \theta = \exp\left(\frac{nF}{RT}(E_i - E^o)\right)$$

The equations describing diffusion in the boundary layer close to the electrode are

$$\frac{\partial C_o(x,t)}{\partial t} = D_o \frac{\partial^2 C_o(x,t)}{\partial x^2} \quad \text{and} \quad \frac{\partial C_R(x,t)}{\partial t} = D_R \frac{\partial^2 C_R(x,t)}{\partial x^2}$$

while it is also known that at the commencement of the experiment, $t = 0$

$C_o(x,o) = C_o^*$ and $C_R(x,o) = 0$ (R initially absent)

and some distance from the electrode, the solution will be unchanged by the electrode reaction i.e.

$$\lim_{x\to\infty} C_o(x,t) = C_o^* \qquad \lim_{x\to\infty} C_R(x,t) = 0$$

At the electrode surface the flux balance must also balance

$$D_o\left[\frac{\partial C_o(x,t)}{\partial x}\right]_{x=0} + D_R\left[\frac{\partial C_R(x,t)}{\partial x}\right]_{x=0} = 0$$

The application of the Laplace transform to the diffusion equations and boundary conditions, the combination with the equation of flux at the electrode, and further inversion yields (12)

$$C_o(o,t) = C_o^* - (\pi D_o)^{\frac{1}{2}} \int_o^t f(\tau)(t-\tau)^{-\frac{1}{2}} d\tau \;,\; \text{with } f(\tau) = \frac{i(\tau)}{nFA}$$

$$C_R(o,t) = (\pi D_R)^{-\frac{1}{2}} \int_o^t f(\tau)(t-\tau)^{-\frac{1}{2}} d\tau$$

from these equations and the boundary condition (eq.1) we obtain

$$i = nF\ A\ Co^{*}\ (\pi\, Do\ J)^{\frac{1}{2}} X\ (Jt)$$

the function X(Jt) has been tabulated, and it reaches a maximum $\pi^{\frac{1}{2}} X_p(Jt) = 0.446$ at $n(E_p - E_{\frac{1}{2}}) = -28.5$ mV (for 26°). The peak current is then given by

$$i_p = 2.7 \times 10^5\ n^{3/2} A\ Do^{\frac{1}{2}}\ \mathcal{V}^{\frac{1}{2}}\ Co^{*}$$

and

$$E_p - E_{\frac{1}{2}} = E_p - E^{o} + \frac{RT}{nF} \operatorname{Ln} \left(\frac{Do}{D_R}\right)^{\frac{1}{2}} = -1.11 \left(\frac{RT}{nF}\right) = -28.5/n \text{ mV (at } 25^{o}\text{C)}$$

and $$\left| E_p - E_{p/2} \right| = 2.2\ \frac{RT}{nF} = 56.6/n \text{ mV (at } 25^{o}\text{C)}.$$

For a totally irreversible reaction:

$$O + ne \longrightarrow R$$

the Nernstian boundary condition is replaced by

$$\frac{i}{nFA} = Do \left(\frac{\partial Co(x,t)}{\partial x}\right)_{x=o} = K_f(t)\ Co(o,t)$$

where $K_f(t)$ is the rate constant for electron transfer and it is potential dependent, i.e.

$$K_f(t) = K^{o} \exp \left\{ -\alpha n_a \frac{F}{RT} \left[E(t) - E^{o} \right] \right\}$$

where α is the transfer coefficient and n_a the number of electrons transferred during and before the rate determining step.

Following a similar procedure to that above

$$i = nFACo^{*}Do^{\frac{1}{2}} \mathcal{V}^{\frac{1}{2}} \left(\frac{\alpha n a F}{RT}\right)^{\frac{1}{2}} \pi^{\frac{1}{2}} X(bt)$$

the function $\pi^{\frac{1}{2}} X(bt)$ goes through a maximum at $\pi^{\frac{1}{2}} X(bt) = 0.496$.

The peak current is then

$$i_p = 3.10^5 \, n \, (\alpha n_a)^{\frac{1}{2}} \, A \, Co^* \, Do^{\frac{1}{2}} \nu^{\frac{1}{2}}$$

this value occurs when

$$\alpha n_a \, (E_p - E^o) + \frac{RT}{F} \, Ln\left(\frac{(\pi Do \; b)^{\frac{1}{2}}}{K^o}\right) = -5.34 \text{ mV}$$

or

$$E_p - E_{p/2} = \frac{1.857 \; RT}{\alpha n_a F} = \frac{47.7}{\alpha n_a} \text{ mV at } 25^oC$$

It may be noted that:

1) If the rate of change of the potential is low enough, the result (I-E response) is effectively a steady state experiment (similar to that using a point by point technique), leading to a characteristic smooth S-shape I-E response. A rapid change in potential introduces non-steady state diffusion, and consequently the I-E curve shows a marked current peak.

2) If the electrode reaction is of the type $O + ne \rightleftharpoons R$ and Nernstian equilibrium is maintained at the electrode surface (reversible case), the peak current is given by $I_p = 2.7 \times 10^5 n^{3/2} D_o^{\frac{1}{2}} C_o^{\infty} \nu^{\frac{1}{2}}$. The peak potential is independent of the sweep rate, and it is related to the polarographic halfwave potential by $E_p = E_{\frac{1}{2}} - \frac{0.029}{n}$ volts. The cathodic and anodic peaks are not coincident, but separated by $\frac{0.059}{n}$ volts.

3) If the reaction is sufficiently slow that the rate determining step is charge transfer (irreversible case), the peak current is now given by $I_p = 3 \times 10^5 n (\alpha n_a)^{\frac{1}{2}} D_o^{\frac{1}{2}} C_o^{\infty} \nu^{\frac{1}{2}}$ and the peak potential varies with the sweep rate as

$$E_p = E^o - \frac{RT}{\alpha n_a F}\left(0.78 + \mathrm{Ln}\ \frac{Do^{\frac{1}{2}}}{K^o} + \mathrm{Ln}\left(\frac{\alpha n_a F \nu}{RT}\right)^{\frac{1}{2}} \right)$$

$$\left| E_p - E_{p/2} \right| = \frac{47.7}{\alpha n_a} \text{ mV at } 25^oC$$

The peak separation exceeds $0.059/n$ Volts and the separation increases as ν increases.

Mechanistic hypotheses can be made from the simple observation of the voltammogram (13) (i.e. the number of peaks, their relative positions, the appearance and disappearance of peaks with potential limits and potential scan rate, differences in the voltammogram between the first and nth sweep, etc.), and these can be confirmed using the quantitative information available from this and other techniques. The mechanism must also be compatible with the identified reaction products. The behaviour of a system can be studied over a wide potential range, intermediates can be directly observed and possibly be identified by the potentials at which they oxidise or reduce, and even the participation of preceding or following chemical reactions can be detected by altering the sweep rate to compete with the rate of the chemical reaction by varying the potential sweep range.

A great deal of work has been done by Nicholson and Shain (14,15) on the theoretical development and the practical utilization of the results obtained by using this technique. The quantitative way in which a number of characteristics (I_p^a/I_p^c, $I/\nu^{\frac{1}{2}}$, $\Delta E_{p/2}/\Delta \log \nu$,etc.) of the cyclic voltammogram should depend on scan rate for a given electrode mechanism, was demonstrated. The effects of coupled chemical reactions on the shapes of voltammograms, and methods of obtaining the rate constants for the chemical reactions from cyclic voltammetric data were also described.

Rotating Disc Electrode (R.D.E.).- The rotating disc electrode is an example of a convective diffusion system (16,17) where a complete hydrodynamic solution has been obtained (18). The basic differential equation for convective diffusion to a rotating disc electrode in its reduced form for the steady state (12) is

$$\frac{\partial Co}{\partial t} = D_o \frac{\partial^2 Co}{\partial Z^2} - V_Z \frac{\partial Co}{\partial Z} = 0$$

or

$$V_Z \frac{\partial Co}{\partial Z} = D_o \frac{\partial^2 Co}{\partial Z^2}$$

and substituting V_Z for the value obtained by Karman and Cochran (18).

$$V_Z = -0.51\, W^{3/2}\, V^{-\frac{1}{2}}\, Z^2$$

where W is the rotation rate in rad.s^{-1} and V is the kinematic viscosity, yields

$$-0.51\, W^{3/2}\, V^{-\frac{1}{2}}\, Z^2 \frac{\partial Co}{\partial Z} = D_o \frac{\partial^2 Co}{\partial Z^2}$$

$$\frac{\partial^2 Co}{\partial Z^2} = -\frac{Z^2}{B}\frac{\partial Co}{\partial Z} \qquad B = D_o\, W^{-3/2}\, V^{\frac{1}{2}}/0.51$$

by integration we obtain

$$Co^* = \left(\frac{\partial Co}{\partial Z}\right)_{Z=0} 0.89 \left(\frac{3D_oW^{-3/2}V^{\frac{1}{2}}}{0.51}\right)^{\frac{1}{3}}$$

the current, is related to the flux at the electrode surface, so

$$i = nFA\, D_o \left(\frac{\partial Co}{\partial Z}\right)_{Z=0}$$

where, under the limiting current conditions

$$i_L = i_{Levich} = 0.62\, n\, F\, A\, D_o^{\frac{2}{3}} W^{\frac{1}{2}} V^{-1/6}\, Co^*$$

for non-limiting current conditions, a change in the integration limits is required and

$$C_o^* - C_o(Z=0) = \left(\frac{\partial C_o}{\partial Z}\right)_{Z=0} \int_0^\infty \exp\left(\frac{-Z^3}{3B}\right) dZ$$ is obtained (12).

From this equation and the flux at the electrode surface, we obtain

$$i = 0.62\ nFAD_o^{\frac{2}{3}}W^{\frac{1}{2}}V^{-1/6}\left(C_o^* - C_o\ (Z=0)\right)$$

or $$i = i_{L,a}\ \frac{C_o^* - C_o(Z=0)}{C_o^*}$$

the equivalent expressions for the reduced form (O + ne = R) are

$$i = i_{L,c}\ \frac{C_R^* - C_r(Z=0)}{C_R^*}$$

$$i_{L,c} = -0.62\ nFA\ D_R^{\frac{2}{3}}W^{\frac{1}{2}}V^{-1/6}C_R^*$$

For a totally irreversible reaction, the disc current is

$$i = nFA\ K_f(E)C_o(Z=0)$$

where $K_f(E) = K^o\exp\left(-\alpha N_a F(E-E^o)/RT\right)$

and it can be expressed

$$i = nFAK_f(E)C_o^*\left(1 - \frac{i}{i_{L,a}}\right)$$

The general i-E equation (for a quasi-reversible reaction) can be derived in a similar manner, and the final expression for i is

$$1/i = \frac{1}{nFA(K_fC_o^* - K_bC_R^*)}\left(1 + \frac{D_o^{-\frac{2}{3}}K_f + D_R^{-\frac{2}{3}}K_b}{0.62\ V^{-1/6}W^{\frac{1}{2}}}\right)$$

If the reverse reaction can be ignored, then

$$i = \frac{nFAK_fC_o^*}{1+K_f/0.62\ V^{-1/6}D_o^{\frac{2}{3}}W^{\frac{1}{2}}}$$

Again, the following conclusions may be drawn from these equations:

1) For large K_f (i.e. large overpotentials) the electrode process is mass transfer controlled and the relation $I = 0.621\ nF\ D_o^{\frac{2}{3}}\ V^{-1/6} C_o^{\infty}\ W^{\frac{1}{2}}$ is valid and a plot of I vs $W^{\frac{1}{2}}$ should be linear. In this case no kinetic data may be obtained.

2) For small values of K_f (i.e. when working at low overpotentials) the electron transfer is slow compared with mass transfer and $I = nF\ K\ C_o^{\infty}$. In this case the current does not depend on the rotation rate of the disc, and it can be used directly to calculate kinetic data.

3) For intermediate values of K_f the full equation must be used, and a plot of 1/I vs $1/W^{\frac{1}{2}}$ will be linear and the value of K_f may be obtained from the intercept.

4) For the electrode reactions where the reverse reaction must be considered $O + ne \underset{K_b}{\overset{K_f}{\rightleftharpoons}} R$ the 1/I vs $1/W^{\frac{1}{2}}$ plot is still linear and both K_f and K_b can be obtained from the slope and intercept.

The rotating disc electrode is also a useful tool for the qualitative investigation of electrode reactions. Simple diffusion controlled processes result in the function $I/W^{\frac{1}{2}}$ being independent of W but this is not always the case when chemical reactions are involved in the overall process (19).

<u>Coulometry</u>.- In controlled potential coulometry, the substance of interest is electrolyzed at a working electrode the potential of which is maintained constant during the electrolysis by means of a potentiostat.

Consider the electrolysis of the species O initially present in bulk solution at a concentration C_o^*, at a potential E corresponding to the limiting current region. The current at any time is given by

$$i_1(t) = n\ F\ A\ M_o C_o^*(t)$$

where M_o is the mass-transport parameter for the reactant species, and depends on the reactant diffusion coefficient, solution viscosity, and the mass transport regime. The current also indicates the total rate of consumption of O, due to electrolysis

$$i_1(t) = -nF \frac{dN_o(t)}{dt}$$

where N_o is the total number of moles of O in the system.

$$C_o^*(t) = \frac{N_o(t)}{V} \qquad V = \text{solution volume}$$

then $$i_1(t) = -nFV \frac{dC_o^*(t)}{dt}$$

and $$nFA\ M_o\ C_o^*(t) = -nFV \frac{dC_o^*(t)}{dt}$$

$$\frac{dC_o^*(t)}{dt} = -\frac{M_o A}{V} C_o^*(t) = -PC_o^*(t) \qquad P = \frac{M_o A}{V}$$

with the initial condition $C_o^*(t) = C_o^*(0)$ at $t = 0$, the solution of this ordinary differential equation is

$$C_o^*(t) = C_o^*(o) \exp(-Pt)$$

and

$$i_1(t) = nFA\ M_o C_o^*(o) \exp(-Pt)$$

$$i_1(t) = i(o) \exp(-Pt)$$

The total quantity of electricity Q(t) consumed in the electrolysis is given by the area under the i-t curve

$$Q(t) = \int_0^t i(t)dt$$

and the weight of substance electrolysed is related to the quantity of electricity consumed and the initial concentration of the electroactive speciesby the Faraday's Law.

$$W = \frac{W_{eq}}{F} \int_0^t i(t)dt$$

from which W_{eq} is the equivalent weight of the substance electrolysed.

The conclusions are:

1) Rapid electrolyses are achieved by maximising the stirring rate and the ratio A/V, these are two of the principal objectives in the design of cells for controlled-potential coulometry.

2) n, the number of electrons transferred in the overall electrode reaction can be determined.

3) The final products of the electrode reaction can then be identified bythe usual techniques of inorganic and organic chemistry.

More theoretical and experimental aspects of the technique are described in the works of Bard and Meites (20-23), Harrison and Thirsk (24) and J. E. Harrar (25).

In this work, the n-value was determined by slightly improved technique. During the experiment, the current was monitored as a function of charge passed and n was calculated by extrapolating I-Q plot to I = 0 and using Faraday's Law on the intercept. For a simple reaction the I-Q plot is linear.

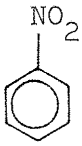
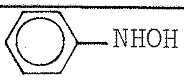
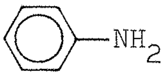
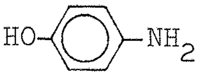
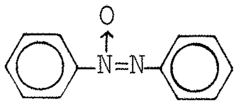
I.3.- Electrochemical reduction of Nitrobenzene and halonitrobenzenes

The literature contains many papers, some dating back to the last century, which describe the reduction of nitrobenzene and its derivatives in both aqueous and nonaqueous solutions (7-10, 26-63). It is clear that many products may be formed and, indeed, under all but the most carefully controlled conditions, the reduction yields a complex mixture of products. Relatively few papers fully characterise products and where this has been done it has been shown that products and mechanisms concluded from I-E curves alone are not reliable. Furthermore the literature would suggest that the products are dependent on solvent (27,28), pH (27,29-31), potential (32), cathode material (33,34), the presence of trace oxygen (28), etc., and many of these factors are not taken into account when mechanisms have been proposed.

The reduction of nitrobenzene at mercury in the pH range 4-6 requires four electrons to produce phenylhydroxylamine (29). Below a pH value of 4 and by using a high overvoltage cathode, phenylhydroxylamine is further reduced to aniline (27,30); this reduction occurs at more negative potential than that which produces phenylhydroxylamine. The reduction of nitrobenzene under basic or neutral conditions gives azoxybenzene (31) which can be reduced irreversibly to give azobenzene (36,37). Other products have been reported in this reaction (p-aminophenol, hydrazobenzene, benzidine) which made this a quite complex reaction ((37) and Table 1.5.).

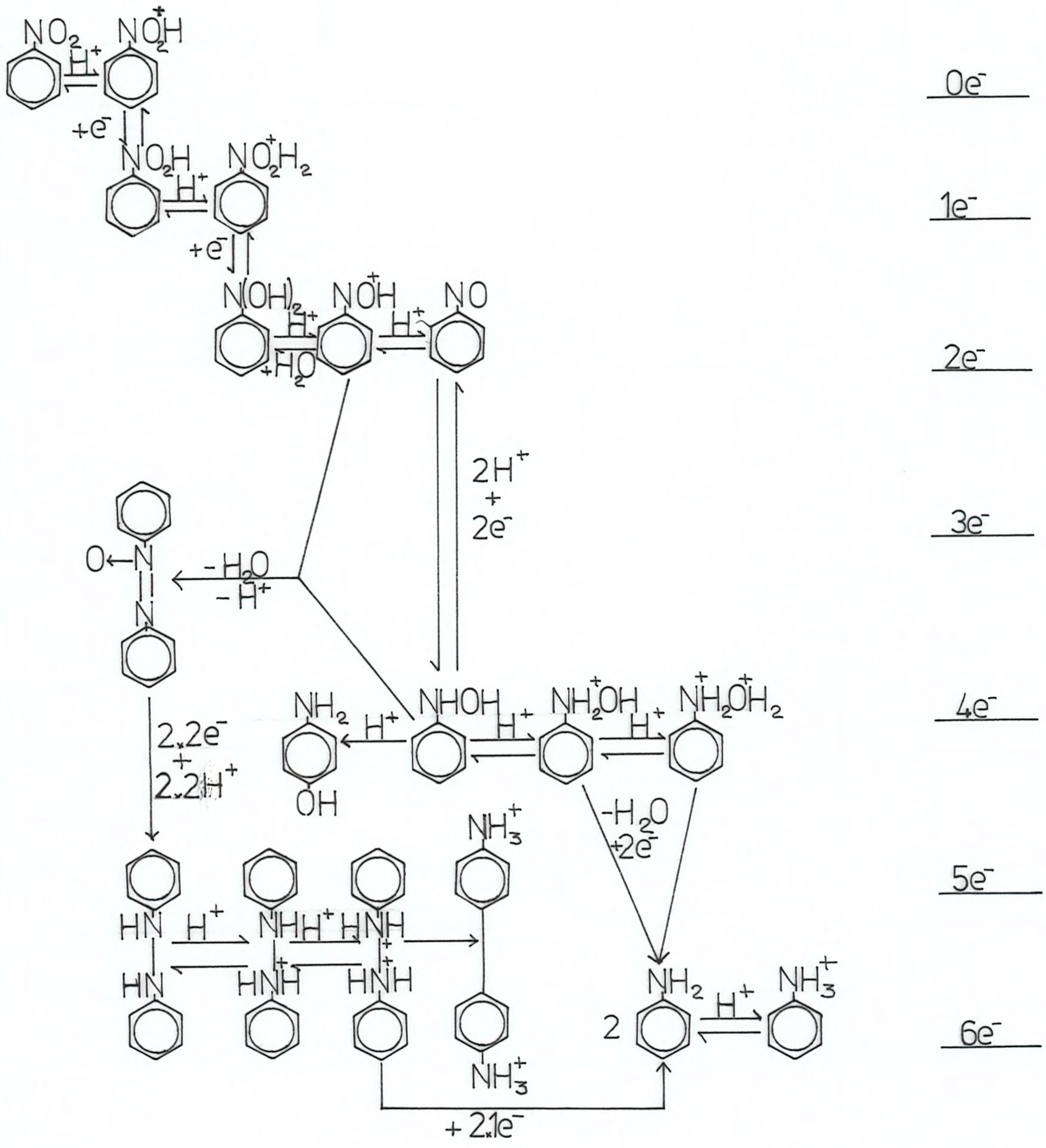
The mechanism of nitrobenzene reduction in acidic media has been extensively studied (26-52) and a general reaction scheme has

Table 1.5

Reagent	Cathode	Reaction medium	Products	Yield %	Ref.
	Zn	aq. acid		29	38
	Pt	10% HCl		90	39
	Monel	aq. acid		72	40
	Ni	aq. C_2H_5OH NaOAc. reflux		95	41
	Monel Zn,Sn	Basic C_2H_5OH		90	38
	Phosphor Bronze	Salt of Org. Acid H_2O		95	42

been proposed on the basis of polarographic studies by Heyrovsky and Vavricka (43,44, scheme below). A possible reaction product under these conditions is p-aminophenol, important from an industrial point of view (photographic applications, car industry, pharmaceutical interest, etc.), and good results in its synthesis have been obtained by electrolytic reduction of nitrobenzene using simple electrodes such as graphite, copper and nickel (45,46). It was found that agitation of either the electrode or the electrolytic medium and elevation of the temperature of the system increased production efficiencies and the use of redox compounds provided further improvement (29). It was also found that control of the electrode potential improves the electrolytic process (32). In effect, Wilson and Udupa (34) made studies of the influence of various factors on the material yield of the aminophenol, from the electrochemical reduction of nitrocompounds. They found the most significant efficiency increase in a well agitated medium attained by high speed rotation of a disc cathode, at a high temperature and high acid strength. They attributed the increase in the yield of aminophenol to the relative rates of two reactions, the further reduction of the hydroxylamine, or the rearrangement to aminophenol. The reduction occurs only at the cathode surface and hence strong convection permits the 4e product to be transported away from the electrode before further reduction can occur. Rearrangement occurs in the solution and is acid catalysed, and an increase in the temperature does facilitate the rearrangement over the further reduction of the hydroxylamine. Under conditions of 20% acid, a rotating amalgamated monel cathode, 90°C and

General reaction scheme for the electrochemical reduction of nitrobenzene based on that proposed by Heyrovský and Vavřička.



2.7 A/dm^2 the yield of aminophenols ranged between 72 and 82% material yield for the different nitrocompounds studied. Rance and Coulson (32) emphasise the importance of control of the electrode potential in the efficiency of the preparation, and also described in a quantitative way the effects of the addition of redox compounds to the catholyte and of elevating the temperature. They concluded that the rate and the products of the electrolytic reduction of nitrobenzene depends on the cathode potential, and that with improved control of potential, the reaction to aniline can be restricted and the phenylhydroxylamine formed would rearrange to p-aminophenol. Furthermore, with the addition of a redox compound, the oxidised species is reduced at the cathode and then acts as a reducing agent for nitrobenzene in the bulk of the solution, improving the efficiency of production of p-aminophenol. In their system, the most efficient conditions for the production of p-aminophenol were -0.15V, 85°C, with the addition of stannous ions to the catholyte; under these conditions, p-aminophenol was produced at a rate of 0.306 g/cm^{2}h^{-1}. Jayaraman, Udupa and Udupa (33) tried various addition agents like Sn^{+2}, Bi^{+3}, Tl^{+}, at electrodes of monel, brass and copper, in 10-30% acid and 15-35 A/dm^2. The best conditions for the aminophenol production were the reduction of 20% w/v nitrobenzene in 20% sulphuric acid, on bismuth-deposited copper cathode, at 90-95°C and 20-25 A/dm^2; under these conditions, the material yield of the aminophenol was 75%.

Because the chemical methods of manufacture of p-aminophenol are expensive and it is difficult to obtain a really pure product, the electrochemical method for aminophenols looks interesting and several attempts at its synthesis in large scale can be found in the literature (47-50). The main limitation appears in the requirement of high efficiency at a high rate of aminophenol preparation, i.e. current density. In general, the development of industrial electroorganic processes require cells of high capacity (high space-time yield) which can be achieved (i) by the use of high ratios of electrode area to cell volume, (ii) by increasing the mass transfer rate (by flowing the electrolyte or by the rotation of the working electrode) when the process is limited by mass transfer rate of the substrate. Considerably important in this area are the studies of H. Udupa (47) in the design and operation of a high amperage cell with a rotating electrode for electroorganic preparations, including the p-aminophenol synthesis, and that of Goodridge and Hamilton (48) in their use of a fixed bed porous flow-through electrode during the production of p-aminophenol. In both cases improvements in efficiency and cell capacity are reported. In Chapters 3 and 5 of this thesis the study of an optimization of p-aminophenol yield and the design and operation of a flow system is described.

The electrochemical reduction of the nitrobenzene derivatives has also been widely studied, and numerous reviews can be found in the literature (7-10). Studies in nonaqueous media by ESR coupled with electrochemical generation of radicals allowed the identification of radical ion intermediates in the electrochemical reduction of nitrobenzene and its derivatives (53,54). In general, it has been observed that the reduction of substituted aromatic nitrocompounds leads to the corresponding substituted anion radicals (55,56). With certain halonitrobenzenes elimination of halogen occurs during the electrolytic reduction (57,58). Thus the isomeric chloronitrobenzenes all yield the expected chloronitroanion radical upon reduction in dimethylformamide. With the ortho-bromo and all three iodo-nitrobenzenes the halogen atom is ejected and one identifies the nitrobenzene anion radical. These eliminations are solvent dependent (59) and by using mixtures of water-dimethylformamide, the halogen can be partially or fully retained. The studies made by Kitagawa, Layloff and Adams (57), and those of Fujinaga, Deguchi and Umemoto (58) allowed the establishment of an order for the dehalogenation of halonitrobenzenes during the electrolytic reduction

p,m-Cl, m-Br < O-Cl < p-Br < O-Br, p,m,o-I

Their results are consistent with the known ease of cleavage of carbon-halogen and the steric effects of bulky ortho groups.

The products of the electrochemical reduction of the halonitrobenzenes are dependent upon the halogen substituent (57,58), electrolyte (57), solvent (59), and the applied potentials (58), and while some studies (57,58,60) report the carbon-halogen bond cleavage to be an overall three electron process, Lawless and Hawley (61) have found an n value of two from chronoamperometric experiments for the electrochemical reduction of several halonitrobenzenes in different solvents (dimethylformamide, acetonitrile and dimethylsulfoxide). They found also that the stabilities of the anion radicals in the three solvent systems decrease in the order DMSO > AN > DMF and the order of the decomposition of the anion radicals in all the three solvents to be o-iodo > o-bromo >> p-iodo > m-iodo nitrobenzene. Nelson, Carpenter and Seo (62) made studies of these compounds in nonaqueous media using various electrochemical and spectroscopic methods and their results agree with those of Lawless and Hawley. The rate constants for the intermediate decomposition reaction were measured by chronoamperometric methods using digital simulation working curves, and the order they followed in terms of isomers was

$$K_m < K_p < K_o$$

and in terms of the halosubstituent,

$$K_F < K_{Cl} < K_{Br} < K_I.$$

In aqueous media, the reduction of the nitro group present in these compounds is facilitated, the anion radicals will tend to protonate before halide ion expulsion can occur, and according with the reaction conditions, a compromise will exist between these two possible routes, the carbon-halogen rupture or the nitro group reduction.

Of particular interest in this work was the synthesis of o-fluoroaniline, an intermediate for an aspirin replacement drug. It is necessary to reduce the nitrogroup without any cleavage of the C-F bond because the compound resulting from further reaction of aniline is a poison. Catalytic reduction always leads to the cleavage of the C-F bond to the extent of a few % and this means that metal/acid reduction has to be used; this is environmentally undesirable. Hence it seemed an appropriate reaction for electrochemical reduction. The objective of chapter 4 was to seek conditions for the complete $6e^-$ reduction of the halonitrobenzenes to the corresponding anilines.

I.4.- The Scope of this work

This work is concerned with the investigation of the electrochemical reduction of nitrobenzene and the o-halonitrobenzenes in acidic media. It is known that the reduction of these compounds is a potential route to a wide variety of species of possible commercial interest (scheme below). Furthermore, more mechanistic information is required for a complete understanding of the process. Hence the present study was undertaken and its aims were:

1) To study the variation of products as a function of several electrolysis parameters and to optimise the yields of desired products.

2) To investigate reaction mechanisms under the conditions of the preparative electrolysis.

3) To carry out the reactions in a range of cells with different mass transport regimes and electrode geometries.

The investigation carried out falls into three headings.

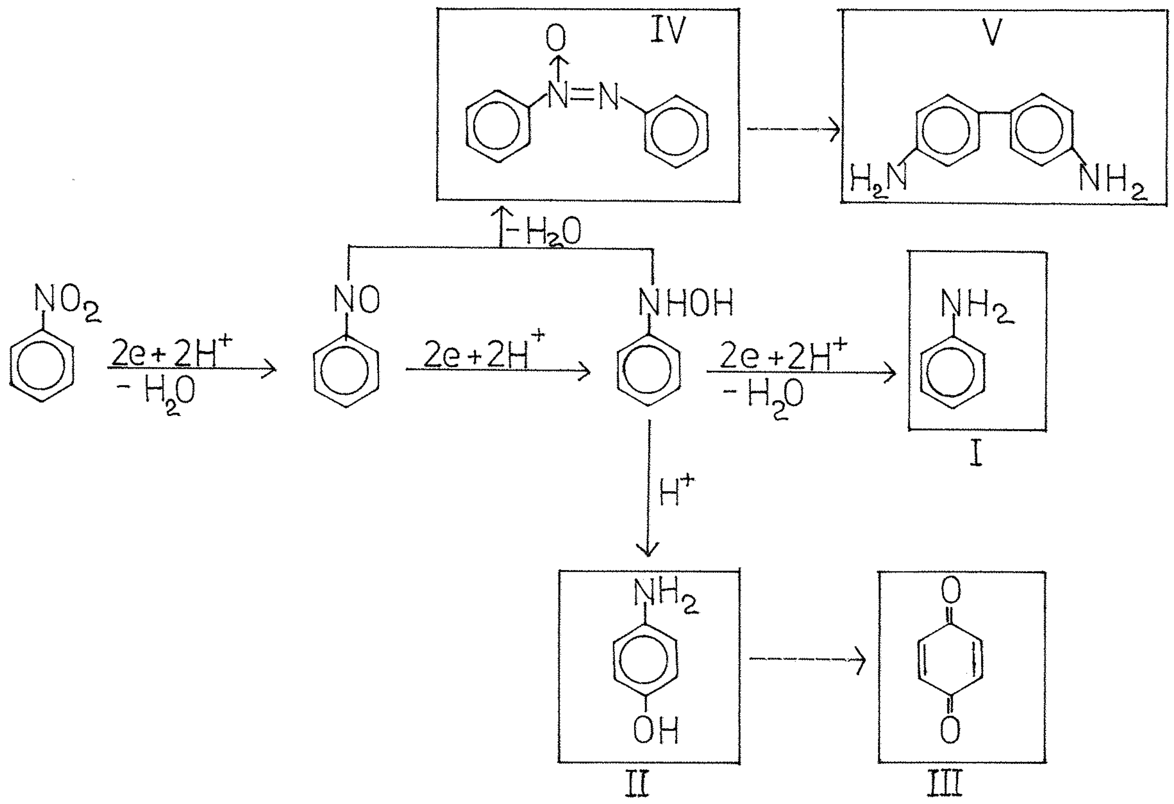
a) The electrochemical reduction of nitrobenzene to p-aminophenol.

b) The electrochemical reduction of o-halonitrobenzenes.

c) Preliminary scale-up of these reactions in a parallel plate cell.

In the first investigation, electroanalytical techniques have been used to investigate the mechanism of the reduction of nitrobenzene. The conditions were chosen so that the major product was likely to be p-aminophenol. As a continuation of this study, the conditions were optimised.

Products of interest derived from the Nitrobenzene reduction



I, aniline. II, p-aminophenol. III, benzoquinone. IV, azoxybenzene. V, benzidine.

It was the intention of the work with o-halonitrobenzenes to carry out the complete $6e^-$ reduction to the corresponding anilines. The fluoroderivative was of particular interest. Again electroanalytical and product analysis has been used to optimise the conditions.

In the initial scale-up, a parallel plate reactor with an ion exchange membrane and a flowing electrolyte was employed. These conditions reflect more closely those to be expected in an industrial scale electrolyser.

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CHAPTER II

CHAPTER II

EXPERIMENTAL

II.1. - General

A fifty-fifty mixture of distilled water-organic solvent was used as the medium for all experiments. The low pH solutions were prepared with sulphuric acid and sodium sulphate was used, where necessary, to make the higher pH solutions conducting. In a few experiments, the electrolyte was ammonium chloride. All the solutions were deoxygenated with nitrogen (BOC Ltd. OFN) in the electrochemical cells for, at least, 15 min. Except where otherwise stated, the experiments were performed at room temperature. The geometrical area of the electrodes was used for the calculation of current densities.

II.2. - Cells and Electrodes

Cells. - Several different designs of cell were used in the experiments. Except for voltammetric measurements and polarization curves at mercury, the working electrode was separated from the secondary electrode by means of a sintered disc or a membrane. For the measurement of the polarization curves of nitrobenzene and o-halonitrobenzenes at mercury, a conventional type of three electrode, two-compartment cell was found suitable (fig.2.1). The working electrode was in the form of a sphere formed on the end of a capillary fed from a micrometer operated syringe. Using this arrangement the electrode could be rapidly changed and its area controlled. For experiments with copper and lead, a three electrode, three compartment cell, volume 20 cm^3, was used (fig.2.2). The

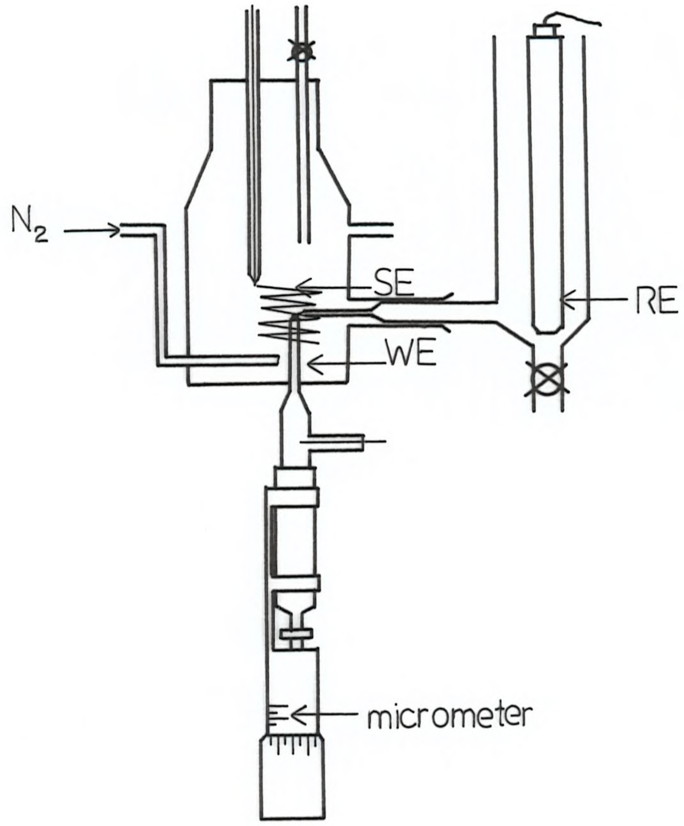

Fig 2.1

Three electrode two compartment cell used for electroanalytical experiments on mercury.
WE compartment volume 40 cm³

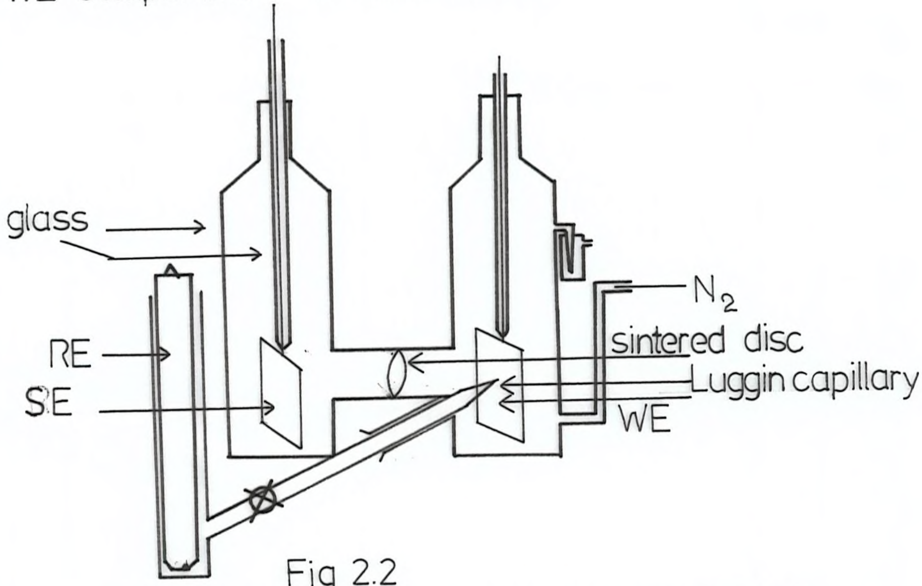

Fig 2.2

Three electrode three compartment cell used for steady state experiments and some coulometry and product studies on copper and lead.
WE compartment volume 20 cm³

working electrode was copper or lead wire and the secondary electrode was a platinum gauze electrode. The reference electrode was a Radiometer type K401 saturated calomel electrode in a compartment separated from the working electrode by a Luggin capillary.

For cyclic voltammetry on copper, the cell shown in fig.2.3 was used. It incorporates a copper wire at the centre of a long helical platinum secondary electrode making a proper symmetrical cell geometry. This cell was also used for experiments with a rotating disc electrode with little modification. The cell shown in fig.2.1 was also used for voltammetric measurements on mercury.

Coulometry measurements and product studies were performed with the cell shown in fig.2.4. It gives a high ratio of electrode surface to solution volume as required for these experiments. When using a flow system, the cell shown in fig.2.5 was used, in this case the cell was designed considering the exigences of an uniform flow distribution of the electrolytic medium and potential on the cathode (1,2). The anodic compartment was separated from the cathodic compartment by means of a Nafion cation membrane. The cells were cleaned, firstly, by using detergent and then chromic acid solution in order to remove grease and oxidisable compounds (3). After that a 1:3 mixture of nitric acid and hydrochloric acid was used, and finally, distilled water and acetone.

Electrodes. - In order to get the polarization curves on mercury, the working electrode was in the form of a sitting mercury drop, which could be rapidly changed and made reproducible in area with the help of the micrometer screw gauge (see fig.2.1). For larger scale electrolysis,

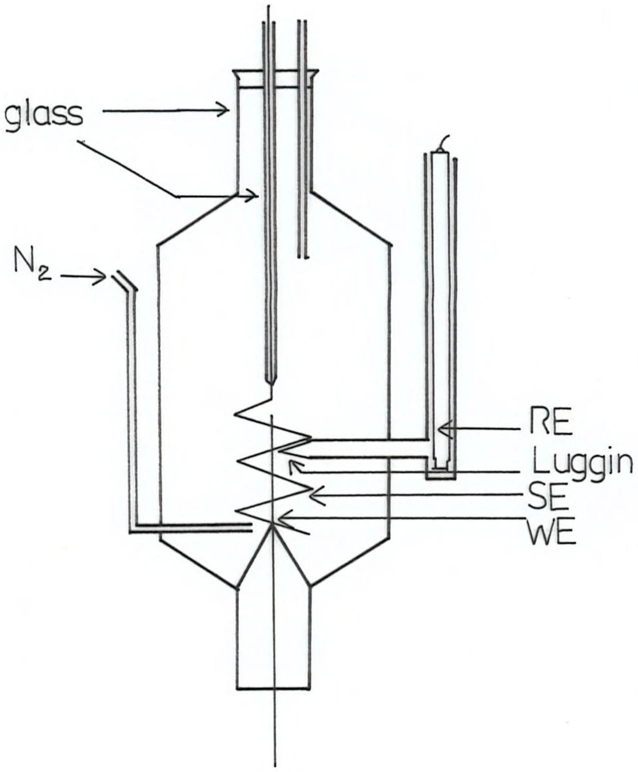

Fig 2.3
Cell used for voltammetric measurements with wire electrodes. WE compartment 20 cm^3.

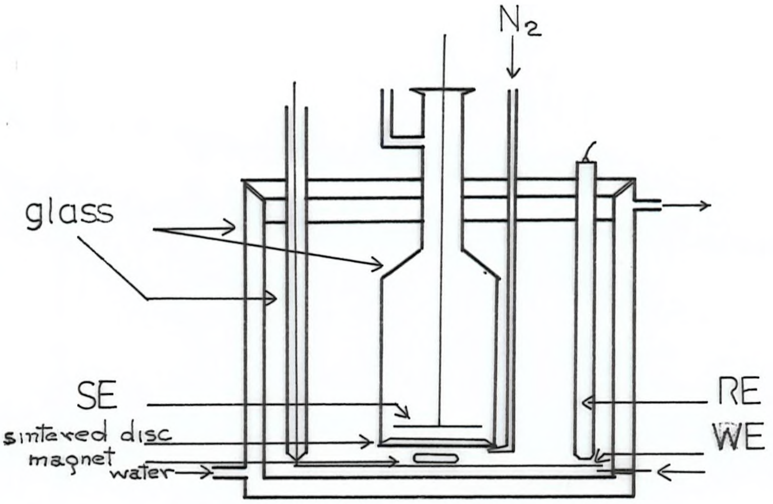

Fig 2.4
Cell used for coulometry at a mercury cathode. For some experiments the mercury pool was replaced by a Cu gauze or a Pb or Zn sheet.
WE compartment 100 cm^3.

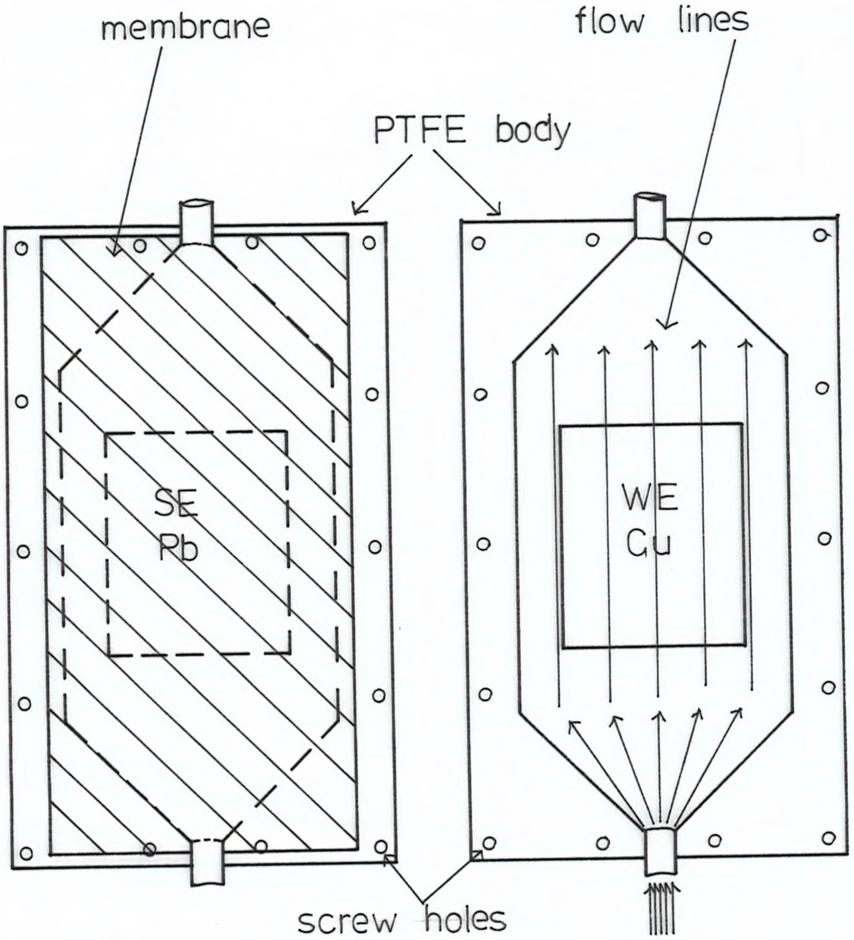

Fig 2.5
Two electrode two compartment cell used for electrolysis in a flow system.
Electrode area 70 cm^2.

the working electrode was a pool of mercury with an external contact through a platinum wire. Mercury was chemically purified and triply distilled under reduced pressure before use.

Copper and lead wires were used in steady state and voltammetric measurements. For electrolyses, a gauze copper electrode and circular sheet lead, copper and zinc electrodes were used as working electrodes; these electrodes were prepared by making a copper wire - metal join with tin and insulating the copper wire from the solution by glass and epoxy resin (fig.2.6). Emery polishing papers (5/0 and 3/0) and nitric acid or aqua regia were used to clean these electrodes. The copper rotating electrode (prepared in the workshop) was a disc of copper, area 1 cm^2, fixed into a PTFE cylinder. For cleaning, it was polished with emery paper and then 1 micron and 0.05 micron polishing alumina. Platinum was used as a secondary electrode throughout this work and the area was chosen to ensure that the reaction at secondary electrode does not limit the current. The potential of the working electrode was, in all cases, controlled with respect to a SCE and was placed in a compartment separated from the working electrode compartment by a Luggin capillary.

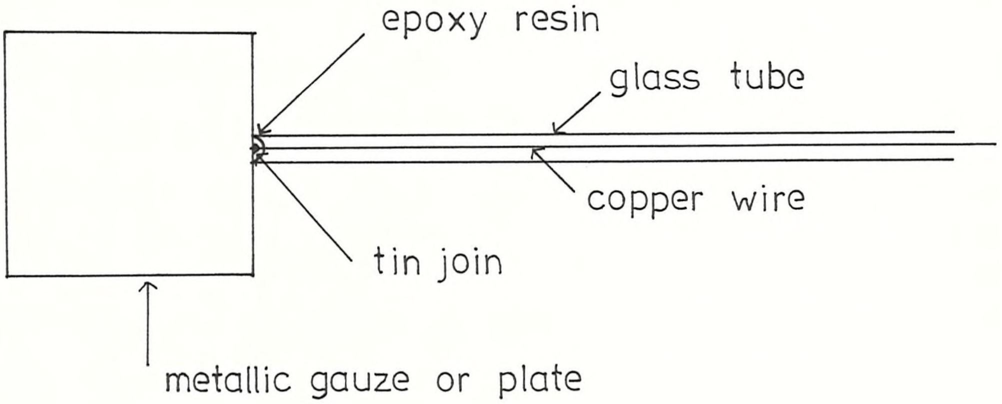

Fig.2.6
Electrode Preparation

II.3. - Chemicals and Instrumentation

Chemicals.- 1:1 mixtures of distilled water/organic solvent were used as the media for all experiments. The organic solvents used were of high purity from BDH Ltd. Nitrobenzene, aniline, p-aminophenol, azobenzene, azoxybenzene and o-chloroaniline used for electrolysis and analysis were all BDH laboratory reagents. The 1,2-diphenylhydrazine, the o-halonitrobenzenes (except o-F-$C_6H_5NO_2$) and the o-haloanilines (except o-Cl-$C_6H_5NH_2$) were Aldrich reagents. Orthofluoronitrobenzene of high purity was from Fluorochem Ltd. Sulphuric acid was Hopkin and Williams LTD GPR grade. Sodium sulphate and ammonium chloride (GPR grade) were added to some solutions. The diethylether (used for the extractions) and sodium hydrocarbonate (used for neutralization) were Koch-Light Laboratories for Lab. use. All the chemicals were used directly, without any pretreatment.

Instrumentation.- The early electrochemical experiments were carried out using a modified Chemical Electronics valve potentiostat and a HI-TEK Type DT2101 was used in later experiments. For voltammetric measurements a Chemical Electronics waveform generator type RB1, a Hewlett-Packard 7015 X-Y recorder and a Hewlett-Packard 1201-A oscilloscope were used. For coulometry, an electronic integrator from Chemical Electronics International and a sensitive ammeter from Cambridge Instruments Co. Ltd. were used. Rotating disc electrode experiments used a motor controller MC43. Two pumps from Totton Electrical Ltd. model EMP 40/4; two flowmeters type from GAP Meter, Basingstoke; a Sorensen power supply SRL 60-35 and a Philips conductivity bridge (to measure the cell resistance) model GM 4249 were used in experiments with the flow system. The analysis of products was carried out using a programmable Pye Unicam 104 chromatograph, a Unicam SP 1700 U.V. Spectrometer and an AEI-MS12 mass spectrometer coupled with a Pye 104 chromatograph.

II.4.- Procedures for experiments.

Steady state experiments.- Solutions of nitrobenzene (range 10^{-3} - 10^{-1}M) in 50% organic solvent/water, 0.1M in sodium sulphate and solutions of o-halonitrobenzene (range 10^{-3} - 10^{-1}M) in 50% 1-propanol/water were used for these experiments. Polarization curves on copper, lead, zinc and mercury were obtained - potentiostatically using a point by point or a slow scan rate (0.01 V/s) technique in acid medium and at room temperature ($\simeq$ 20°C). Nitrogen was bubbled through the cell during the experiment. On mercury, each reading was recorded with a fresh drop of mercury. For copper, polarization curves were recorded with several concentrations of nitrobenzene at one concentration (5M) of H_2SO_4. Values of current were read from the ammeter one minute after each change in the potential.

Cyclic voltammetry.- Cyclic voltammograms were recorded for dilute solutions of nitrobenzene and o-halonitrobenzenes (10^{-3} - 10^{-1}M) using a copper wire or a mercury drop as working electrode in a symmetrically arranged cell. The potential was cycled between 0 and -1 volts at different potential scan rates (ν). The effects of changing the concentration, pH, and the potential scan rate on the peak potential and peak current were also studied by cyclic voltammetry. For low potential scan rates, the X-Y recorder was found suitable; for high scan rates, an oscilloscope was necessary.

Rotating disc electrode.- For experiments with rotating disc electrode, a cell as shown in fig.2.3 was used. The disc electrode was fixed at the WE position showed in the figure, and very close to the Luggin capillary. It was rotated with a constant speed motor. The secondary electrode was a platinum plate, parallel to the working electrode. The experiments were carried out with a copper electrode in a 5.10^{-2}M nitrobenzene in acetone-water solution, 3M in sulphuric acid and using a slow linear potential sweep. The rotation rate of the disc electrode was varied between 3.10^{2}-3.10^{3} rpm.

Coulometry.- In these experiments, a cell with relatively large electrode area to solution volume ratio was employed (4). The potential of the working electrode was chosen on the basis of steady state or potential sweep experiments. The effect of changing the potential and the effect of stirring and heating the solution were studied. A volume of 100 cm^3 of 8.10^{-2}M nitrobenzene in organic solvent-water solution, 3M in sulphuric acid, and 100 cm^3 of 4.5×10^{-2}M o-halonitrobenzene in 1-propanol-water solution were used in these experiments. The working electrode was copper gauze with a 30 cm^2 geometric area. Experiments with lead (20 cm^2 geometric area), mercury (30 cm^2 geometric area) and zinc (3 cm^2 geometric area) were also carried out. The average time for electrolysis was 2.5 hours and the total number of coulombs passed through the cell were measured by an electronic integrator.

Use of a flow system.- In flow experiments, a system as shown in fig.2.7 was used. The cell was designed following the exigencies of the bibliography (1,2) and was made in the workshop of the department. The assembly incorporates two pumps in order to keep and control the flow of the electrolyte in each of the compartments of the cell separately, and the rate of the flow was controlled by using a flowmeter. Overpressure in the system was avoided by the use of lateral arms as can be seen in the diagram. The total catholyte volume was 600 ml, the system could be deoxygenated by using nitrogen gas and indeed it was bubbled throughout the experiment. The temperature of the electrolyte could be changed by means of an additional arrangement made between the pump and the reservoir in the side of the cathodic compartment. The experiments were run at a constant current and the internal cell resistance was measured under the working conditions by the use of a conductivity bridge.

II.5. - Method of Analysis

Analysis.- The solutions in the WE compartment after the completion of the coulometry were analysed. After the electrolysis, the acid solutions were neutralised with sodium hydrogen carbonate in a cooling system and the solid formed (Na_2SO_4) was separated by decantation and filtration and then washed with ether. The aqueous solution was reduced in volume on the rotary evaporator and the organic compounds extracted with diethyl ether. The diethyl ether was reduced in volume and injected into the chromatograph, the aqueous layer was also analysed by GLC.

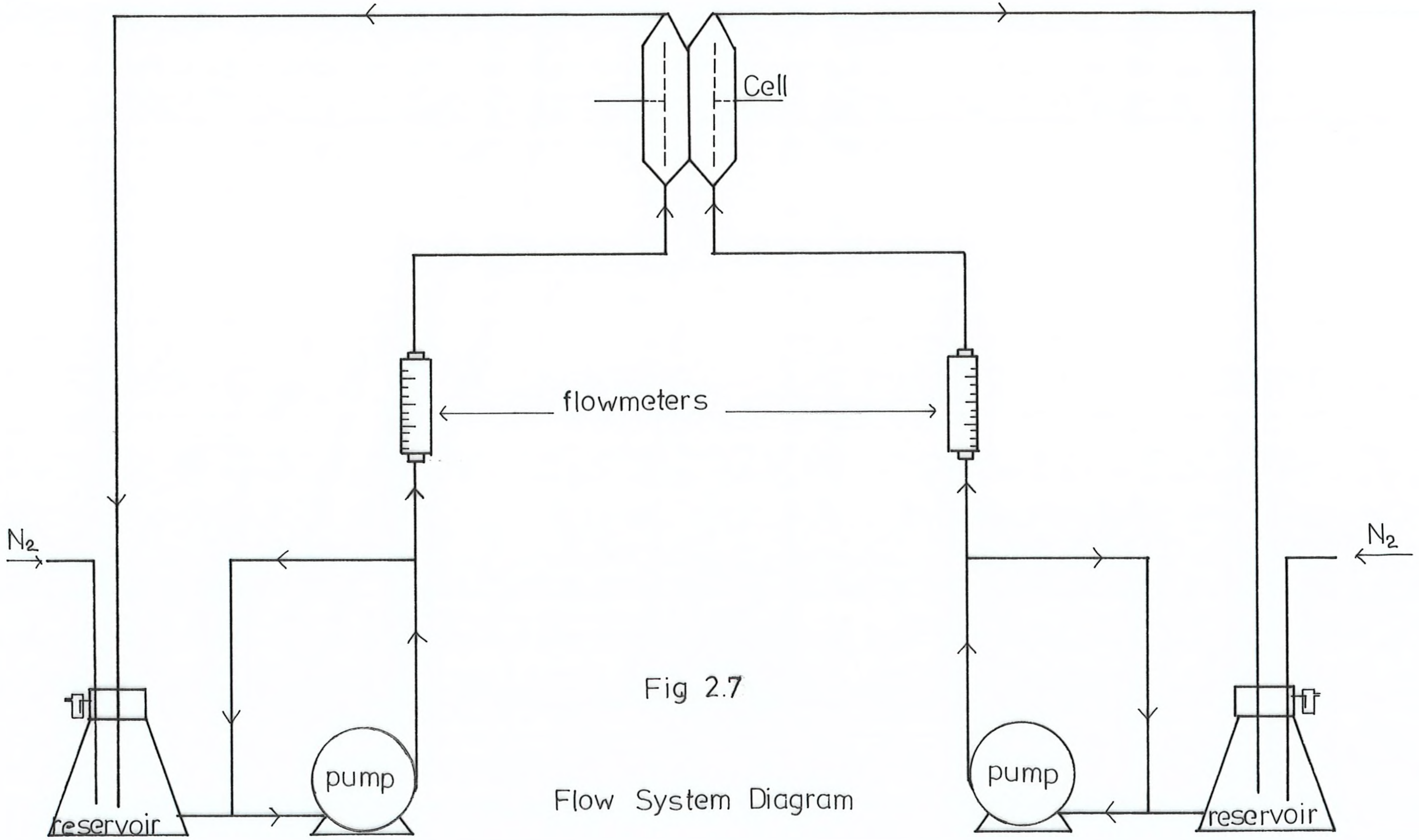

Fig 2.7

Flow System Diagram

The analysis was carried out by gas-liquid chromatography, mass spectrometry and a colorimetric method. Several glass columns with different stationary phases were tested for the g.l.c. analysis and a 5% OV-17 silicone column (1.5 m long and 3 mm diameter) was chosen. The separation was effected by a temperature programme, 140°C for 3 minutes, then 140 to 250° at 48°/min. and finally 250°C for 5 minutes. The retention time of unknown peaks were compared with those for standard compounds and the identification was confirmed by mass spectrometry (5). Quantitative analysis was based upon an integration technique (6); the area under the g.l.c. peaks were compared with those for standards of known concentration. For the purpose of colorimetric analysis (7) a 100 ml of saturated silver nitrate solution in acetone-water and several standard solutions of p-aminophenol (range 0.02-0.2 mg ml^{-1}) in the same solvent as that used in the electrolysis, were prepared. The standard solutions of p-aminophenol and the electrolytic sample (after the neutralisation) were mixed with the silver nitrate solution and their absorption measured with a photocolorimeter at 400 nm. From the standard curve (see fig.2.8) and the sample absorption value, the actual concentration of p-aminophenol in the sample was determined.

Typical electrolysis.-

(a) Procedure for p-aminophenol electrosynthesis:

100 ml of 0.1M nitrobenzene in 50% 1-propanol/water solution, 3M H_2SO_4 was placed in the electrolysis cell as shown in fig.2.4. Nitrogen gas was bubbled through the cell for 15 min. before starting the electrolysis, and the nitrogen was passed throughout the experiment.

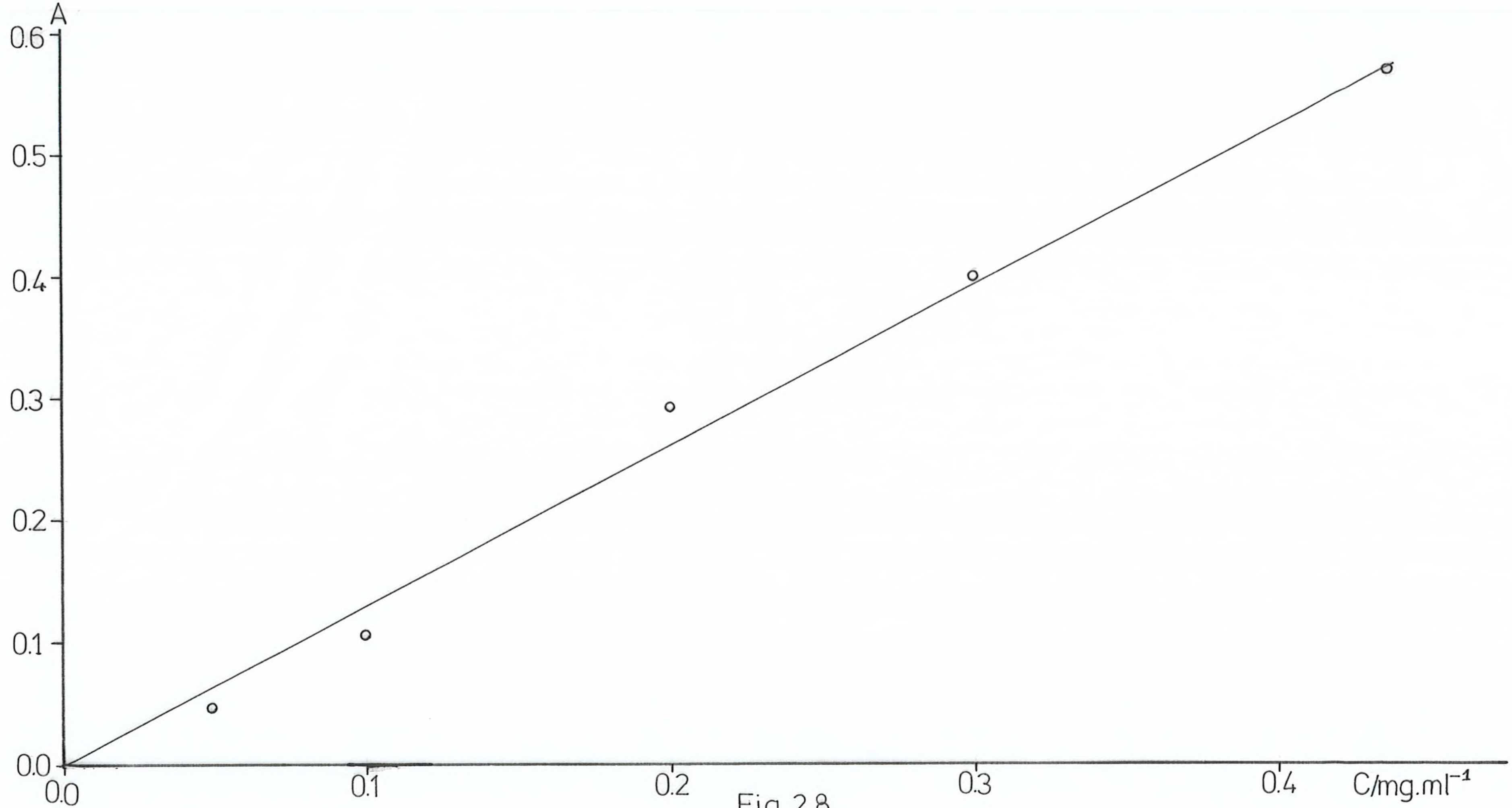

Fig 2.8

Colorimetric analysis of p-aminophenol. Plot of absorbance at 400nm vs concentration of p-aminophenol.

A potential of -0.35 Volts Vs SCE was applied to the copper gauze electrode (30 cm^2). Initially the current was 0.3 Amps and after 3 hours and the passage of 3800 C it had dropped to 10 mA. During the electrolysis the solution was well stirred and in addition to the nitrogen a magnetic stirrer was used. When the electrolysis had finished, the catholyte was neutralised with sodium hydrogen carbonate (the cathodic compartment was designed so that it could be cooled during the neutralisation process), the solid formed (Na_2SO_4) was filtered off on a water pump and washed with ether (2 or 3 times with 100 ml portions). Meanwhile the volume of the aqueous solution was reduced on the rotary evaporator at reduced pressure and the solution was then extracted three or four times with portions of 100 ml of ether in a separating funnel. All the ethereal solutions were combined and reduced to about 200 ml. Both the ether and aqueous layer were analysed by g.l.c. The standard solution was aniline, nitrobenzene, p-aminophenol and azoxybenzene each 10^{-2}M in ether, the retention times for each possible product under normal conditions are those shown in page 60 . The product identification was sometimes checked by g.l.c. - mass spectroscopy and the yield of p-aminophenol by the colorimetric method. In the electrolysis described the total organic yield was 80% (16% in H_2O layer and 64% in ether layer) and the current yield was 84%

(b) Procedure for the electrosynthesis of o-fluoroaniline.

100 ml of 45 mM o-fluoronitrobenzene in 50% 1-propanol/water solution, 0.1M in H_2SO_4 was placed in the electrolytic cell. Nitrogen was bubbled through the cell for 15 mins. before starting the experiment

and throughout the experiment, and the electrolytic medium was stirred by means of a magnetic stirrer. A potential of -0.9 volts Vs SCE was applied to the mercury electrode (30 cm^2). Initially the current was 900 mA and after 1 hour and the passage of 2150 C, it had dropped to zero mA. When the electrolysis had finished, the solution was neutralised with $NaHCO_3$ and the organic products were isolated with ether (4 x 100 ml portions). The ether extract was reduced in volume and analysed by g.l.c. The o-fluoroaniline organic yield under these conditions was 78% and the current yield 93%.

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CHAPTER III

CHAPTER III

Electrochemical Reduction of nitrobenzene to p-aminophenol

III.1.- Results

III.1.1.- Electroanalytical Experiments

Steady State. Current-Potential Curves.- The polarization curve for the reduction of nitrobenzene on copper in acid medium and its dependence on the concentration of nitrobenzene is shown in fig. 3.1. The I-E curves show a single well formed reduction wave, $E_{\frac{1}{2}} = -.35V$, and the current is proportional to the concentration of nitrobenzene both in the Tafel region and on the limiting Plateau. A replot of the data as log I v_sE gives a linear Tafel region as shown in fig.3.2. The slope is approximately 170 mV^{-1}.

The current-potential curves for mercury and lead under similar conditions (3M H_2SO_4 + 10mM nitrobenzene) were also recorded (fig.3.3). Mercury shows two reduction processes, the first occurring at potentials positive to that for mercury dissolution and the second at $E_{\frac{1}{2}} = -0.55V$. The ratio of the limiting currents for these two processes is 2:1 and the total current density is close to that for the single process on copper. On lead there is one reduction process, $E_{\frac{1}{2}} = -0.53V$. Surprisingly, the current density on lead is lower than that on both mercury and copper although it should be noted that in the experimental conditions the surface is covered by a thick layer of lead sulphate.

Cyclic Voltammetry.- Cyclic voltammograms were recorded for solutions in acid medium and at a copper electrode. A well formed reduction peak is found at approximately -0.35V ($\nu = 0.03V.s^{-1}$, 5M H_2SO_4) but the reduction process is totally irreversible (fig.3.4). In a series of experiments the concentration of nitrobenzene (10^{-3} - 10^{-1}M), concentration of sulphuric

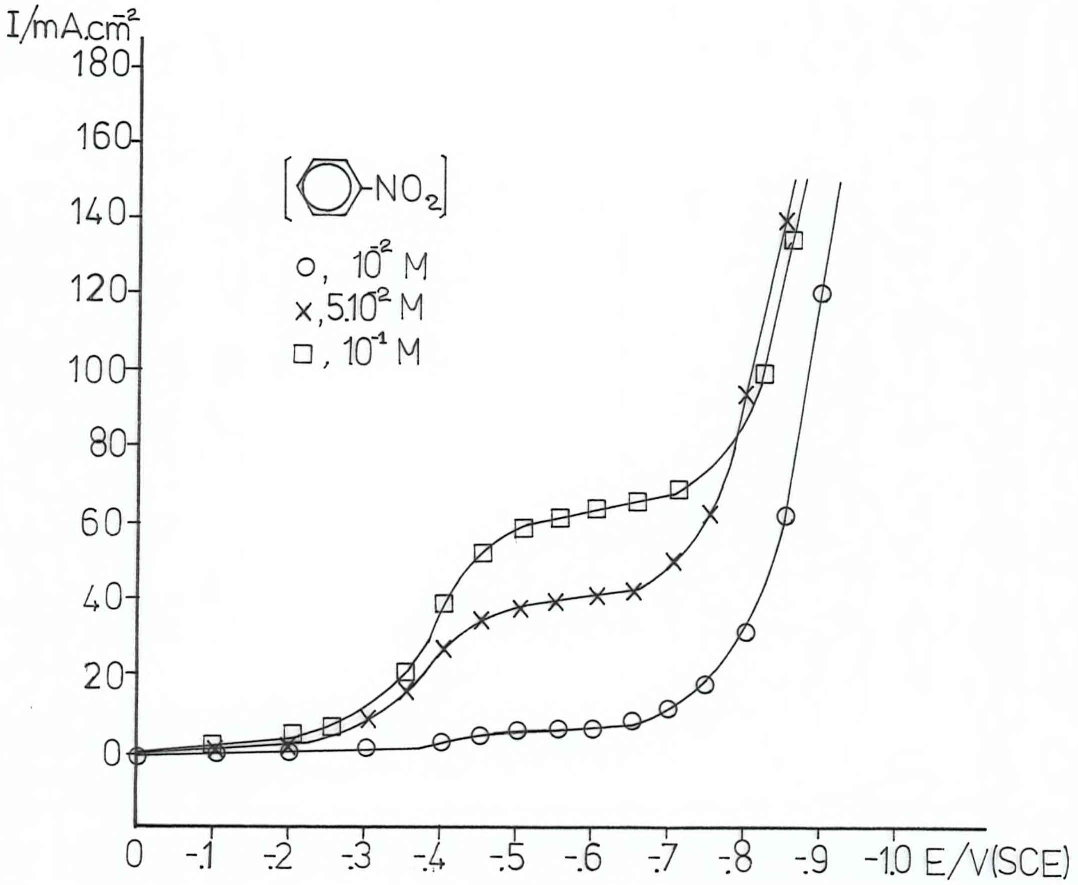


Fig 3.1
Polarization curves at copper. Solution of nitrobenzene in 50% acetone-water, 5M in H_2SO_4.

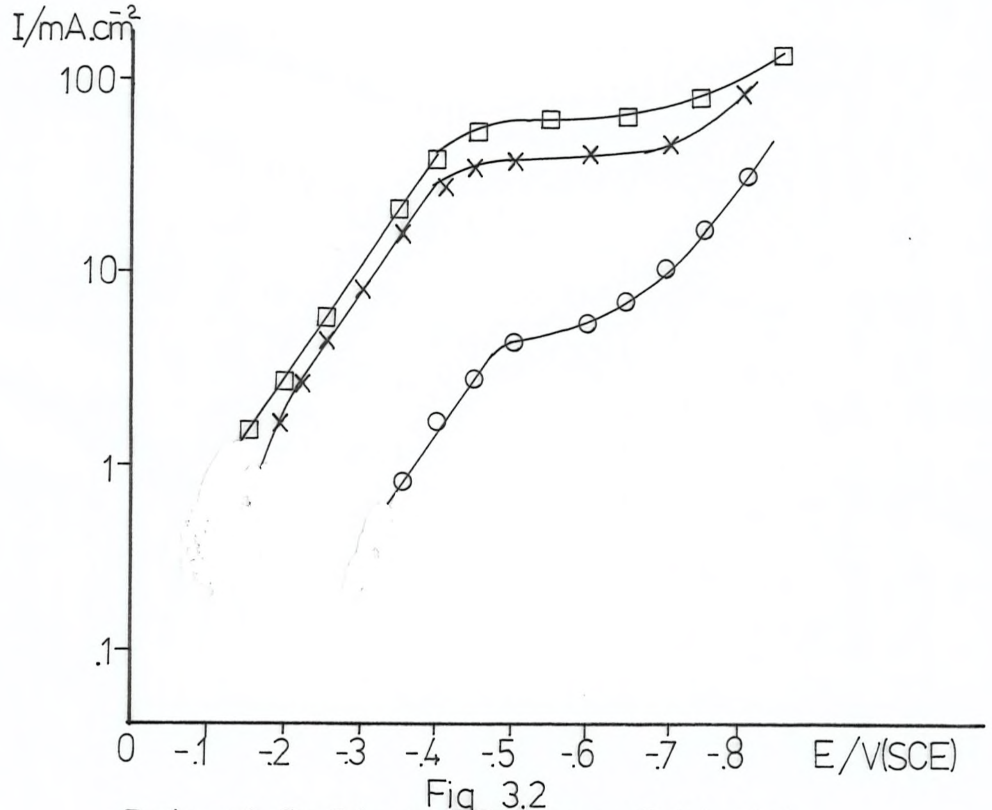


Fig 3.2
Data of fig. 3.1 replotted as a Tafel plot.

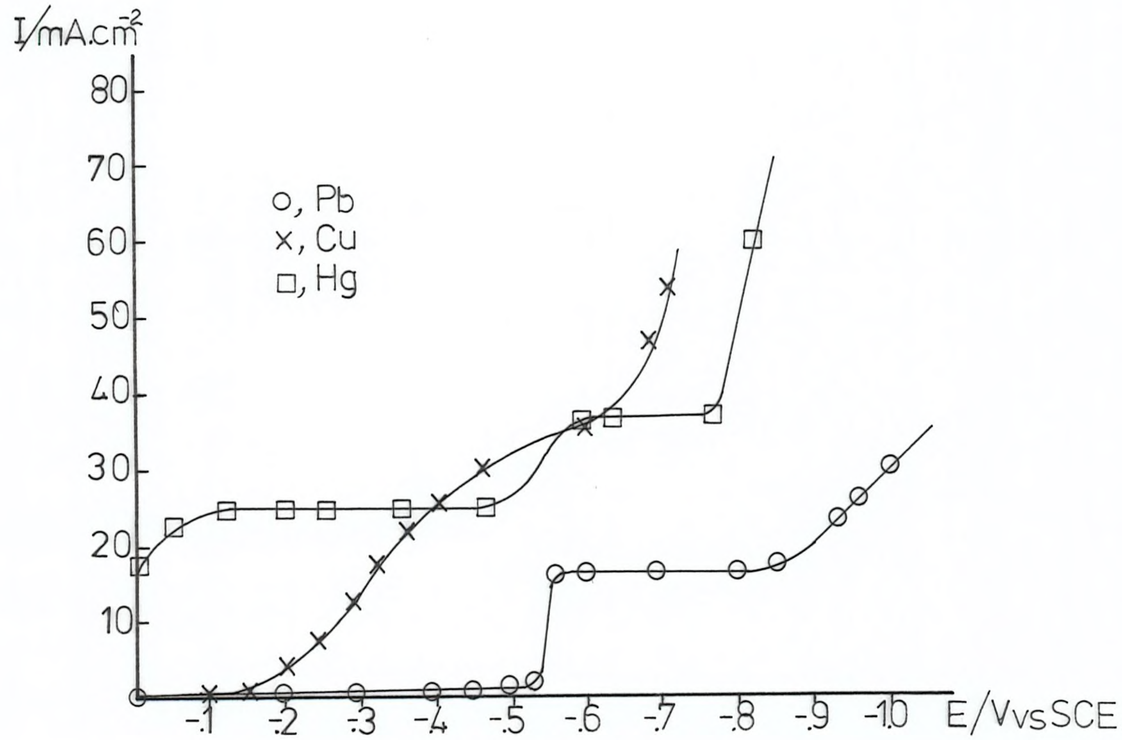


Fig 3.3
Polarization curves. Nitrobenzene (5×10^{-2}M) in 50% acetone - water, 3M H_2SO_4.

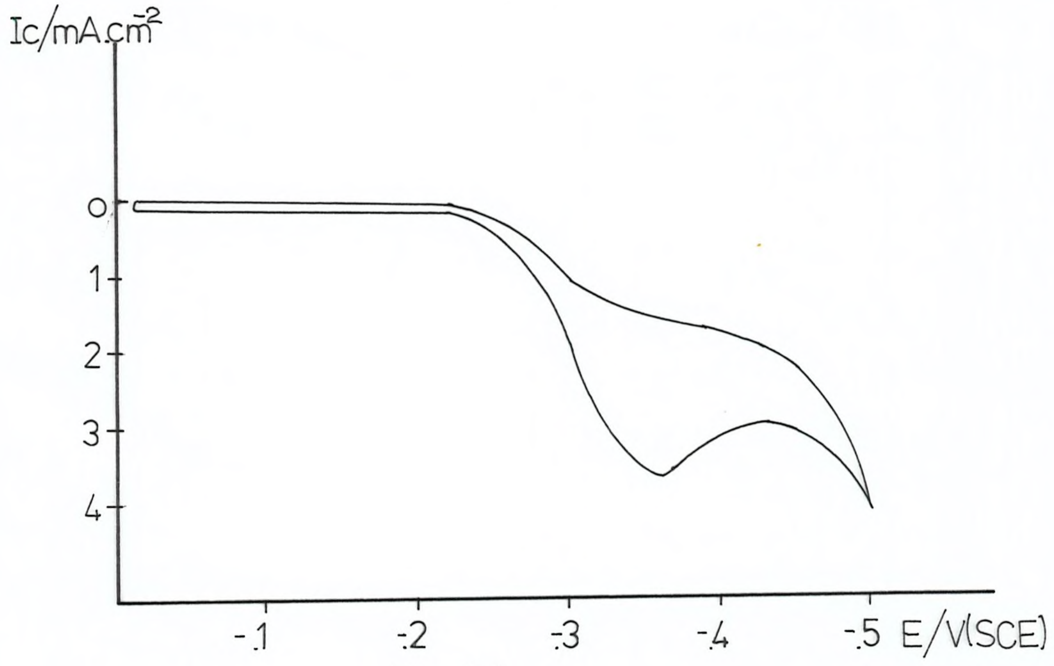


Fig 3.4
Cyclic voltammogram. Solution 5×10^{-3}M of nitrobenzene in 50% acetone-water, 5M H_2SO_4. WE=Cu, ν=0.03 Vs^{-1}

acid (0.1M - 10M) and potential scan rate (0.01 - 1 Vs^{-1}) were varied. The peak potential does not change with the concentration of nitrobenzene and it has a constant value in strongly acid solutions; on the other hand, the peak shifts to negative potentials at pH above 1 (Table 3.1). The Ep Vs log ν graph is linear with a slope of -28 mV (fig.3.5, Table 3.2). The peak current is independent of the pH but it does change with the potential scan rate (ν) as shown in fig.3.6. Indeed, the plot of Ip Vs $\nu^{\frac{1}{2}}$ is linear passing through the origin, showing that the reaction is diffusion controlled. The value calculated for D is 0.9×10^{-5} cm^2s^{-1} (assuming n = 6 and taking $n_\alpha\alpha = 0.65$ from $E_p - E_{p/2}$). The peak current also changes with the concentration of nitrobenzene (fig.3.7) and the slope of the log I_p - log C plot is one.

The potential limits on copper in strong sulphuric acid extend from 0.1V (Cu dissolution) to -0.8V (hydrogen evolution) and within this potential range we were unable to identify any further reduction or oxidation peaks under any acidic conditions or potential scan rates. Hence cyclic voltammetry gives little information on the intermediates in this reaction.

Rotating Disc Electrode.- In a rotating disc electrode experiment, one can be said to be comparing the rate of mass transfer with the rate of other processes. When the mass transfer is the slowest step in the reaction, the current varies linearly with the square root of the rotation rate (ω) and an I Vs $\omega^{\frac{1}{2}}$ plot passes through the origin, i.e. $I/\omega^{\frac{1}{2}}$ should be independent of ω. An experiment using a slow linear potential sweep on a copper disc electrode in a 5.10^{-2}M nitrobenzene in acetone-water, 3M sulphuric acid solution give the results shown in fig.3.8 and table 3.3.

Table 3.1

Effect of acidity on the peak potential. Solution 5 x 10^{-3}M $C_6H_5NO_2$ in acetone-water (1:1 mixture).

Working electrode: copper

Sweep rate, ν = 0.03 Vs^{-1}.

E_p (volts)	$[H_2SO_4]$
-0.53	0.1
-0.32	1.0
-0.35	5.0
-0.33	10.0

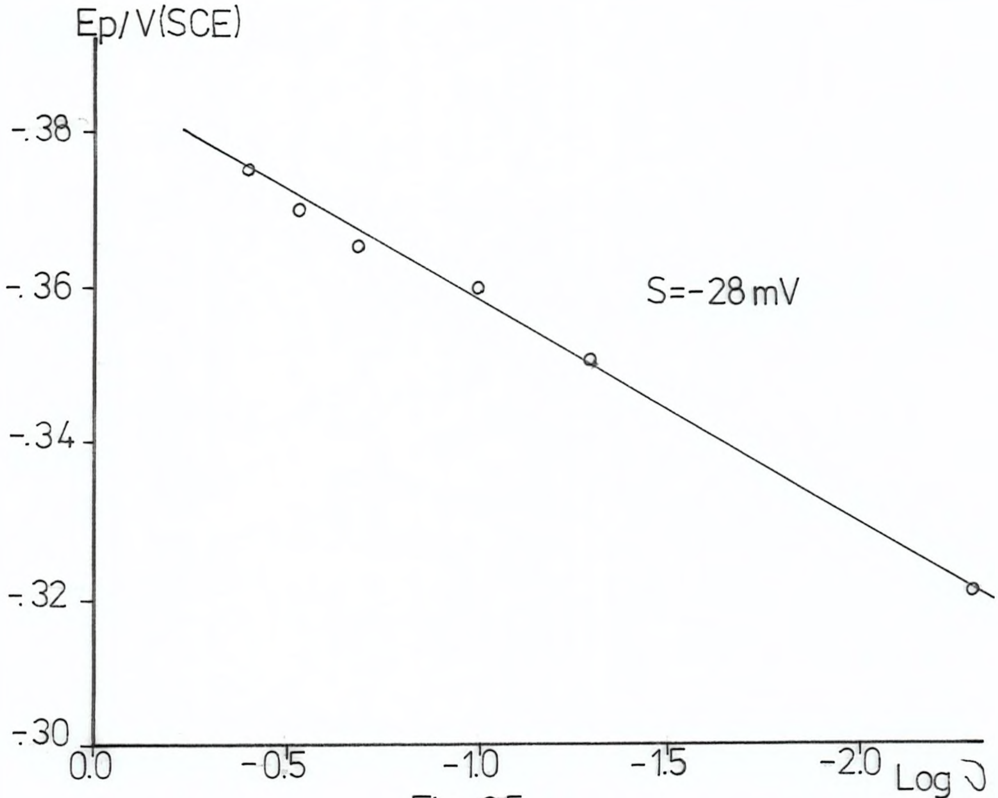


Fig 3.5

Plot of Ep vs. Log ν. Solution 4.10^{-3}M nitrobenzene in acetone-water, 1M H_2SO_4. WE=Cu.

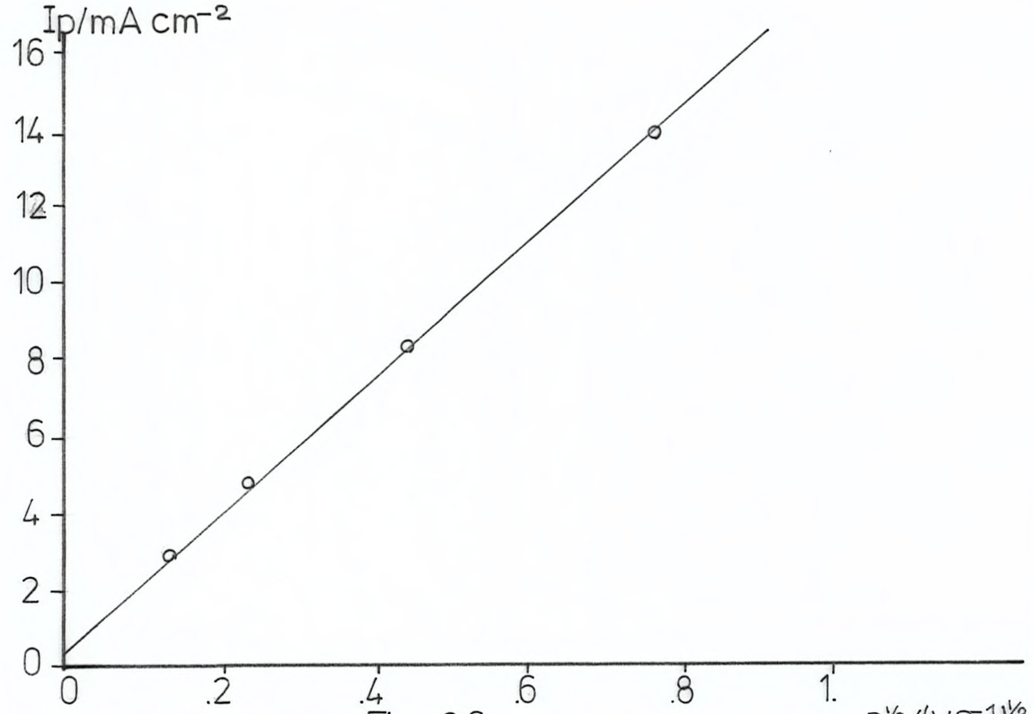


Fig 3.6

Plot of Ip vs. $\nu^{1/2}$. Solution 4.10^{-3}M nitrobenzene in acetone-water, 1M H_2SO_4. WE=Cu.

Table 3.2

Dependence of E_p with experimental parameters

$$\left(\frac{\partial E_p}{\partial C}\right)_{H^+,\nu} = 0 \qquad \left(\frac{\partial E_p}{\partial pH}\right)_{\substack{\nu,C \\ pH < 1}} = 0$$

$$\left(\frac{\partial E_p}{\partial \log \nu}\right)_{H^+,C} = -28 \text{ mV} \qquad \left(\frac{\partial E_p}{\partial pH}\right)_{\substack{\nu,C \\ pH > 1}} \neq 0$$

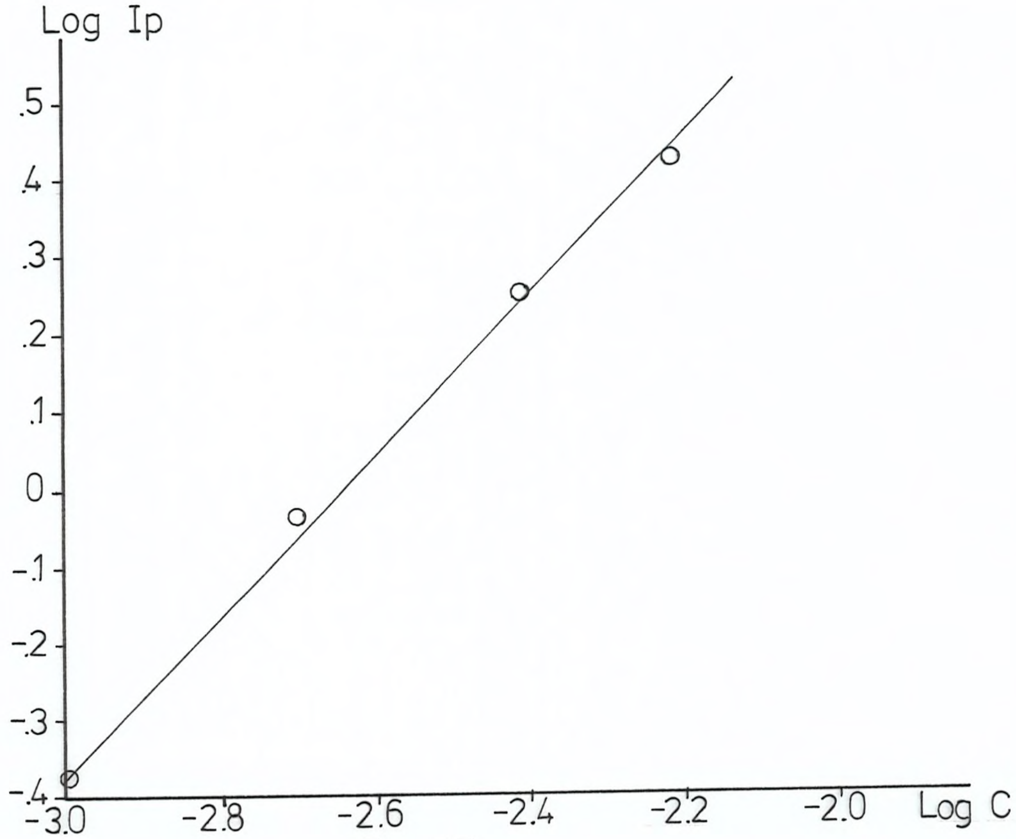


Fig 3.7

Plot of Log Ip vs Log C. Solution of nitrobenzene in acetone-water, 1M H_2SO_4. WE=Cu. $\nu = 0.03 VS^{-1}$

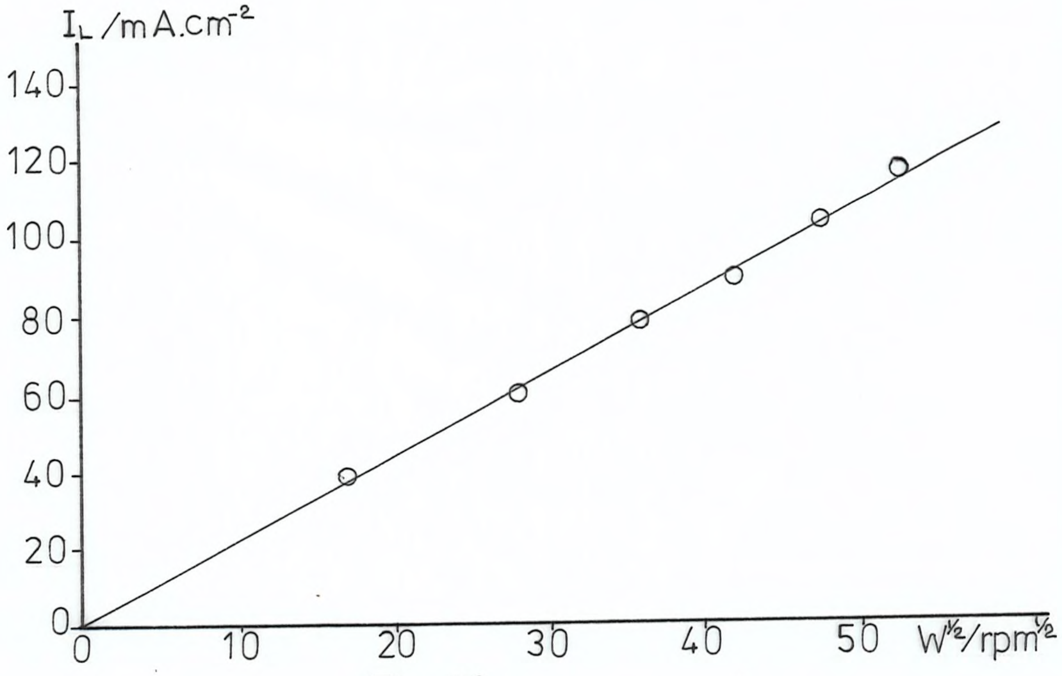


Fig 3.8

RDE experiment, plot of I_L vs $w^{1/2}$. Solut. 5.10^{-2}M nitrobenzene in acetone-water, 3M H_2SO_4. WE=Cu, $\nu = 0.03 VS^{-1}$, E=−0.51 V

Table 3.3

R.D.E. experiment on copper electrode in a 5×10^{-2} M nitrobenzene in acetone-water, 3M sulphuric acid solution.
$\nu = 0.03$ V sec^{-1}. $E = -0.51$V.

I(mA cm^{-2})	w(rpm)	$I/w^{\frac{1}{2}}$
37.1	300	2.14
59.8	800	2.11
76.3	1300	2.11
86.6	1800	2.04
101.1	2300	2.11
115.5	2800	2.18

In the limiting current plateau, the reaction is clearly mass controlled. The constancy of $I/w^{\frac{1}{2}}$ also shows that the number of electrons involved in the electrode reaction is the same at all rotation rates. Again assuming $n = 6$, a value for the diffusion coefficient of $0.96 \times 10^{-5} cm^2 s^{-1}$ could be estimated.

Coulometry.- Controlled potential coulometry was carried out to determine 1) n, the number of electrons transferred in the overall electrode reaction and 2) the final products of the electrode reaction.

Coulometry experiments were carried out at different concentrations of nitrobenzene in organic solvent-water and acidic medium. A typical curve is shown in fig.3.9 for a copper cathode, the data are presented in the form of an I-Q plot, and it can be seen that a good linear plot is obtained and the extrapolation to I=0 leads to a n value of 4.

III.1.2. - Product Identification

Several glass columns with different liquid phases (table 3.4) were tested for the GLC analysis. A 5% OV-17 column was found suitable for the determination of the electrolysis products. By using a temperature programme (details in page 43) the analysis could be completed in 11 min, and good resolved peaks were obtained for aniline, nitrobenzene, p-aminophenol, azobenzene and azoxybenzene. Mass spectrometry was used to confirm the identity of the products, and the yield of p-aminophenol was frequently checked by the colorimetric method based on complexation with Ag^+.

Analyses were performed for electrolyses on copper, lead and mercury. The tables 3.6, 3.7 and 3.8 show the products and their organic yield in the conditions indicated. Table 3.5 shows the retention times and the mass

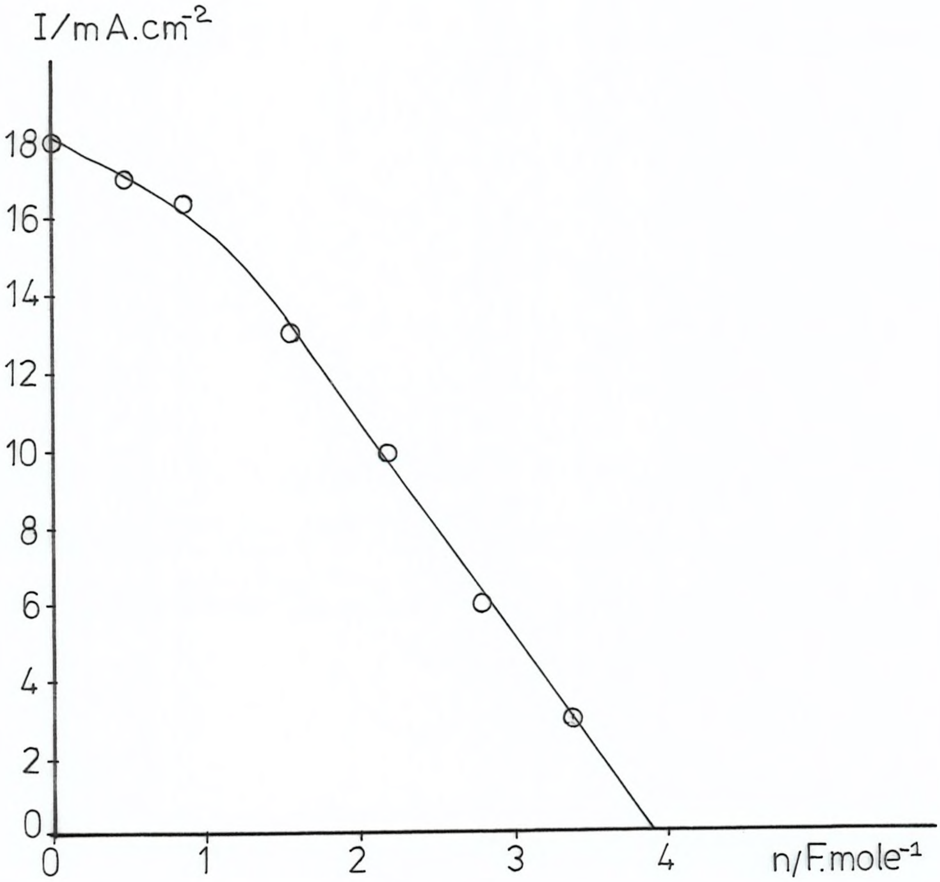


Fig 3.9

Coulometry. Solution 8.10^{-2}M of nitrobenzene in acetone-water, 3M H_2SO_4. WE=Cu, V=-0.33 volts, T=70°C, with agitation.

Table 3.4

Chromatographic Columns

Liquid Phase	Polarity
Carbowax	most polar
Diglycerol	most polar
OV-17	intermediate
OV-1	non-polar

Table 3.5

Retention times and mass spectra data for standards and electrolysis products from the nitrobenzene electrochemical reduction

Compound		MW	Retention time(min)	m/e ratio(intensities)
aniline	(s)	93	1.6	93(100), 66(20), 65(11), 92(10), 46.5(3), 39(3)
aniline	(p)	93	1.6	93(100), 66(23), 65(12), 92(11), 46.5(3), 39(6)
p-aminophenol	(s)	109	4.7	109(66),108(25),81(51),55(37), 53(13), 52(6)
p-aminophenol	(p)	109	4.8	109(16),108(5), 81(18),55(23), 53(3), 52(2)
azoxybenzene	(s)	198	9.1	198(92), 77(100),91(40),105(30), 65(16), 64(11)
azoxybenzene	(p)	198	9.0	198(31), 77(100),91(33),105(18), 65(20), 64(13)

MW = molecular weight, s = standard sample, p = electrolysis product.

spectrometry data for standards and electrolysis products, some typical chromatograms and mass spectras are shown in the appendix.

III.1.3. Product studies

Controlled potential experiments were carried out in 50% acetone/water to identify the dependence of the products on cathode metal, electrode potential, concentration of sulphuric acid, stirring, temperature and oxygen contamination. Table 3.6 shows the effect of the cathode metal on the yield of p-aminophenol. In each of those experiments the current was monitored as a function of the charge passed during the electrolysis and n, the number of electrons involved in the reduction, was determined by extrapolating the I-Q data to zero current; generally the I-Q plot was linear and a typical plot was shown in fig.3.9.

The effect of changing the potential on the p-aminophenol-aniline ratio (the two main products) for electrolysis on copper electrode and its relationship with the n value is shown in table 3.7. It can be seen that at copper only two major products are formed and that their yields are dependent on the potential. As the potential is made more negative, the yield of p-aminophenol decreases and that of aniline increases. This change is also reflected in the n value (increases from 4 to 6). The highest yields of p-aminophenol occur at potentials corresponding to the foot of the reduction wave, below $E_{\frac{1}{4}}$, on the steady state curve; the high yield is, however, obtained at the cost of a low current density. It is also clear that on both mercury and lead (Table 3.6) the yield of aniline is high when the potential corresponds to the second reduction process. Even at lower potentials there is a considerable formation of aniline at mercury and lead - electrodes compared with the

Table 3.6

Reduction of Nitrobenzene (80 mM) in 50% acetone/50% water containing sulphuric acid (3M). Effect of cathode metal.

Cathode	Potential	n	Products (% of $C_6H_5NO_2$ added) p-aminophenol	Aniline	Azoxybenzene
Cu	-0.30	3.9	81	14	5
	-0.40	4.6	46	29	21
Pb	-0.60	5.3	16	60	16
	-0.85	5.7	15	76	5
Hg	-0.20	4.2	39	29	10
	-0.80	5.7	0	78	13

Table 3.7

Solution 4.10^{-2}M of nitrobenzene in 50% acetone-water, 3M H_2SO_4

Electrode	Potential(V)	Initial (mA/cm^2)	% Aniline	% p-aminophenol	% azoxybenzene	n
Cu	-0.40	19.7	29	46	21	4.6
	-0.35	15.9	24	67	5	4.4
	-0.33	14.0	15	79	5	4.1
	-0.30	10.9	14	81	5	3.9
	-0.25	6.0	5	82	5	3.6

results on copper. The results (table 3.8) also show that stirring and heating improves the p-aminophenol yield. The effect of the acidity of the medium in the p-aminophenol yield is shown in table 3.9, it shows the advantage of a strong acidic medium for the p-aminophenol production.

It can be seen that the selection of several electrolysis parameters is critical and in all further electrolyses, copper was used as the cathode, the concentration of acid was fixed at 3M and the reactions were carried out in a well stirred (by a stream of N_2 gas and a magnetic stirrer) and oxygen free solution. While it would be advantageous to use a higher temperature, the design of the experimental cell determined the use of ambient temperature.

III.1.4.- Effect of the solvent.

Since the electrolysis must be carried out at a potential where the current is well below the limiting current plateau, it is particularly important for any practical system to maximise the concentration of nitrobenzene in the electrolyte. Hence the reduction of nitrobenzene was investigated in a range of organic solvent/water mixtures.

Steady state I-E curves were recorded using a point by point technique for solutions of nitrobenzene (50 mM) at a copper cathode in several 50% organic solvent/water mixtures containing sulphuric acid (3M). In each solution a single reduction wave was obtained, the limiting currents were similar and the half-wave potentials were close to -0.4V Vs SCE indicating that the reduction mechanism probably does not depend on the solvent. The solubility of nitrobenzene in these

Table 3.8

Electrolytic reduction of nitrobenzene (80mM) in 50% acetone/50% water containing sulphuric acid.

Effect of stirring, temperature and oxygen contamination.

Electrode	E	Products (% $C_6H_5NO_2$ added)	Comments
Hg	-0.20	p-aminophenol(39) aniline (29) azoxybenzene (10)	All O_2 removed
Hg	-0.20	Aniline (20) azoxybenzene (76)	with trace O_2
Cu	-0.33	p-aminophenol (80) aniline (8)	well stirred
Cu	-0.33	p-aminophenol (45) aniline (45)	No stirring
Cu	-0.33	p-aminophenol (87) aniline (4)	well stirred, 70°C

Table 3.9

Electrolysis of Nitrobenzene (50mM) in 50% acetone/50% water containing sulphuric acid. Effect of acidity. Cu cathode, electrode potential: -0.3V

H_2SO_4(M)	Products (% Nitrobenzene added) p-Aminophenol	Azoxybenzene	Aniline
0.3	0	43	52
1.0	45	28	27
3.0	80	12	8

aqueous organic media, however, varies substantially and in consequence the limiting current densities for saturated solutions of nitrobenzene are markedly solvent dependent. The solvents used and the maximum limiting current densities are reported in table 3.10.

Table 3.11 shows the effect of the organic solvent on the yield of p-aminophenol for four promising solvents and in view of these results and the data in table 3.10, later experiments were carried out in n-propanol. Figs.3.10 and 3.11 report the results of a further series of electrolyses at various potentials. It can be seen that the yield of p-aminophenol and the ratio of p-aminophenol to aniline decreases as the potential is made more negative, but the choice of a more positive potential is again at the cost of a lower current density, the data in acetone are also included to emphasise the lack of sensitivity to the solvent. At a potential where the initial current is about a third of the limiting current for the concentration of nitrobenzene used, the organic yield and the current efficiency are both in excess of 80%.

Table 3.12 shows the yield of p-aminophenol in experiments with much increased initial concentrations of nitrobenzene. The electrolyses were carried out in 1-propanol/water and it can be seen that a high organic yield and current efficiency is possible even when the concentration of nitrobenzene is 0.6M (i.e. saturated). Moreover the current density reaches an acceptable range, 100-200 mA cm^{-2}, with the saturated solution of nitrobenzene; even higher values should be possible in a cell where the stirring regime produces a higher rate of mass transport.

Table 3.10

Limiting currents for the reduction of saturated nitrobenzene in 50% Organic solvent/50% water mixtures, containing sulphuric acid. 3M Copper cathode

Organic Solvent	$I_L (mA.cm^{-2})$
Acetic acid	560
Acetone	250
1,2-dimethoxyethane	470
Dimethylsulphoxide	160
Dioxan	400
1,2-ethanediol	110
Ethanol	320
Methanol	280
1-Propanol	800

Table 3.11

Electrolytic reduction of Nitrobenzene (40mM) in various 50% solvent/50% water mixtures containing sulphuric acid (3M). Electrolysis at potential where initial current density is 10 $mAcm^{-2}$, i.e. at approximately 0.33 I_L. Copper Cathode.

Solvent	n	Yield of p-aminophenol
Acetone	3.9	81
1-Propanol	3.6	85
Dioxan	3.5	52
Acetic acid	3.9	58

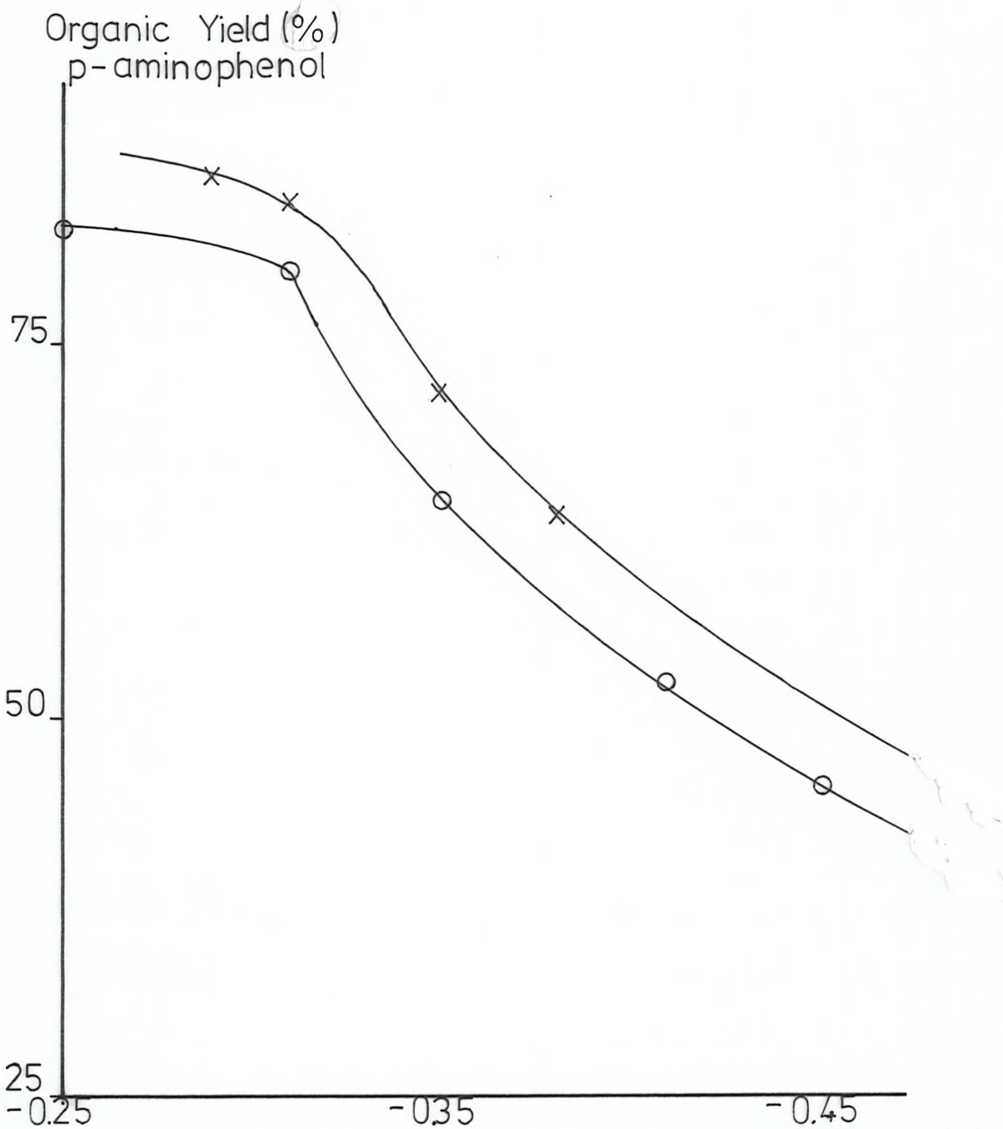


Fig 3.10

Yield of p-aminophenol as a function of electrolysis potential. Nitrobenzene (40 mM) in 50% organic solvent-water, 3M H_2SO_4. x=1-propanol, o=acetone

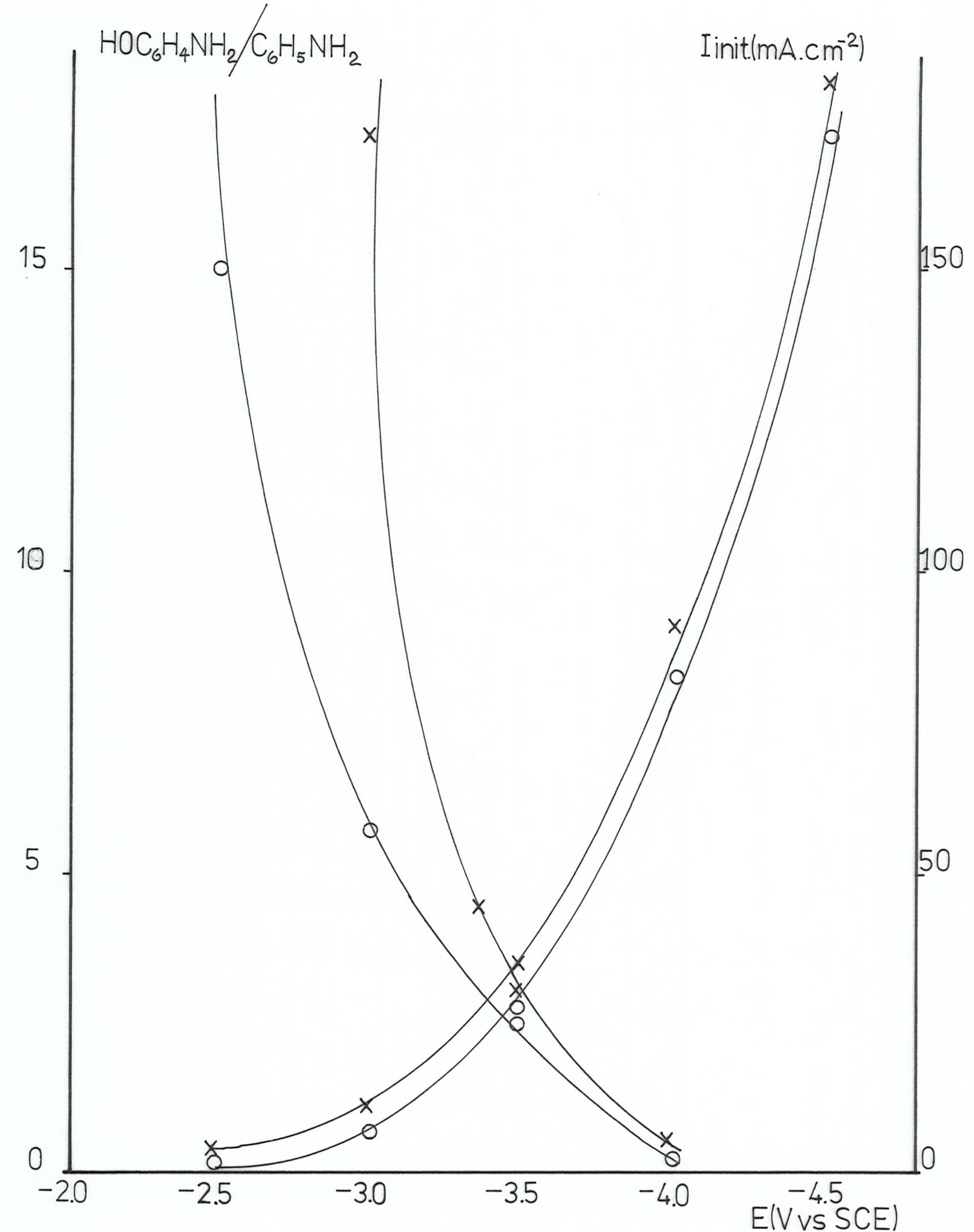


Fig 3.11

Ratio of p-aminophenol/aniline and current density as a function of potential. Nitrobenzene(40mM) in 50% organic solvent/water, 3M H_2SO_4 . x,1-propanol; o,acetone.

Table 3.12

Electrolytic reduction of nitrobenzene at a copper electrode in 50% 1-propanol/50% water containing sulphuric acid (3M)

Concentration of Nitrobenzene (M)	E (V versus SCE)	Initial (mA cm^{-2})	Yield of p-aminophenol(%)
0.04	-0.3	10	85
0.4	-0.3	26	82
0.6(sat.)	-0.4	200	58
	-0.39	150	76
	-0.38	100	82

III.2. Discussion and Conclusions

III.2.1.- Preparative Aspects

The electrochemical reduction of nitrobenzene in acidic media has been the subject of several investigations (1-9) and it is well known that depending on the conditions in which the reaction is effected, different compounds and in different proportions can be obtained. It has been reported that at low cathodic-electrode potentials, nitrobenzene is reduced directly to N-phenylhydroxylamine which rearranges in acid to form p-aminophenol. The percentage of p-aminophenol production depends not only with the cathode potential, but also, of the particular acid used, the cathode material, the temperature and the agitation of the media as was mentioned in the Introduction. Because of previous studies (2) sulphuric acid was used to acidify the solutions, and cathodes of copper, lead and mercury were used. Since the reaction at copper gives a much higher yield of p-aminophenol compared to Hg and Pb, it was studied in more detail, and by using well stirred, oxygen free and hot solutions (70°C , a high yield in p-aminophenol (87%) was obtained which compares well with earlier attempts to prepare this compound by using amalgamated cathodes, redox systems and stronger acidic media (3,4). Table 3.13 compares the results of this and previous studies and the improvement obtained on the p-aminophenol production is believed to depend on the higher solubility of the nitrobenzene in this medium which increases the local concentration of the depolarizer at the electrode surface. Moreover, the solvent does not lead to p-propoxyaniline, and the solubility of intermediates in the process is also increased with the use of these mixtures of solvents.

Table 3.13

Results of the nitrobenzene electrochemical reduction to p-aminophenol

Cathode	Medium	Temperature(^oC)	Cathode Potential(V)	I_{INIT}(mA.cm^{-2})	p-aminophenol organic yield(%)	Ref.
Cu	H_2SO_4 Hg^{+2} added	60	-	25	60	6
Ni,C,Pt	50% H_2SO_4	25-60	-	-	60-90	7
rotating amalgamated monel	20% H_2SO_4	90	-	27	72	5
				200	75	3
rotating Cu	1M H_2SO_4 Sn^{+2} added	85	-0.4	-	80	4
Cu	3-8 NH_2SO_4 bed cell with flow Acetic Acid	90-120	positive than -0.4	-	-	8
Cu	1:1 Acetone/Water 3M H_2SO_4 with agitation	70	-0.33	40	87	this study
	1:1 n-propanol/water 3M H_2SO_4 with agitation	room	-0.38	100	82	this study
		room	-0.39	150	76	this study

Because of the limitations in the current density obtained (order of 40 $mA.cm^{-2}$) and the instability of the acetone as a solvent in acidic solutions (it went brown during electrolysis or on standing) in further experiments several organic cosolvents were used (table 3.10) and good results were obtained in 1-propanol/water mixtures, where the current density reached the highest value. Saturated solutions of nitrobenzene in this medium were electrolysed and high values of current density (100-200 mA/cm^2), organic yield (80-90%) and current yield (95-100%) were obtained. The time for the electrolysis was also reduced considerably compared with earlier experiments, and the formation of tarry or dimeric products were not observed under these conditions.

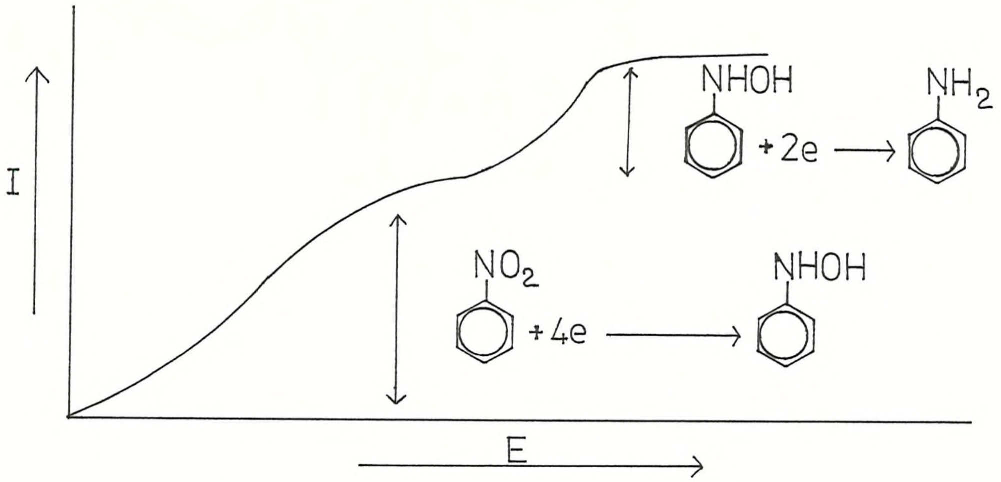
In summary, it can be said that the best conditions for p-aminophenol production were, the use of a copper cathode and a saturated solution of nitrobenzene in 1:1 mixture of 1-propanol/water (where the depolarizer was more soluble), 3M in sulphuric acid, at low cathode potential (-.39V), in a well agitated medium and at a high temperature. Under these conditions, the current density was over 150 $mA.cm^{-2}$, the organic yield over 80% and the current yield close to 100%.

While the analysis, in the laboratory, of the products is straightforward, their isolation on an industrial scale is difficult because the p-aminophenol is present as an ammonium salt. It is probably necessary to neutralise the sulphuric acid and this is wasteful and creates unwanted heat. The presence of a cosolvent complicates these problems since it must be recycled and as well as increasing the solubility of nitrobenzene, it also increases the solubility of the product.

Several attempts to industrialise the electrochemical production of p-aminophenol have been reported (2,10,11) and these failed probably because of the low current densities which are possible in all aqueous media. This work has shown that a cosolvent overcomes this problem. With a suitable work-up and a modern cell design, this synthesis of p-aminophenol has a promising future.

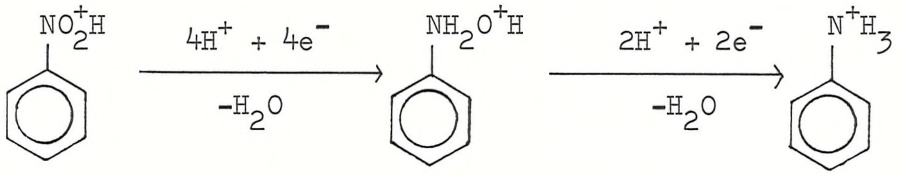
III.2.2. - Mechanism

Although the electrochemical reduction of nitrobenzene has been studied since the last century (12), conclusions concerning reaction mechanism drawn from electroanalytical experiments are not always consistent with the products of preparative scale electrolyses. For instance, the results of the experiments on Hg electrode show an appreciable yield of aniline at the first wave where it was not expected, while the p-aminophenol yield at Cu electrode (one wave) is much better than that on mercury where two well defined reduction processes are observed. A good deal of work has been done on the polarographic behaviour of nitrobenzene (1,13-20) and in general, the results obtained show a two wave reduction process in acid media with n values of 4 for the first wave and 2 for the second, and a single process in basic media with an n value of 4. The electrochemical reactions associated with these processes were thought to be the formation of phenylhydroxylamine and aniline respectively (see below).



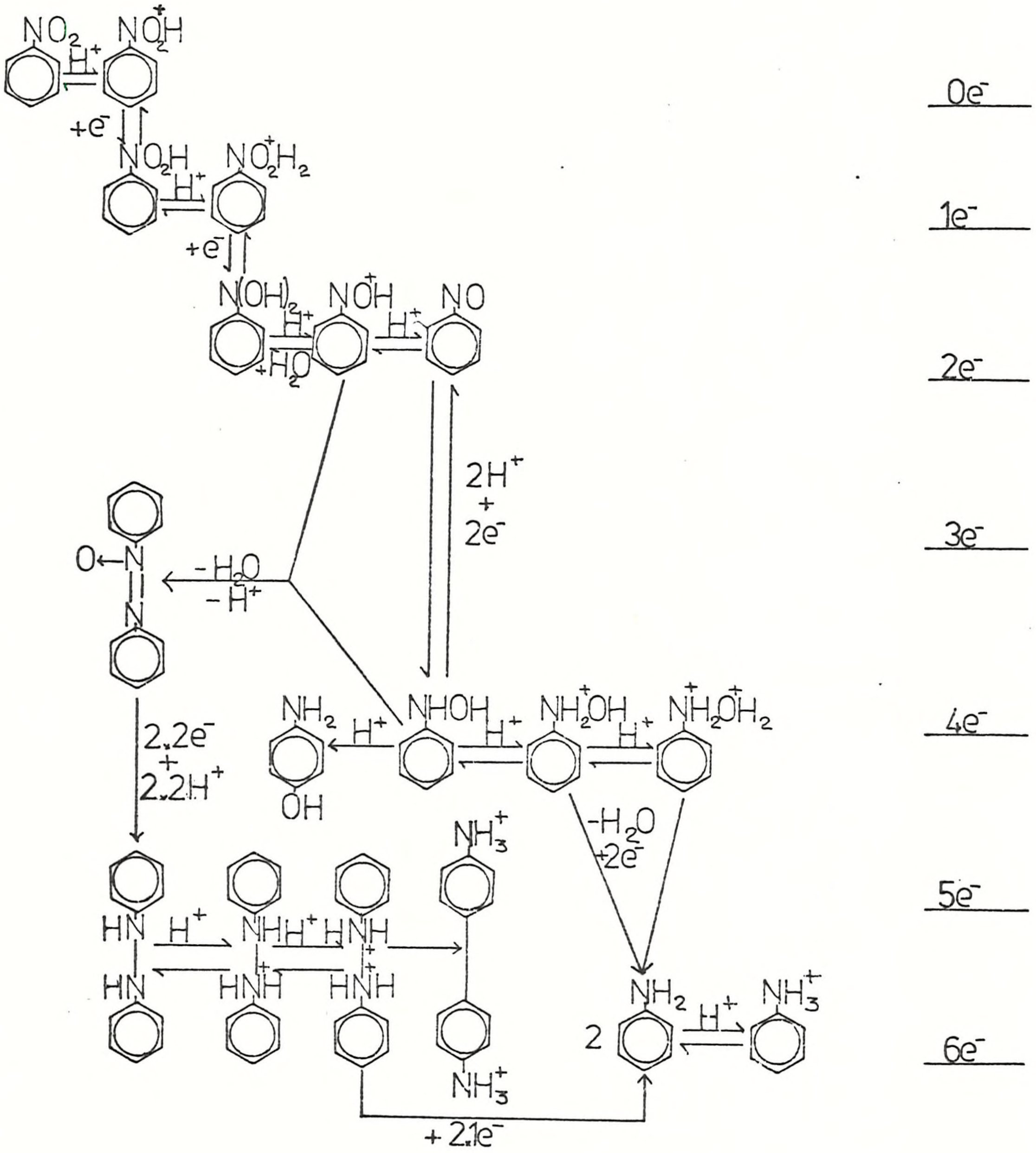
A detailed polarographic investigation of the reaction in acid solution is that of Heyrovsky and coworkers (1), and they have proposed a general reaction scheme (see below).

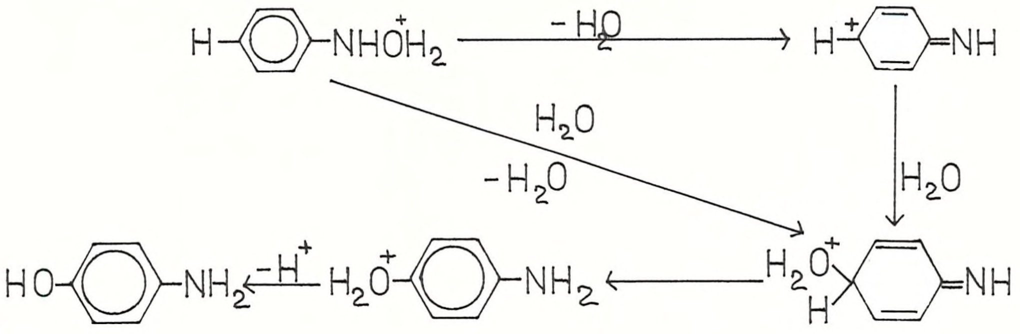
In general, the results of this study, with respect to electron uptake, on a stirred mercury surface, agree with earlier work in a similar system (15), and those obtained using polarographic means. The reduction is principally a two step process to phenylhydroxylamine and aniline.



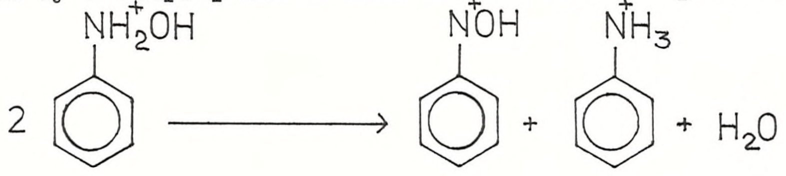
Nevertheless, electrolyses at potentials in the first region give a mixture of products (table 3.6 and 3.8), with p-aminophenol and aniline as main compounds. The p-aminophenol formation, as stated by Wawzonek (21) in solutions of high acidity must occur by the acid-catalysed rearrangement of phenylhydroxylamine. The reaction scheme proposed by L. Finar (22) is:

General reaction scheme for the electrochemical reduction of nitrobenzene based on that proposed by Heyrovský and Vavřička.



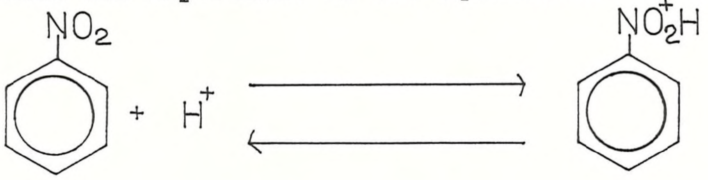


since the electroanalytical experiments give an n value of 4 in this region, the aniline formation at this stage can only be explained by a disproportionation of a 4e reduced product e.g.

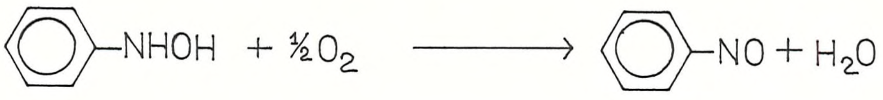


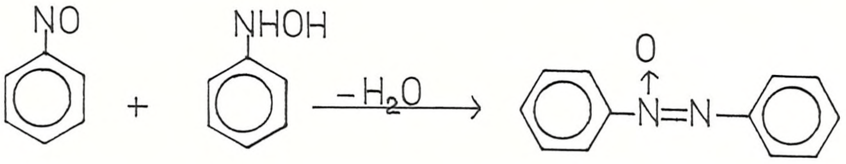
When the electrolysis is carried out at a potential in the second region and well deoxygenated solutions, the main product, as mentioned before, is aniline (table 3.6). The results of this and earlier work clearly indicate that the yield of p-aminophenol from the 4e reduction product is a function of the electrode material. Hence it may be that a part of the acid catalysed rearrangement may occur while an intermediate is adsorbed on the electrode surface e.g. the protonation of phenylhydroxylamine may occur while the latter is adsorbed. Moreover, it has been suggested by Lund (2) that the rearrangement of phenylhydroxylamine to p-aminophenol occurs more rapidly during electrolysis than in homogeneous solution. The observation that the yield of p-aminophenol is increased by stirring, however, may be evidence that the rearrangement occurs away from the electrode surface.

It has been reported by J. Pearson (13) and Pezzatini and Guidelli (20) that the polarographic $E_{\frac{1}{2}}$ is independent of $[H^+]$ below pH = 1, but shifts negative with increasing the pH value, and the same dependence was found for Cu in this work (tables 3.1 and 3.2). This indicates the importance of the equilibrium in the pH range

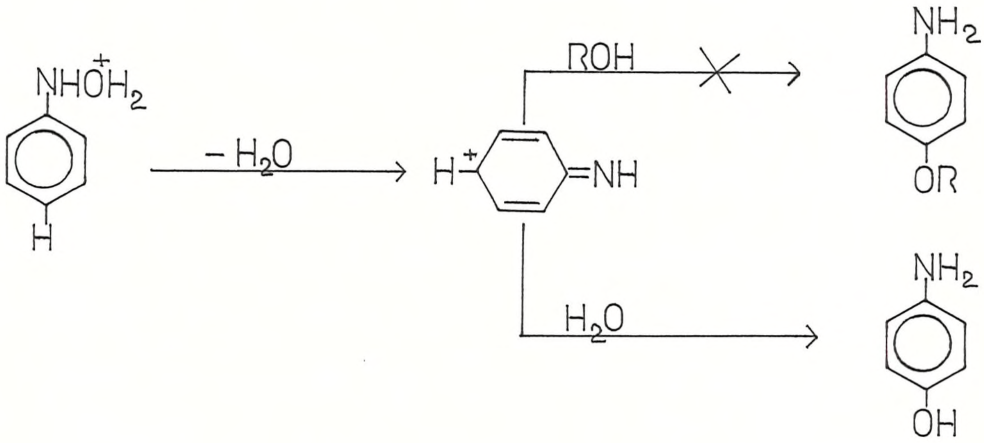


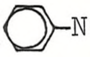
1 to 5. Below pH one, however, the nitrobenzene in solution is fully protonated and it is the electroactive species in the process. The steady state and cyclic voltammetry experiments on copper showed a single irreversible reduction peak. On the other hand, controlled potential electrolyses in the limiting plateau region confirm the transfer of 6 F mol^{-1} with aniline as the product, while at potentials in the lower half of the reduction wave the transfer of 4 F mol^{-1} and p-aminophenol as the products (tables 3.7 and 3.8). Hence, although the reduction appears to be a single process, the wave in fact, consists of two overlying processes, one $4e^-$ and one $2e^-$ reduction. Whether or not the reduction is to p-aminophenol depends on the use of low potentials to avoid further reduction of phenylhydroxylamine to aniline as previously reported by Rance and Coulson (4) and confirmed for the results in this study (Fig.3.10 and 3.11 and Table 3.12). It is also necessary to use highly acidic solutions to ensure the protonation of phenylhydroxylamine (the literature reports the acid-catalysed rearrangement) and to keep the catholyte completely free from oxygen. In not well deoxygenated solutions, azoxybenzene formation is increased (table 3.8); the phenylhydroxylamine is oxidised by oxygen in solution to nitrosobenzene which reacts with more phenylhydroxylamine as previously reported by Fleischmann et al (23). It is also noted (table 3.8) that an increase in temperature

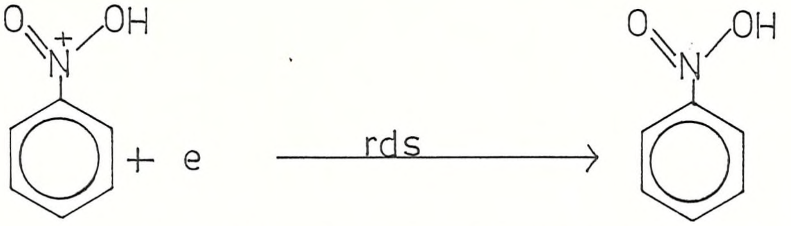




enhanced the yield of p-aminophenol, it is believed to occur by an increase in the rate of the rearrangement. In experiments with 1-propanol, p-propoxyaniline was not found amongst the products. Hence during the rearrangement of phenylhydroxylamine to p-aminophenol, the alcohol must be a poor nucleophile compared to water.

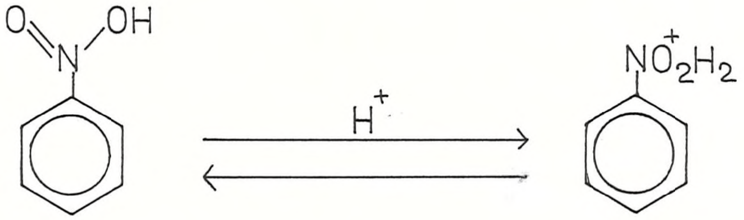


The cyclic voltammetry and rotating disc electrode experiments confirm a diffusion controlled process; however, a well defined Tafel region is observed when the I-E data are replotted as log I vs E, suggesting the existence of a region where the process is controlled by the e^- transfer step, and the slope value is consistent with $\alpha = 0.35$ and a single electron transferred before and during the rate determining step. These data, and those obtained for $[H^+]$ and[$-NO_2$] reaction orders in the region studies are consistent with an electrode process in which the first electron transfer is the rate determining step in the reaction.



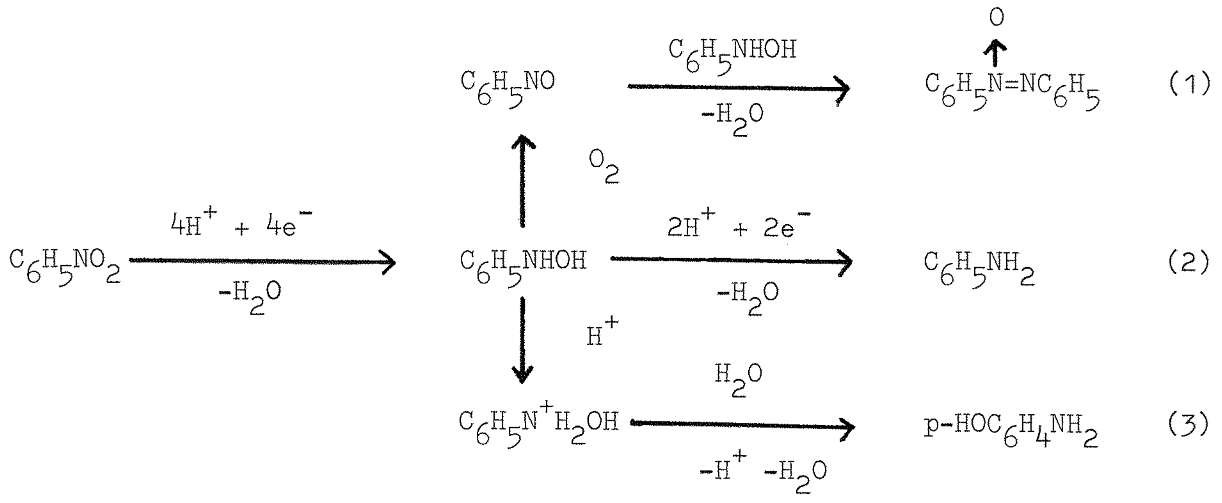
and the value obtained from cyclic voltammetry for $(\partial E_p/\partial \log \nu)$ $= -28$ mV also suggests an irreversible process.

The next step could be the further protonation of the species resulting from the first e^- transfer step



The data reported in table 3.6 show that there is a strong dependence of the products on the cathode metal. Hence at least the initial protonation step required for the rearrangement may well occur while the phenylhydroxylamine is adsorbed on the electrode surface. On the other hand, the increase in yield of p-aminophenol with increased convection would argue that it is favourable to remove from the cathode an intermediate in the rearrangement. All these observations are compatible with a competition between routes 1 to 3 (Scheme below) for the fate of the phenylhydroxylamine.

Scheme


$C_6H_5NO_2$
$4H^+ + 4e^-$
$-H_2O$
C_6H_5NO
O_2
C_6H_5NHOH
H^+
$C_6H_5N^+H_2OH$
C_6H_5NHOH
$-H_2O$
$2H^+ + 2e^-$
$-H_2O$
H_2O
$-H^+ \; -H_2O$
O
$C_6H_5N{=}NC_6H_5$
$C_6H_5NH_2$
$p\text{-}HOC_6H_4NH_2$
(1)
(2)
(3)

III.2.3.- Conclusion

It is the conclusion of this work that the best yield of p-aminophenol is obtained with a low potential at a copper cathode, using a well stirred oxygen-free solution in 1-propanol/water containing sulphuric acid (3M). Indeed, under these conditions the organic yield and current efficiency for p-aminophenol compare well with earlier investigations (table 3.13). It can be seen from those results that using a saturated solution of 50% 1-propanol/50% water it was possible to obtain p-aminophenol yield of 82% at a current density of 100 $mA.cm^{-2}$ and 76% at 150 $mA.cm^{-2}$.

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CHAPTER IV

CHAPTER IV

Electrochemical reduction of the o-halonitrobenzenes to the aniline

IV.1.- Results o-fluoronitrobenzene reduction

IV.1.1.- Electroanalytical Experiments.

Steady State. Current-Potential relationship.-

Polarization curves for solutions of o-fluoronitrobenzene on Hg at different pH values were obtained and typical results are shown in fig.4.1. In weakly acidic medium (pH = 5), one wave is observed, $E_{\frac{1}{2}} = -.66V$. The current initially increases exponentially with potential then reaches a value which is independent of potential before finally it again increases due to hydrogen evolution. In more acidic solution (pH = 1), two waves are observed, with half wave potential values of $E^1_{\frac{1}{2}} = -.14V$ and $E^2_{\frac{1}{2}} = -.65V$, the ratio between the limiting currents is approximately two (I^1_L/I^2_L). The concentration dependence in weakly and strongly acidic medium is linear with slopes of one, fig.4.2. A replot of the I-E data give a Tafel region with slopes of 110 mV^{-1}.

The current-potential curves for the reduction on copper and zinc, under similar conditions were also obtained and a single reduction process was observed in acidic media, fig.4.3. In the case of Zn, the I-E curve is distorted by the anodic current for the dissolution of the metal which is observed at potentials positive to -0.8V.

Steady state curves for nitrobenzene, o-chloro- and o-bromo-nitrobenzene on mercury were also obtained by linear sweep voltammetry at a very low sweep rate ($\nu = 0.005\ vs^{-1}$)and the results are shown in table 4.1.

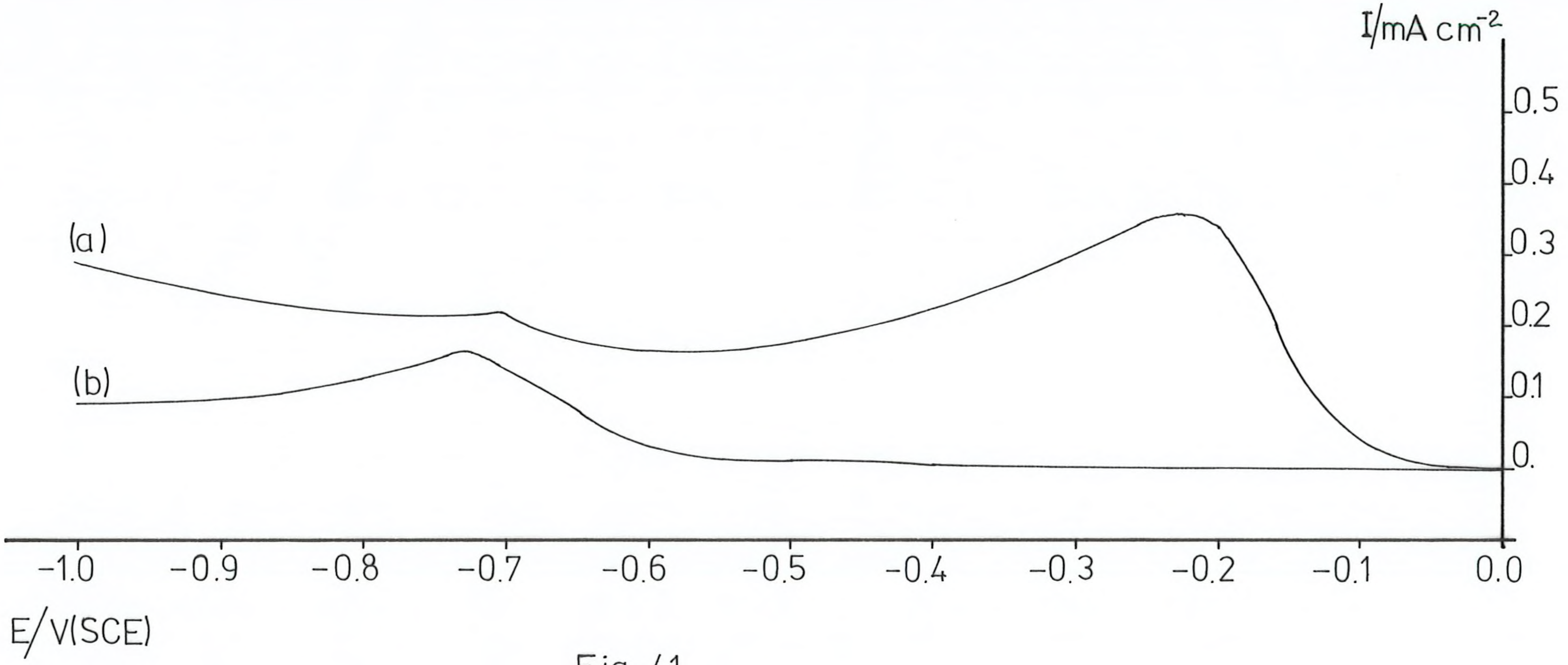


Fig 4.1

Steady state. Current-potential curves. Solut. 10^{-3}M o-$FC_6H_4NO_2$ in 50% 1-propanol-water

(a)= .1M H_2SO_4 (b)=1M NH_4Cl

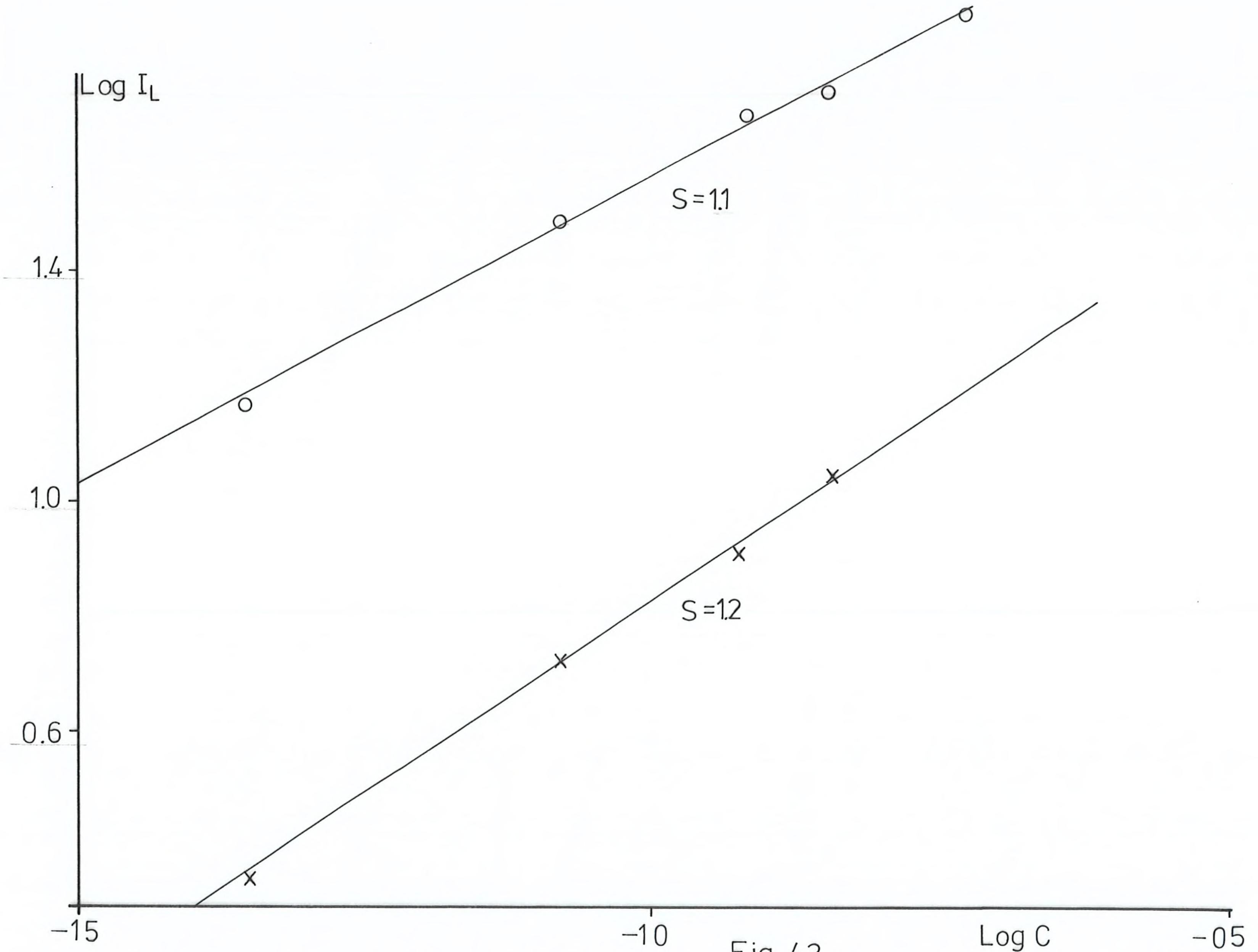


Fig 4.2
Plot. of Log I_L vs Log C. Solution of o-$FC_6H_4NO_2$ in 1-propanol – water. WE = Hg. $\nu = 0.01\,VS^{-1}$
o = H_2SO_4(pH=1), x = NH_4Cl (pH=5).

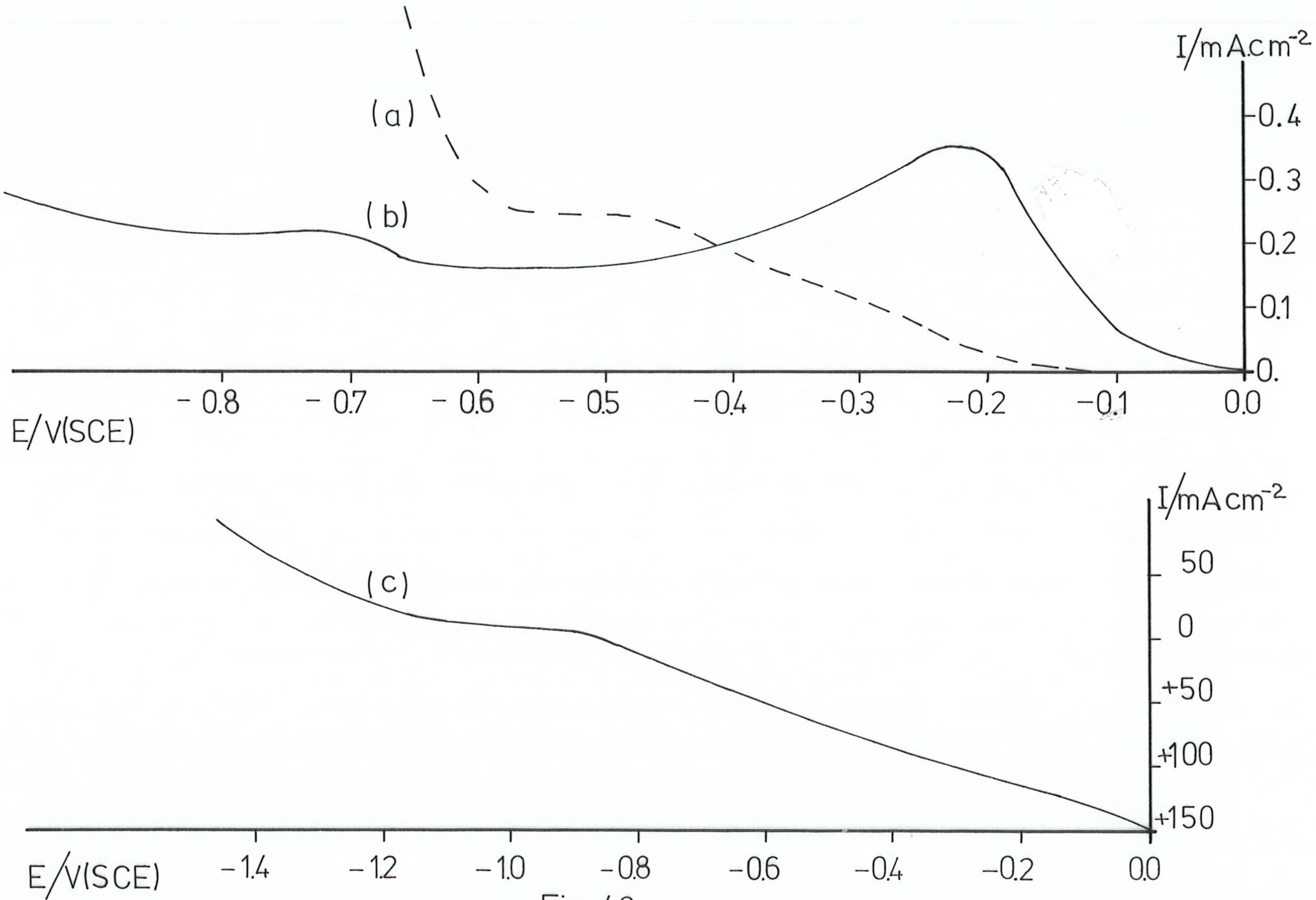


Fig 4.3

Current-potential curves. Solut.10^{-3}M o-$FC_6H_4NO_2$ in 50% 1-propanol-water, 0.1M H_2SO_4
(a)=Cu , (b)=Hg , (c)=Zn electrodes.

Table 4.1

X	E^1_p/V	E^2_p/V	I_2/I_1
H	0.26	0.75	0.56
F	0.22	0.71	0.45
Cl	0.18	0.70	0.75

Cyclic voltammetry of $O\text{-}X\text{-}C_6H_4NO_2$ in 0.1M H_2SO_4. Data taken from voltammograms at a sweep rate of 0.005 $V.s^{-1}$. Hg electrode.

Cyclic Voltammetry.- Cyclic voltammograms were recorded for the o-fluoronitrobenzene compound (10^{-3} - 10^{-1}M) in 50% n-propanol/water, in acid medium (pH : 1-5), on a mercury electrode and over a range of potential scan rates (0.005-0.5 Vs^{-1}). Typical results in acidic medium, figure 4.4. At the slowest potential scan rate, 5 mVs^{-1}, and pH = 1, two reduction processes at E^1_p = -0.22V and E^2_p = -0.71V were observed, both were totally irreversible. With increasing potential sweep rate, however, the reduction process at more negative potentials becomes relatively less important (see fig.4.5) and, indeed, over .3 Vs^{-1} this peak is not observed on the cyclic voltammogram.

The cyclic voltammograms run in an ammonium chloride medium (pH = 5) and an acetate buffer (pH = 4) showed, at all potential scan rates, a single reduction process. The reaction occurs at more negative potentials, i.e. -0.73V in NH_4Cl and the peak current density for the process is at all sweep rates much lower than that for the first reduction in the sulphuric acid solution (fig.4.6).

Over the range of concentration and pH studied, peak currents were directly proportional to concentration. The half wave potential was independent of concentration but shifted to negative potentials as the pH increased. The E_p Vs log ν plot was linear with slope of -30mV (fig.4.7). The peak current depends on the pH in this region and the extent of the variation with pH changed with the potential scan rate. The I_p Vs $\nu^{\frac{1}{2}}$ plot showed that the reaction is diffusion controlled and assuming n=6, a D value of 2.9 x 10^{-5} cm^2s^{-1} was calculated. The variation of some other parameters are shown in Table 4.2.

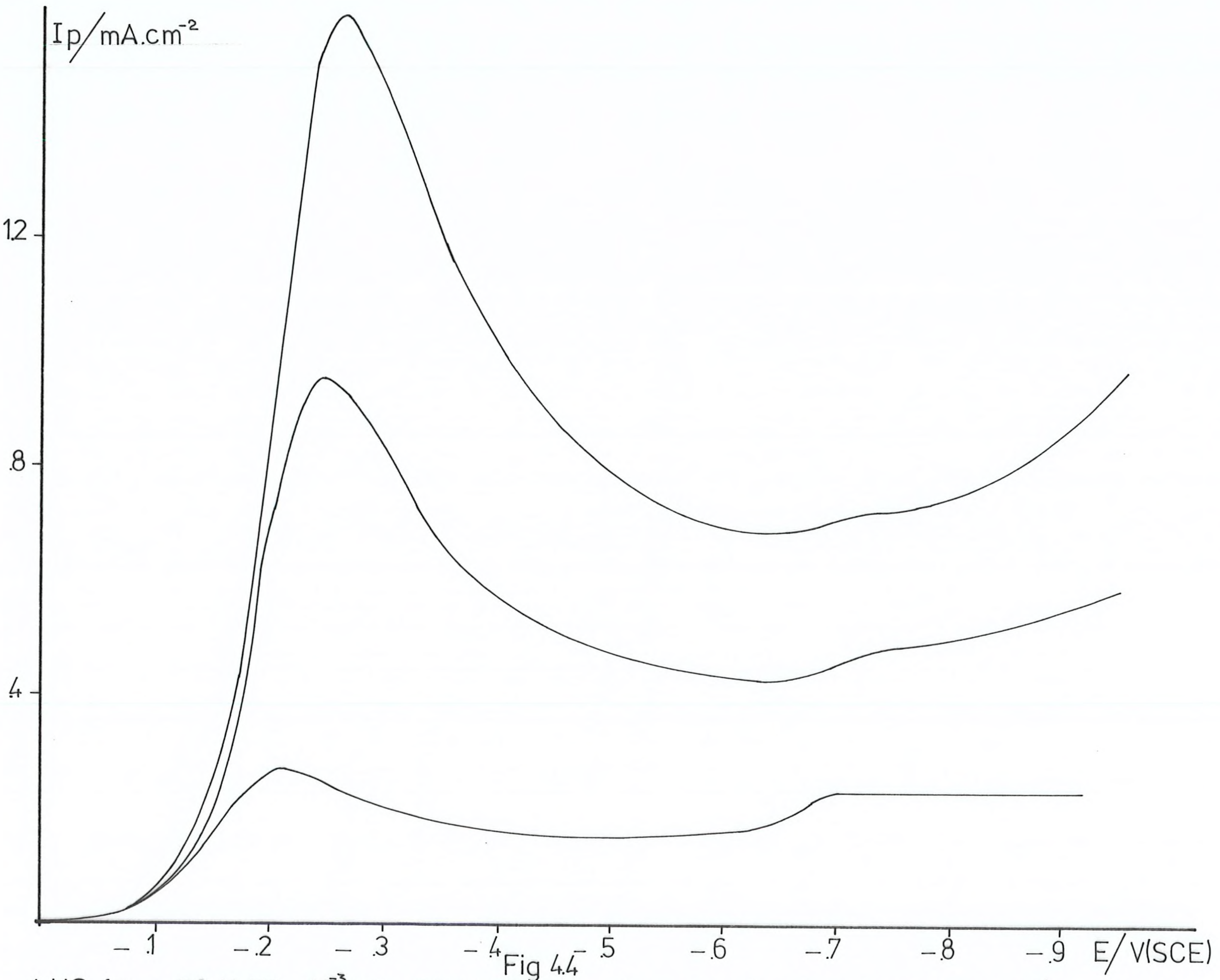


Fig 4.4

LVS for o-$FC_6H_4NO_2$ 10^{-3}M in 0.1M H_2SO_4. Hg electrode. ν = 0.005, 0.1, and 0.3 VS^{-1}

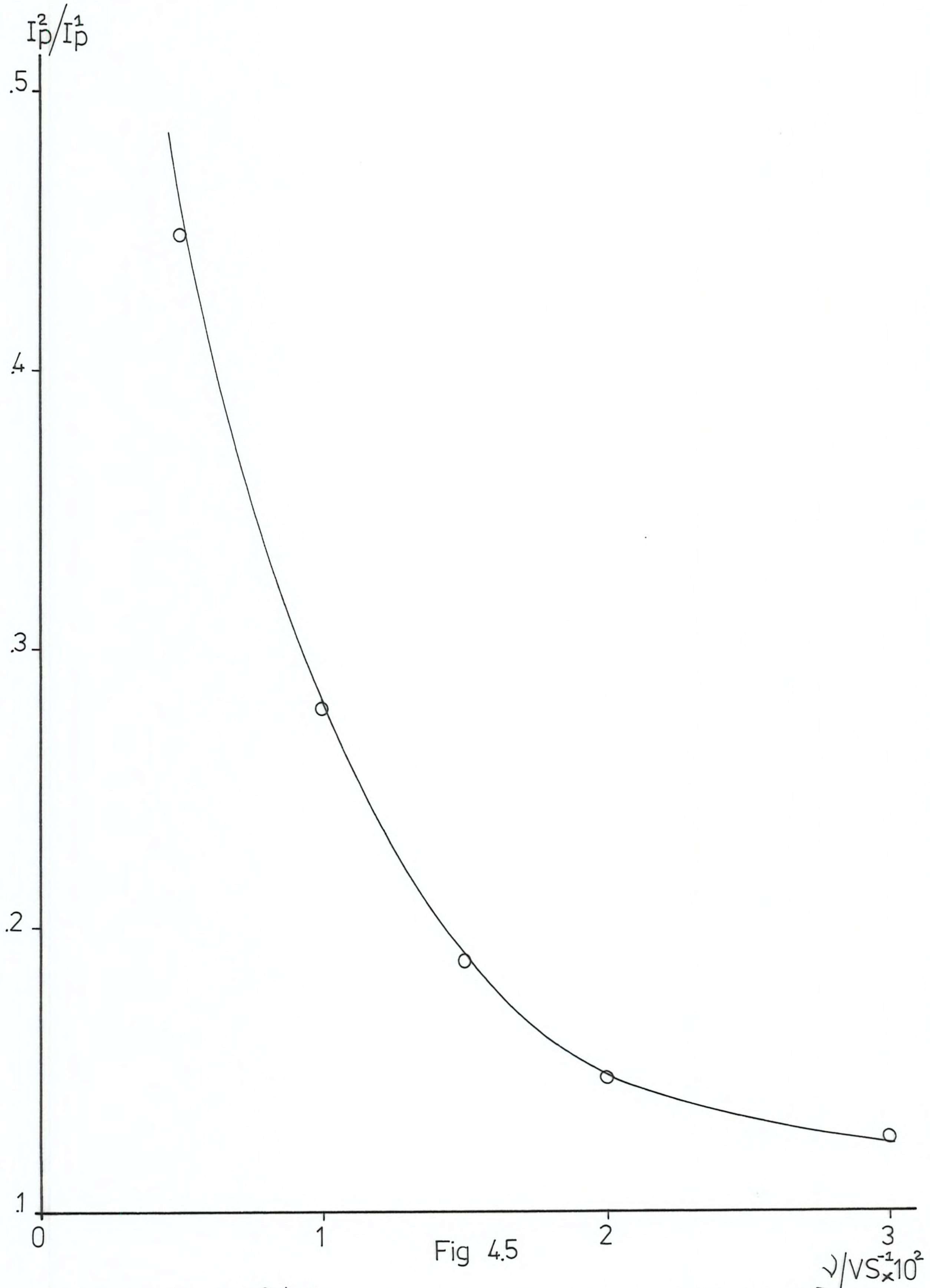


Fig 4.5

Dependence of I_p^2/I_p^1 on potential scan rate, o-$FC_6H_4NO_2$ $10^{-3}M$ in 0.1M H_2SO_4. Hg electrode.

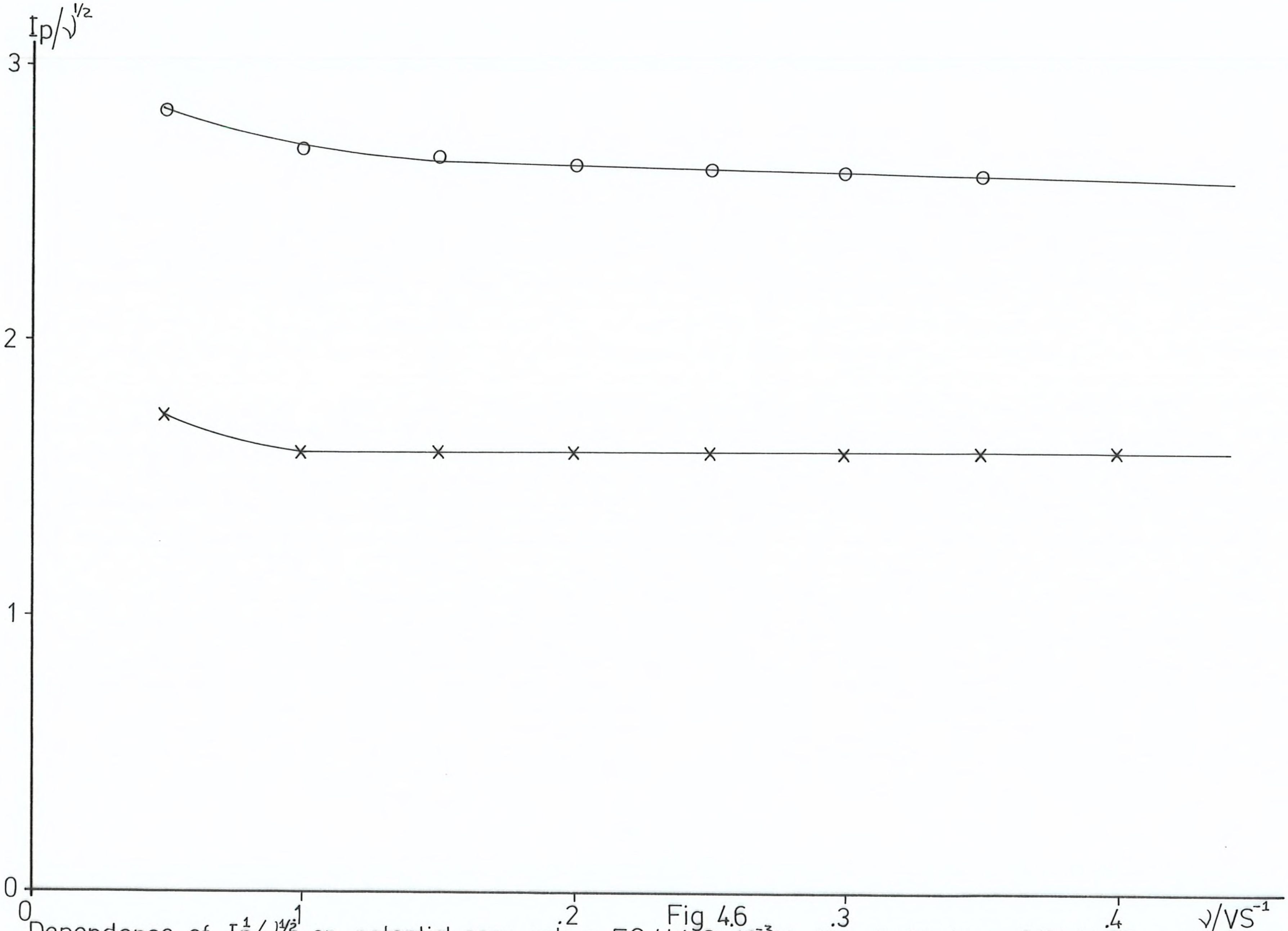


Fig 4.6

Dependence of $I_p/\nu^{1/2}$ on potential scan rate, o-$FC_6H_4NO_2$ 10^{-3}M. Hg electrode. o=0.1M H_2SO_4, x=1M NH_4Cl.

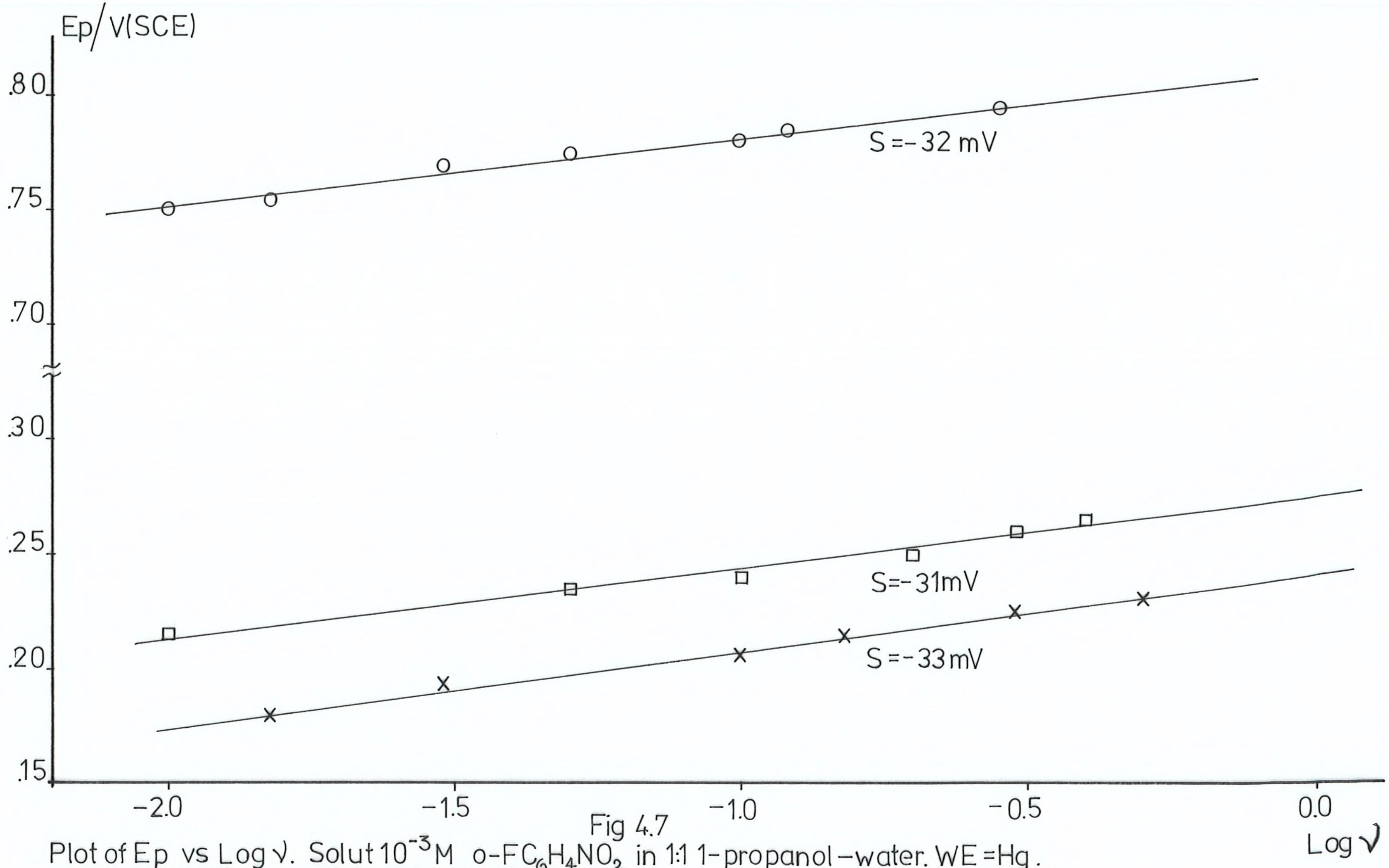


Fig 4.7

Plot of Ep vs Log ν. Solut 10^{-3}M o-$FC_6H_4NO_2$ in 1:1 1-propanol−water. WE = Hg.
o = NH_4Cl(pH=5), □ = H_2SO_4(pH=1), x = H_2SO_4(1M).

Table 4.2

Dependence of $\mathcal{E}_p$ and I_p with experimental parameters. $o\text{-}FC_6H_4NO_2$.

$$\left(\frac{\partial \mathcal{E}p}{\partial C}\right)_{H^+,\nu} = 0 \qquad \left(\frac{\partial \log I_p}{\partial \log C}\right)_{H^+,\nu} = 1$$

$$\left(\frac{\partial \mathcal{E}_p}{\partial pH}\right)_{\nu,C \atop pH > 1} \neq 0 \qquad \left(\frac{\partial \mathcal{E}p}{\partial \log \nu}\right)_{H^+,C} \cong -30 \text{ mV}$$

The I-E curves for o-fluoronitrobenzene at zinc, lead, and copper all apparently show a single reduction process although lead is covered by a lead sulphate layer and the zinc corrodes in the acid medium at the potential when the substrate reduces. Therefore, in view of the low yield at copper, mercury was used as cathode in later experiments. Lead would appear to be a good practical alternative.

The I-E curves for solutions of nitrobenzene and o-chloronitrobenzene have essentially the same form. At pH = 5 only a single irreversible reduction peak is observed while at pH = 1 two reduction processes are seen at slow sweep rates. The peak potentials and the ratio I^2_p/I^1_p vary slightly with the substituent, see Table 4.2, and the electron withdrawing groups assist the reduction to a small extent. The second reduction process for the o-bromocompound was not observed under the conditions of the experiment.

Coulometry.- Coulometry experiments were carried out at 4.5 x 10^{-2}M and saturated o-fluoronitrobenzene solutions in 50% 1-propanol/water at different cathodes and pH values. In each experiment, the current and charge were monitored as a function of time and the products were identified and estimated at the end of the electrolysis. The I-Q data was extrapolated to I = 0 in order to permit the calculation of the number of electrons transferred per molecule of the nitrobenzene. The electrode potential was always chosen to lie in the plateau region of the I-E polarization curve, and the n values obtained from the coulometry experiments range from a value of four in slightly acid solutions to six in stronger acid solutions (0.1M H_2SO_4). Most of the experiments were run on a mercury cathode as the results of the analysis suggested that this was the appropriate cathode for o-fluoroaniline production.

Coulometry experiments on o-chloro and o-bromonitrobenzene in similar conditions to that of the fluorocompound were also performed. In the cases of o-fluoro and o-chloronitrobenzene, the results show a similar behaviour. The results of the bromocompound are different (table 4.7).

IV.1.2.- Analysis.-

The analysis ofproducts was performed in a similar way to that in the previous chapter. For the g.l.c. analysis a 5% OV-17 column was used with the same temperature programme as before (page 43), well resolved peaks were obtained for both, the standards and the reduction products. The organic yield of products was calculated by comparison of the area under the peaks with those for standards of known concentration. Mass spectrometry was again used to confirm the identity of the products.

The table 4.3 shows the g.l.c. retention times and mass spectrometry data for standards and electrolysis products, and some typical chromatograms are shown in the appendix. The analysis was performed for electrolyses on copper, mercury and zinc, at different acid concentrations and these results are shown in tables 4.4, 4.5 and 4.6.

Table 4.3

Retention time and mass spectra dataElectrolysis products from the O-F Nitrobenzene electrochemical reduction

Compound	MW	RT(min)	m/e ratio (intensities)
Nitrosobenzene(l)	107	-	77(100), 51(76), 107(59), 50(25), 30(15), 27(13), 39(9), 38(9)
O-F Nitrosobenzene (p)	125	2.0	95(100), 125(84), 75(78), 43(17), 69(14), 59(14), 50(13), 51(11)
Aniline (l)	93	-	93(100), 66(39), 65(19), 39(13), 92(12), 94(8), 46.5(9), 40(5)
O-F aniline (s)	111		111(100). 83(16), 84(14), 64(10), 91(7), 112(6.5)
O-F aniline (p)	111	2.8	111(100), 83(21), 84(18), 64(16), 95(8.6), 112(8), 75(7.1), 110(4.2)

p = electrolysis product.

l = from the literature.

s = standard

IV.1.3.- Effect of the acidity of the medium

Controlled potential electrolyses were carried out in 4.5×10^{-2}M o-fluoronitrobenzene, 50% 1-propanol/water solutions on a mercury electrode, to identify the dependence of the products on the acidity of the medium. The electrode potential was fixed, as mentioned before, in the plateau region of the I-E curve.

The electrolysis of the fluorocompound at -0.9V and pH = 5 led to a low yield of the aniline and a low n-value (table 4.4). The g.l.c. trace showed the presence of some coupled product but the major product has a retention time just less than that for o-fluoroaniline. The parent peak from the mass spectrum for this product is apparently 125, Table 4.3, which is the molecular weight of o-fluoronitrosobenzene, and the fragmentation pattern is reasonable for this compound. On standing, the catholyte composition changed, the yield of coupled product increased at the expense of this major product, this is also to be expected if the product is the nitrosobenzene.

On increasing the acidity of the medium, the yield of aniline increased, and at 0.1M sulphuric acid solution the yield of the o-fluoroaniline reached its highest value (table 4.4); on further increase in proton concentration, the p-aminophenol began to form. It was also observed, that the o-fluoronitrobenzene concentration could be increased without affecting the yield of the aniline, and using a saturated solution, the yield was 79% and the current density increased to well above 100 mA.cm^{-2}.

Table 4.4

Electrolysis of 4.5×10^{-2}M o-fluoronitrobenzene in 50% 1-propanol-water solution. Effect of acidity.

WE	E	Medium	pH	n	% fluoroaniline
Hg	-.9	NH_4Cl	5.4	4.4	12.6
Hg	-.9	$OA\bar{c}/HOAc$	4.5	5.8	33.1
Hg	-.9	H_2SO_4	1.2	5.9	78.4

IV.1.4.- Effect of the cathode material

Controlled potential electrolysis and coulometry experiments were carried out to determine both the dependence of the products of the reaction with the material of the cathode, and the total number of electrons transferred n. The results are shown in table 4.5, the highest yield value for the o-fluoroaniline production was obtained on a mercury cathode (78.4% organic yield), further electrolysis were run by using this electrode as cathode.

In the case of Zn, the electrode corroded rapidly during the electrolysis, and it was necessary to replace it before each experiment. However, o-fluoroaniline was the major product. Copper gave a lower yield of the aniline.

IV.1.5.- Effect of the ortho substituent

Electrolysis of o-halonitrobenzenes were carried out in sulphuric acid (0.1M) to determine the effect of the substituent on the reduction of the nitro group, the total number of electrons transferred were also determined. The results are shown in table 4.6; as we can see, the highest percentage of the o-haloaniline was obtained for the o-fluoronitrobenzene reduction where the C-X (X = halogen) bond is strong. The yield is, however, not sensitive to substituent except for o-bromonitrobenzene where cleavage of the carbon-halogen bond is a major side reaction. The yield of o-bromoaniline is only 42% and nitrobenzene, aniline and unsubstituted coupled products could be identified in the catholyte after electrolysis, by study of their mass spectra and comparison of their retention times with those of standards or similar compounds.

Table 4.5

Electrolysis of 4.5 x 10^{-2}M o-fluoronitrobenzene in 50% 1-propanol-water solution. Effect of the cathode material

WE	E	Medium	I $mA.cm^{-2}$	n	% fluoroaniline
Hg	Plateau region	.1M H_2SO_4	30	5.9	78.4
Cu	Plateau region	.1M H_2SO_4	48	5.2	35.0
Zn	Plateau region	.1M H_2SO_4	33	5.8	65.0

Table 4.6

Electrolysis of 4.5×10^{-2}M O-X $C_6H_4NO_2$ in 50% 1-propanol-water, .1M in H_2SO_4 solution

WE	X	E(v)	I $mA.cm^{-2}$	n	% O-X aniline
Hg	F	-0.9	30	5.9	78.4
Hg	Cl	-0.9	30	6.0	76
Hg	Br	-0.9	15	4.0	42

IV.2.- Discussion and Conclusions

IV.2.1.- Preparative aspects

The selection of the reaction conditions were based on earlier studies of nitrobenzene reduction (see Chapter III), and the literature which recommended a slightly acidic medium (1). The early experiments were performed in 1-propanol/water, pH:5 solutions on copper and mercury electrodes; under these conditions, the coulometry results showed the transference of 4e in the reduction process, and the g.l.c. and mass spectrometry a high yield ($>$ 70%) of a compound molecular weight 125, thought to be the o-halonitrosobenzene, and a low yield value in the haloamine formation. In further experiments, the effect of the cathode material (table 4.5), the acidity of the medium (table 4.4), and the o-substituent (table 4.6) were studied. The results showed the best yield of the haloamine when working at the mercury electrode, the more acidic medium (.1M H_2SO_4), and the fluoro-compound as the electroactive species. Under these conditions, the organic yield of the amine was 78.4%, at a current density of 30 $mA.cm^{-2}$ (for 45 mM). Experiments using saturated solutions (0.76M) of o-fluoronitrobenzene give an organic yield of 75% at current densities values well over 100 $mA.cm^{-2}$.

The table 4.7 summarises the results of this study, and compare the tendency toward the haloamine formation with other physical properties of the C-X bond. The results show that in the cases of o-fluoro- and o-chloronitrobenzene, carbon-halogen bond cleavage does not occur, and instead good results are obtained for the haloamine formation.

Table 4.7

Tendency to o-haloamines formation by electrochemical reduction of o-halonitrobenzenes

Compound	E.A*(X^-, $Kcalmol^{-1}$)	r X^-(A^o)	$\mathcal{E}_{C-X}$($Kcal.mol^{-1}$)	Tendence observed** for C-X cleavage	% o-halo-aniline***
O-$FC_6H_4NO_2$	79.6	1.33	128	↓	78.4 ↑
O-$ClC_6H_4NO_2$	83.2	1.81	95		76
O-$BrC_6H_4NO_2$	77.4	1.96	67		42
O-$IC_6H_4NO_2$	70.8	2.20	50		-

* The data for electronic affinity (EA), ionic radius(r), and bond energy ($\mathcal{E}_{C-X}$) were taken from ref.2

X = F, Cl, Br, I respectively.

** References 3,4,5.

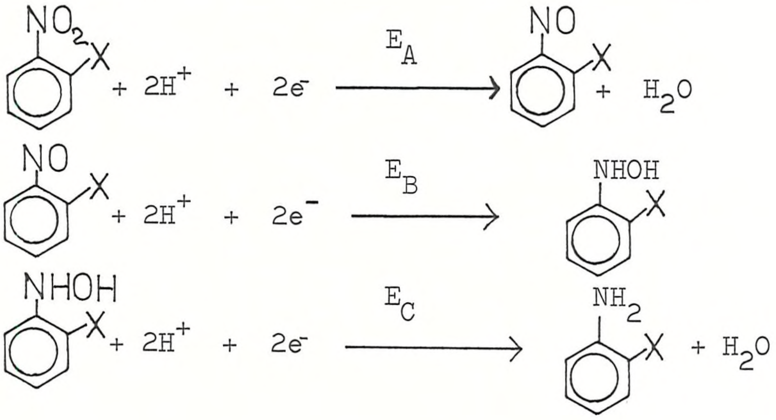
*** From this study.

The table 4.8 shows the dependence of the electrolysis products with the experimental parameters, in the cases of the o-fluoro and o-chloronitrobenzene.

IV.2.2.- Mechanism

IV.2.2.1.- o-fluoro and o-chloronitrobenzene electrochemical reduction

The products identified in the various electrolytes would suggest that the reduction occurs in three overall steps and other products arise from coupled chemical reactions.



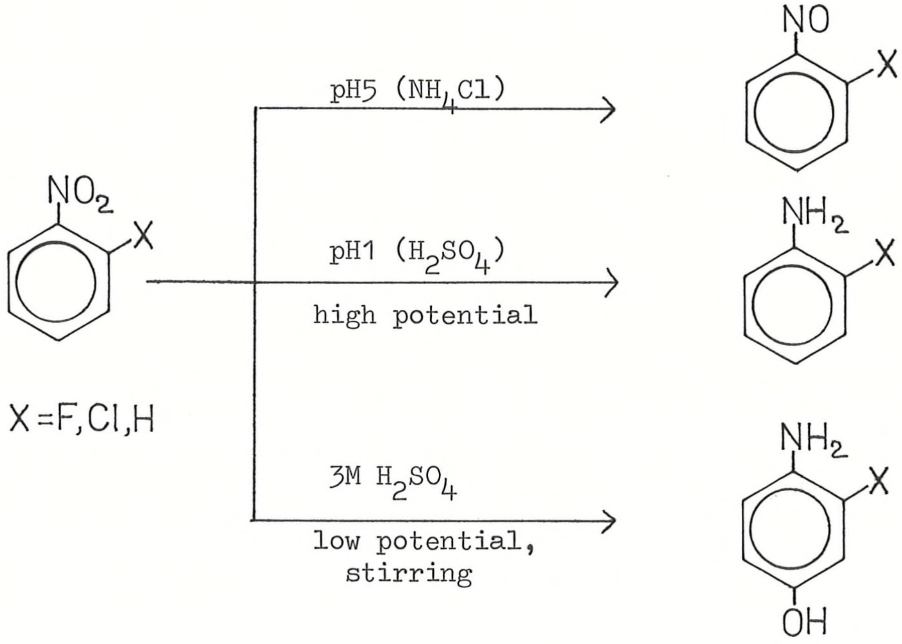
(A)

(B)

(C)

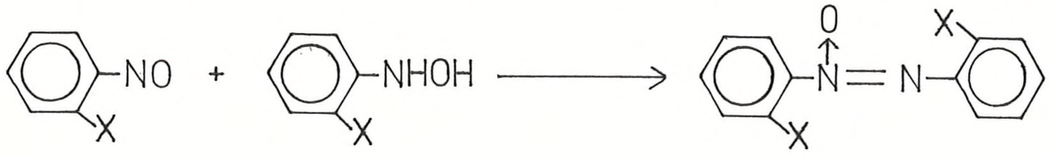
It is clear that the potential for reaction C is always negative to that for the initial reduction. The cyclic voltammograms, however, show that the peak for process C only occurs in quite acid electrolytes and at slow potential scan rates; this indicates that the first step in the reduction of phenylhydroxylamine is protonation and that this is a slow process. It is confirmed by the decrease in yield of aniline when the electrolyte is stirred, stirring causes the 4e product to be convected away from the electrode surface before protonation and further reduction can occur. If the solution is made too acidic, the protonated phenylhydroxylamine rearranges to the p-aminophenol, which can become the major reaction pathway.

Table 4.8



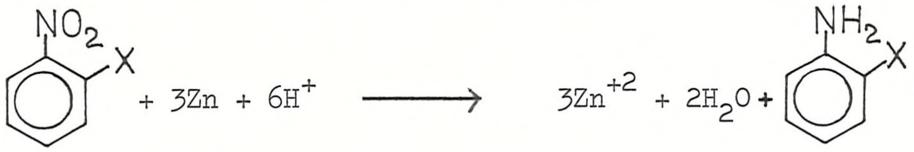
Electrode	Maximum current density mA.cm^{-2}	Yield
Hg	$>$ 100	$>$ 75*
Hg	$>$ 100	$>$ 75
Hg	$>$ 100	$>$ 40
Cu	$>$ 100	$>$ 75

* At pH5, the yield of coupling products increase on standing, as a consequence of reactions like:



It has been found that the potential, E_B, is more positive than E_A (7), and the reduction of nitrobenzene to phenylhydroxylamine never occurs as two distinct processes in the I-E curve for the nitrobenzene. The identification of o-fluoronitrosobenzene as a reduction product at pH5 is, however, good evidence for the two step nature of the reduction of o-fluoronitrobenzene to the phenylhydroxylamine. The results would indicate that the protonation of o-fluoronitrosobenzene is the initial step, and a slow one, in these conditions. This can also be deduced from the $I_p/\nu^{\frac{1}{2}}$ vs ν plot of fig.4.6. where the value of $I_p/\nu^{\frac{1}{2}}$ for the process at pH 5 is much lower than that for the first reduction reaction at pH 1. With the chloro and fluoronitrobenzenes no cleavage of the carbon-halogen bond could be detected during the reduction to aniline.

The reduction of the o-fluorocompound on Zn electrode possibly occurs by reaction of the electrode itself with the halocompound. It could well explain its corrosion under the electrolysis conditions, and previous results in this laboratory (8) show that the reaction



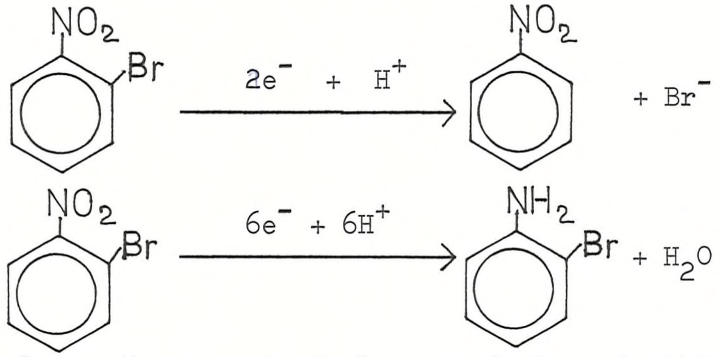
does occur. The cathodic current would in this case be largely

$$Zn^{+2} + 2e^- \longrightarrow Zn.$$

With the other electrodes used in this studies, the metals are not sufficiently strong reducing agents for this mechanism to be observed.

IV.2.2.2.- o-bromonitrobenzene reduction

In the case of o-bromonitrobenzene reduction, the analysis of reaction products showed the presence not only of the haloamine but also of nitrobenzene and aniline. These results added to a coulometric value of four are consistent with parallel processes; one a 2e process, see further, where the weaker carbon-bromine bond suffers considerable cleavage, and the other a 6e transference leading to the aniline formation.

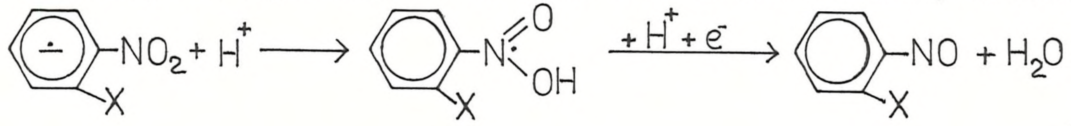


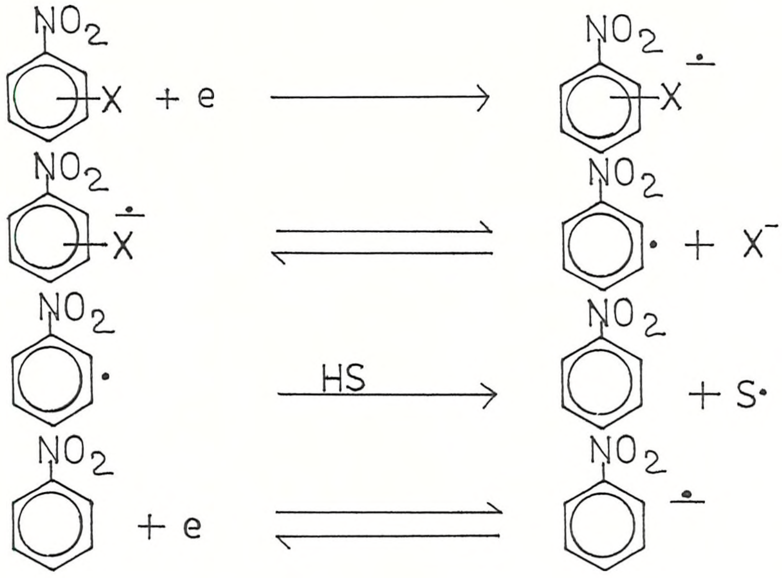
Nevertheless, the amount of cleavage is less in this medium than it is observed in aprotic media (5,9). This is not surprising since in the protonic media the anion radicals will tend to protonate before halide ion expulsion can occur.

IV.2.2.3.- General

Many studies have been reported on the electrochemical reduction of halonitrobenzenes, the most of them in aprotic media (3-6), and a general reaction mechanism (scheme below) has been proposed by Hawley and Lawless (5). They have found, that the rates of the decomposition of the anion radicals follow the order o-iodo > o-bromo >> p-iodo > m-iodonitrobenzene. In the case of electrochemical reduction of these compounds in protic solvents (as in this study), the nitro group is also reduced*, and depending on the conditions of the reaction, selective

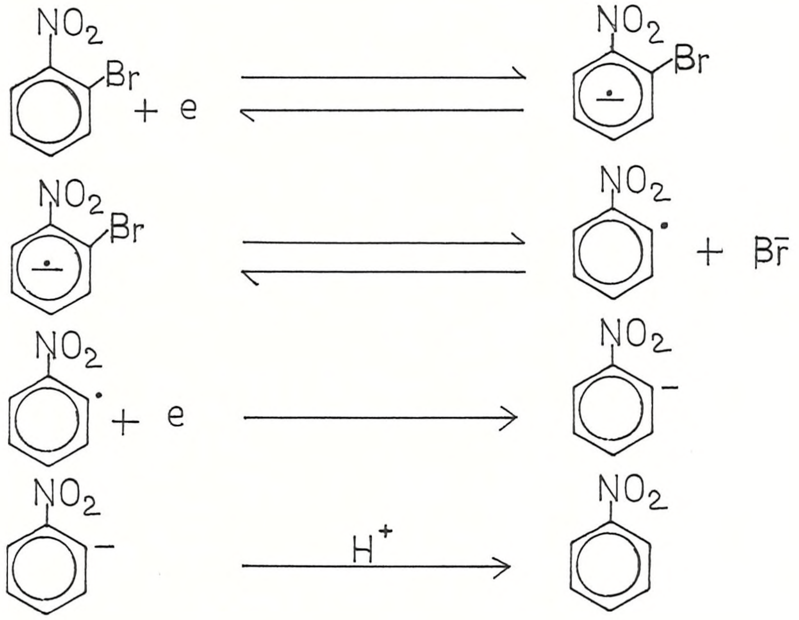
(*)





reduction can be effected. The results of this study reveal that in the cases of o-fluoro and o-chloronitrobenzenes the reduction of the nitro group occurs and no cleavage of the carbon-halogen bond was observed. The consequence was a high yield in the halo-amine product, when working in a relatively high proton concentration (.1M H_2SO_4) or a high yield in the halonitroso compound in weakly acidic medium. In the case of the bromocompound, both processes occur, the nitro group and the C-Br bond reduction, in this case, a mixture of products and a low yield in the haloamine were obtained. It was also found that the nitrobenzene general scheme of the reaction mechanisms proposed by Heyrovsky and Vavricka (10) could explain the reduction of the nitro group in these compounds. The electroanalytical and the preparative experiments from this study emphasise the importance of protonation reactions in the mechanism of this reduction process, and show that these processes are commonly slow.

In the cleavage of the carbon-bromine bond under the conditions of these experiments, it is unlikely the occurrence of the hydrogen abstraction from the solvent (step 3 in the mechanism before), instead of that, the reduction of the neutral radical could occur at the electrode surface and further protonation of the anion to form the nitrobenzene product.



Although more evidence is necessary, it could well explain the $4e^-$ transference and 42% o-bromoaniline obtained from the experiments.

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CHAPTER V

CHAPTER V

Nitrobenzene and o-fluoronitrobenzene electrochemical reduction at a parallel plate reactor with recycled electrolyte

V.1.- Comments and objectives.

The results in previous chapters revealed that the electrochemical reduction of nitrobenzene and the halonitrobenzenes is very much dependent upon the solvent, the cathode material, the electrode potential, the concentration of acid and the rate of stirring of the catholyte. But from the studies reported in Chapter III it is clear that conditions could be found where the material yield for the p-aminophenol production was over 75% at a current density of 150 $mAcm^{-2}$. Similarly from the work described in Chapter IV, conditions where anilines could be obtained in yields exceeding 75% at current densities above 100 $mA.cm^{-2}$ could be defined. In all these experiments, a batch type reactor with agitation was utilised, and after the electrolysis, the catholyte was separated and worked up to isolate the products. The data does not, however, allow any assessment of economic viability.

In this chapter, the initial scale up of these processes is considered. The conditions employed are closer to those in an industrial electrochemical process, and the data obtained allow a more realistic assessment of the economic potential of the reactions.

V.2.- Industrial cells

Cell design is of crucial importance because commercial cells must pass thousands of amperes to allow product in any quantity to be formed. For any reactor to be selected as being suitable for industrial applications, some engineering figures of merit (1) e.g. material efficiency, current efficiency, energy yield and space-time yield must be examined. The material efficiency θ (or material yield), and the current efficience $\emptyset$ (or current yield), previously determined, are defined by

$$\theta = \frac{\text{moles of starting material converted to product}}{\text{moles of starting material consumed}} \times 100 \text{ and}$$

$$\emptyset = \frac{\text{charge used in forming product}}{\text{total charge consumed}} \times 100$$

The energy yield EY (or energy consumption), and the space-time yield STY are defined as the electric power required to make unit weight of the product and the rate of production per unit volume of reactor respectively, and can be calculated from the expressions

$$EY = \frac{\text{total energy consumed}}{\text{weight of product formed}} = \frac{2.8 \times 10^{-2}\ nFV}{\emptyset\ M} \text{ Kwh Kg}^{-1}$$

(V is the cell potential and M the molecular weight of product)

and

$$STY = \frac{\text{moles of product formed}}{\text{reactor volume x electrolysis time}} \quad \text{mol x dm}^{-3} \text{ x h}^{-1}$$

In the light of this examination, a decision can be made as to whether or not the reactor is acceptable for a particular reaction. Normally, high values of these figures are desirable (except for energy yield) but they are not obtained because of parasitic or parallel reactions, high values of cell resistance or low surface area per unit volume of electrolyser. Nevertheless, one can choose the most suitable range of operation of the reactor and then optimise the economics by using a cost equation. Another important factor when designing the reactor is the cost and lifetime of the cell itself, and while this is a figure of merit difficult to quantify, it is clear that the initial cost, performance and lifetime of all cell components will affect the design of the electrolysis cell. Maintenance is another factor to be considered in cell design. Overall, cost studies suggest the use of simple cell designs with simple electrode geometry.

Chemical engineering recognises three broad types of reactor. These are:

a) the batch reactor

b) the plug flow reactor

c) the backmix reactor

and numerous examples of these types of reactor can be found in the electrochemical literature (2,3). They include among others, the capillary gap cell (4), the parallel tubular cell (5), the rotating shear flow cell or pump cell (6), the packed bed cell (7), the bipolar fluidised cell (8), the bipolar trickle tower cell (9), the fluidised bed cell (10), the bipolar packed bed cell (11), etc.

In practice the reactor system may be more complex. It is possible to introduce partial or complete recycle of the outlet stream, to consider the use of multistage setups with reactors in series or parallel and to introduce feed or heat management between stages. In any case all these factors must be taken into account when considering the cost of the electrolytic process.

V.3.- Cell used in this study

In all this work, a parallel plate reactor was utilised. The selection was made on the basis of a qualitative evaluation of practical requirements for an industrial cell i.e. simple electrode geometry, simple cell design, low cost, long life, etc. The two metal plates (WE = Cu, SE = Pb) were 56 cm^2 in area and fixed parallel to each other at a distance of 1 cm, and separated by a Nafion cationic membrane incorporated to avoid the mixture of catholyte and anolyte. The cell body was an acid resistant material (PTFE), and the two ends of the cell were open, with a special design (fig. 25) which allowed a uniform flow distribution of electrolyte over the electrodes. The cell was designed with separated and recycled anolyte and catholyte flows for the same reason as before. In all the experiments, the maximum flow rate was utilised and under these conditions, the Reynolds number defined by

$$Re = \rho \frac{\bar{v}.d}{\mu}$$

where ρ = electrolyte density

$\bar{v}$ = mean linear velocity

d = equivalent diameter

μ = viscosity

was $$Re = 1.1 \times \frac{0.57 \times 1.6}{1.10^{-2}} = 100$$

This corresponds to laminar flow conditions.

V.4.- Results of the parallel plate reactor

The electrochemical reduction of nitrobenzene and o-fluoronitrobenzene were carried out in this flow cell, in order to investigate the dependence of these reactions on scale. The flow circuit was shown in fig.2.7 . The electrochemical reduction of nitrobenzene to p-aminophenol was studied first, and in view of the results in chapter three, the experiments were run in strong acidic media and at the highest flow rate allowed by the arrangement. The results are shown in table 5.1. In the experiment at 100 $mA.cm^{-2}$, the p-aminophenol yield was lower compared with the results in the small batch cell, but an unexpected increase in yield was found at higher current densities. This can only be attributed to local heating caused by the high current circulating through the cell (it is known and confirmed by the previous results that an increase in temperature is favourable for the rearrangement of the phenylhydroxylamine to p-aminophenol). If the current density is further increased (i.e. to 500 $mA.cm^{-2}$) the complete reduction to aniline became the main reaction, and some parallel hydrogen evolution occurs.

The effect of lowering the acid concentration was investigated. The use of a very high sulphuric acid concentration produces problems in any extraction circuit. Hence it was hoped that under rapid flow conditions, where the proton in the reaction layer at the electrode surface is rapidly replaced, p-aminophenol might be formed in less acid conditions. It can be seen that this hope was not fulfilled and, indeed, as at higher current density, aniline is formed in excellent yields, see table 5.2. Particularly at a current density over

Table 5.1

Reduction of Nitrobenzene (0.1M) in 50% 1-propanol/water containing sulphuric acid 3M

Cathode	Flow rate L/h	I(mA.cm^{-2})	Temperature	Products (% $C_6H_5NO_2$)	
				Aniline	p-aminophenol
Cu	18	100	room	25	52
		100	70°C	32	68
		200	room	24	76
		250	room	10	76
		500	room	88	11

300 mA.cm^{-2} the aniline yield is very high, a value as high as 90% organic yield can be obtained at .5 A.cm^{-2}. The electrolysis of o-fluoronitrobenzene at a current density of .2 A.cm^{-2} and .1M H_2SO_4 solution yields 75% organic yield and 70% current yield. Since high material yield and current yield values for the anilines formation were obtained at this high flow rate, the effect of lower flow rates was not studied.

V.5.- Discussion

As discussed above, the development of industrial electroorganic processes remains a challenge, mainly because of the requirements of space-time yield and energy consumption. Although the parallel plate cell fulfils the need for simple and cheap design, these types of cells have a low surface area per unit volume leading to a low space-time yield. For reactions which are limited by the mass transfer of the substrate, the capacity of the cell can be increased by increasing the mass transfer rate and this can be achieved by flowing the electrolyte along the surface of the electrode or by the rotation of the working electrode. In this way high current density values are obtained. From a practical point of view i.e. cell size, system design, etc. flowing electrolyte is, obviously, to be preferred. Since the results obtained in a batch cell (Chapter 3) suggested the use of a well agitated medium for p-aminophenol production, in this system the experiments were performed at the highest possible flow rate (18 L/h). The Reynolds number calculated under these conditions was 100 which indicates

Table 5.2

Reduc tion of Nitrobenzene (0.1M) in 50% 1-propanol-water

Room temperature. Lead anode.

Cathode	Flow rate (Lh^{-1})	I($mA.cm^{-2}$)	Organic yield		Curent Yield (%)	Medium
			Aniline	p-aminophenol		
Cu	18	500	89	11	70	3M H_2SO_4
		200	85	15	75	1M H_2SO_4
		200	95	5	93	0.1M H_2SO_4

flow of electrolyte under laminar conditions. The mass transport rate could be increased substantially by introducing turbulence promoters e.g. a plastic net close to the plate electrode. The results also show the effect of the local heating achieved by the high current passing through the cell and confirmed more effectivity when the electrolyte was heated externally.

In the table 5.3 the results of this study for p-aminophenol production are compared with those from other studies in which different cell designs have been used and we can see that they compare well with these other attempts to produce p-aminophenol.

Electrolyses in more dilute acid solutions led to aniline rather than p-aminophenol. Under the conditions - current density 200 $mA.cm^{-2}$, 18 L/h flow rate and 0.1M sulphuric acid, the aniline is produced at 95% and 93% organic yield and current yield respectively. In the case of o-fluoronitrobenzene reduction to the o-fluoroaniline, these values were 75% and 70%. The energy efficiency was calculated in several of the experiments (table 5.4) and they show that at high current density values the consumption of electric power also increases although there is no appreciable change in the material yield. Hence an increased output of products (STY) is obtained but at the cost of EY. The results reveal that the best conditions for p-aminophenol production in this system are, the use of a high flow rate (18 L/h), a current density in the range .2 to .25 $A.cm^{-2}$ and a strong acidic medium (3M H_2SO_4). Under these conditions, the aminophenol was produced at a 76% material yield and 5.7 Kwh Kg^{-1} energy yield. In the case of the anilines, dilute acid solutions (.1M H_2SO_4) must be used and it was possible to obtain 95% material yield and 10 KwH Kg^{-1} energy yield in these cases.

Table 5.3

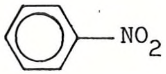
Compound reduced	Product formed	Yield %	Amperage of Cell(A)	Cell Voltage(V)	Operating c.d.(A/dm^2)	Comments	Ref.
	p-aminophenol	-	400	4.5-5.5	20-25	rotating electrode cell WE = Cu	(12)
	p-aminophenol	80 (current yield)	-	-	4	fixed bed porous flow-through electrode. WE = monel	(13)
	p-aminophenol	76 (org.yield)	17	3-8	20-25	parallel plates cell with flow. WE = Cu	this study

Table 5.4

Compound reduced	Product formed	Amperage of cell (A)	Cell Voltage (V)	Operating c.d.(mA.cm^{-2})	Energy Consumption KwH Kg^{-1}
$C_6H_5NO_2$	p-aminophenol	11.2	4	200	5.7
	aniline	11.2	4	200	10
	aniline	28	10	500	27
o-$FC_6H_4NO_2$	o-F aniline	11.2	4	200	14

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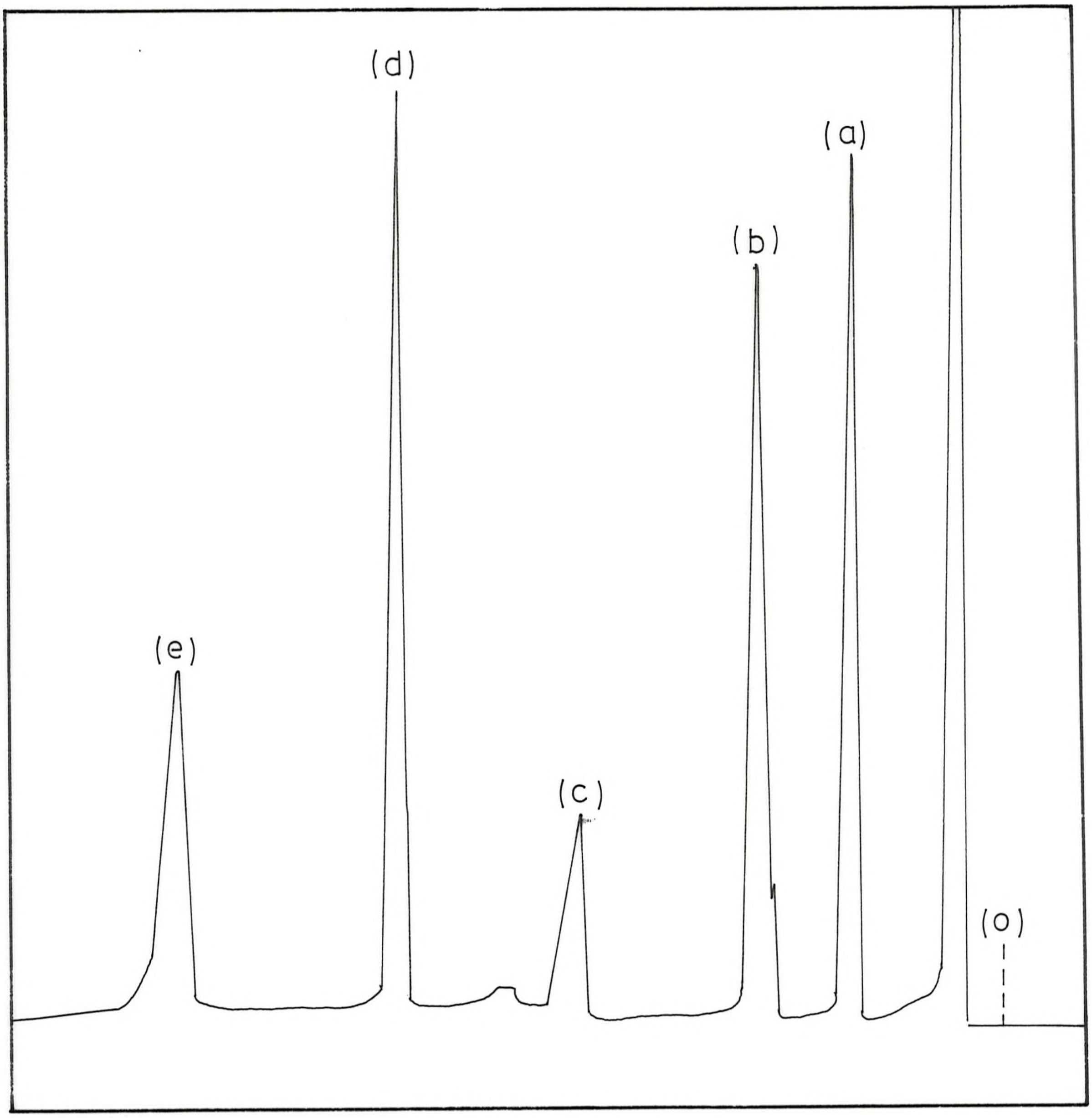
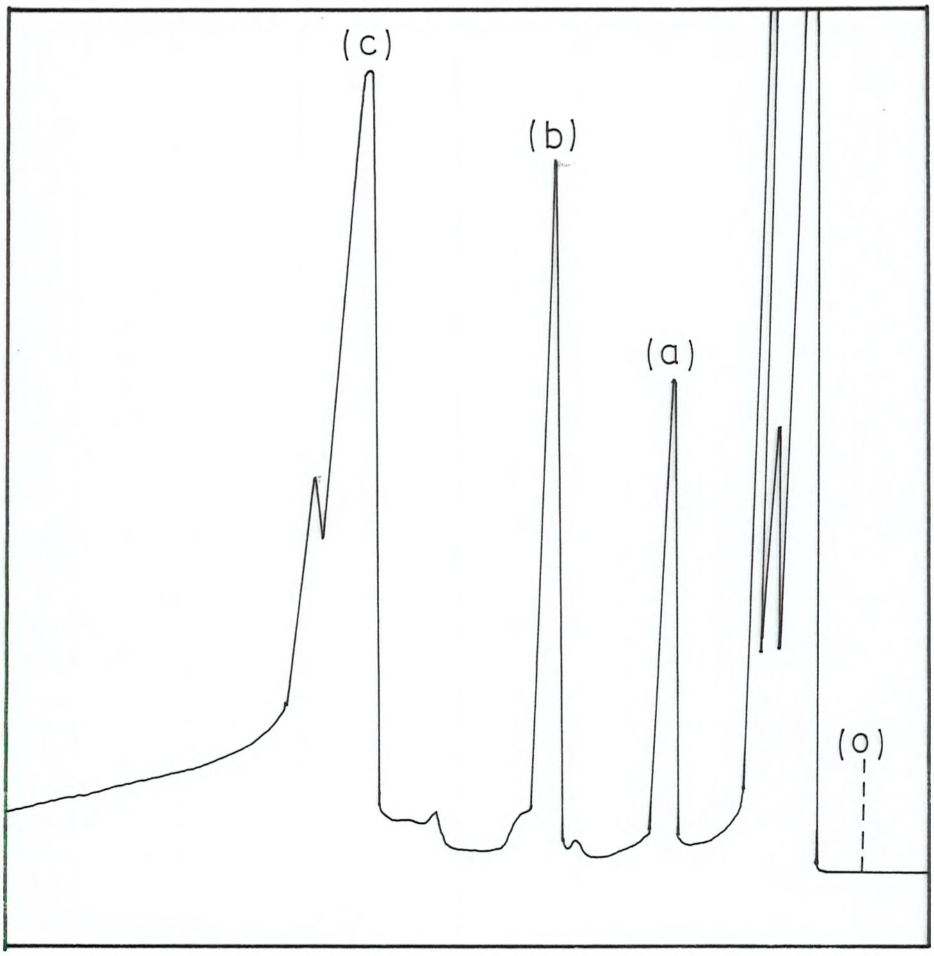
APPENDIX

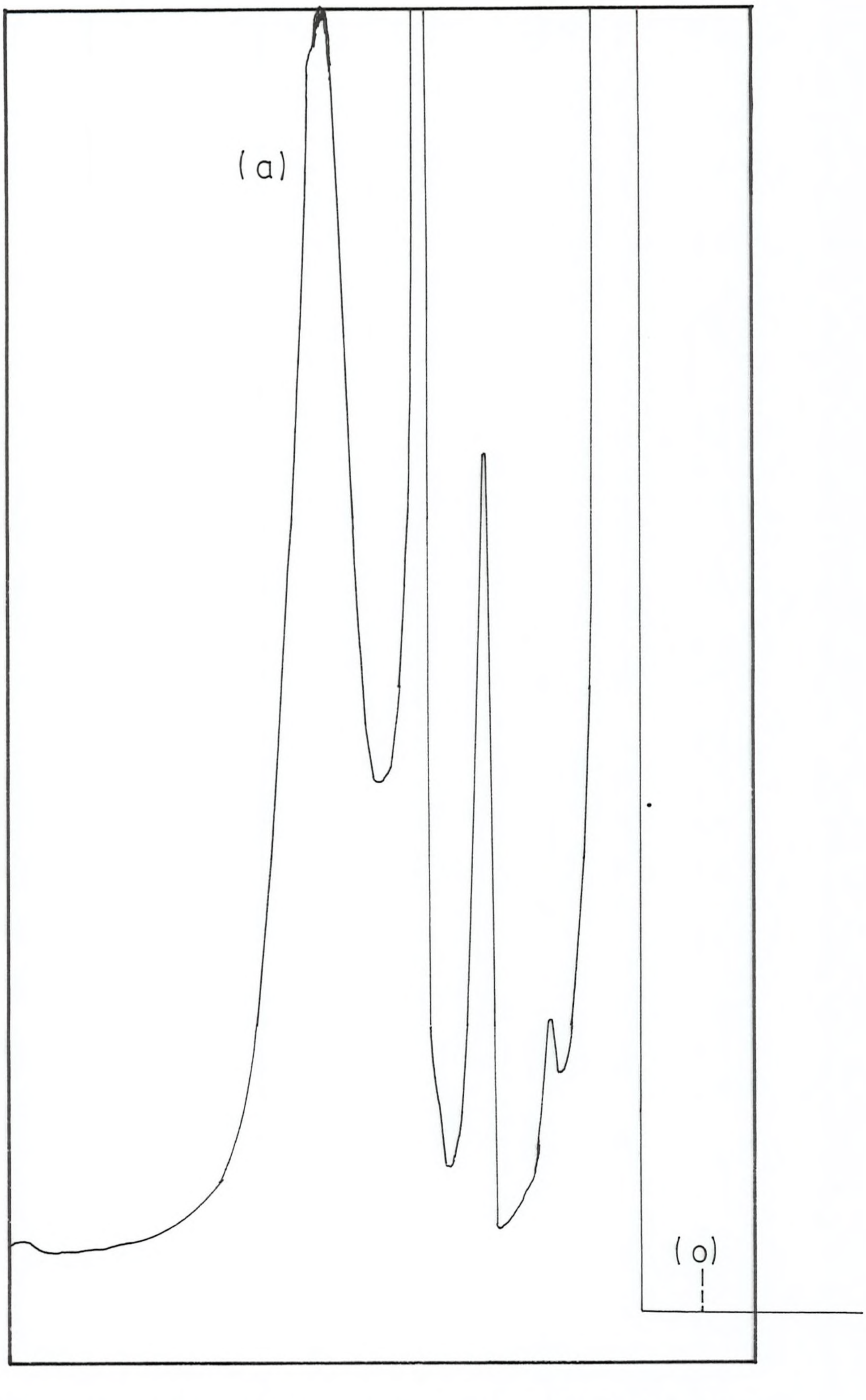
GLC Chromatograms and Mass Spectra of standards and electrolyses products



Chromatogram of standards. (a) aniline, (b) nitrobenzene, (c) p-aminophenol, (d) azobenzene, (e) azoxybenzene. (a) = (b) = (c) = 5×10^{-2} M (d) = (e) = 2.5×10^{-2} M

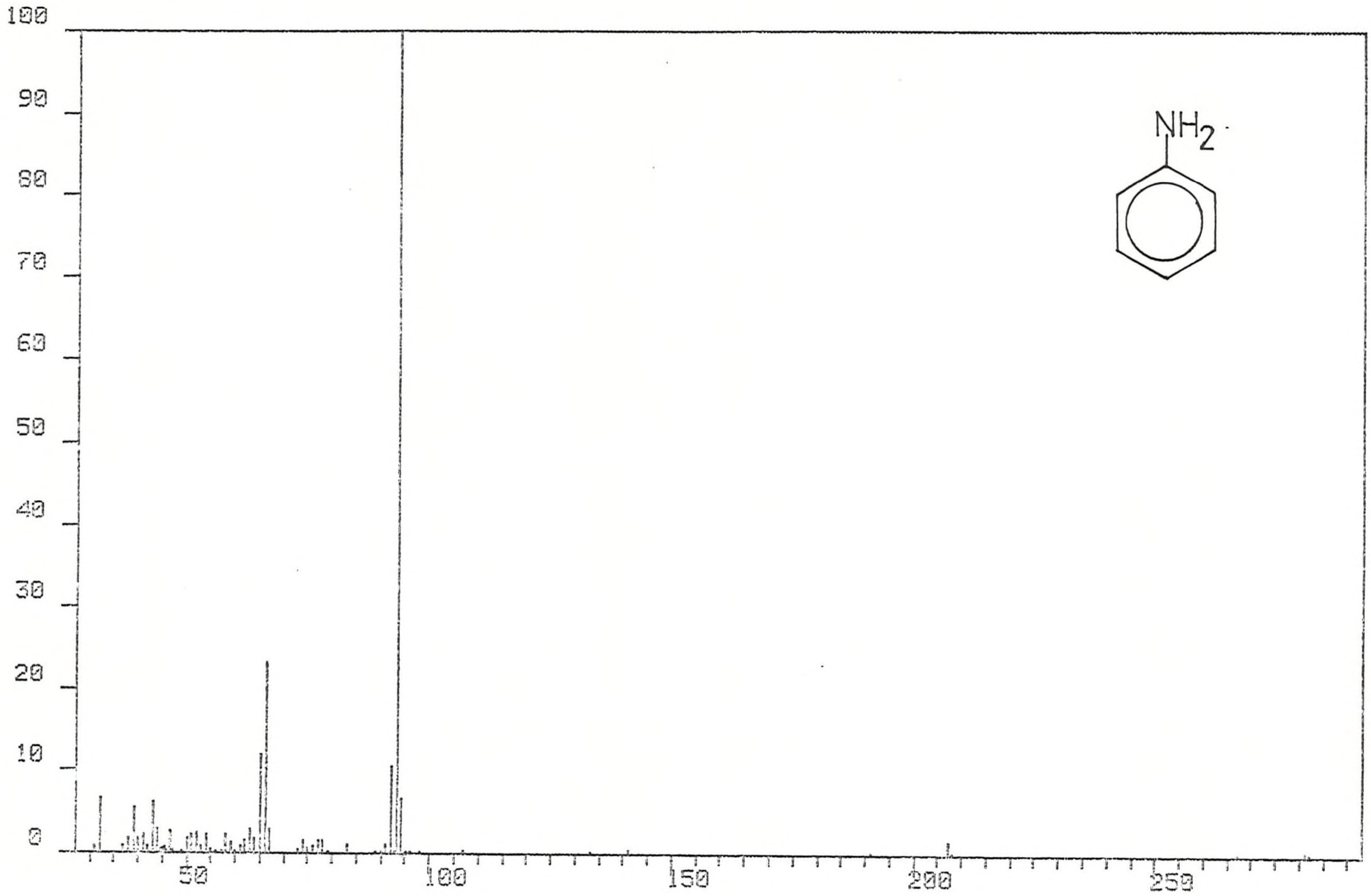


Chromatogram of the electrolysis of nitrobenzene in acetone-water, 3M H_2SO_4 at copper electrode. V=-.33 volts. (a)=aniline, (b)= nitrobenzene, (c) =p-aminophenol.



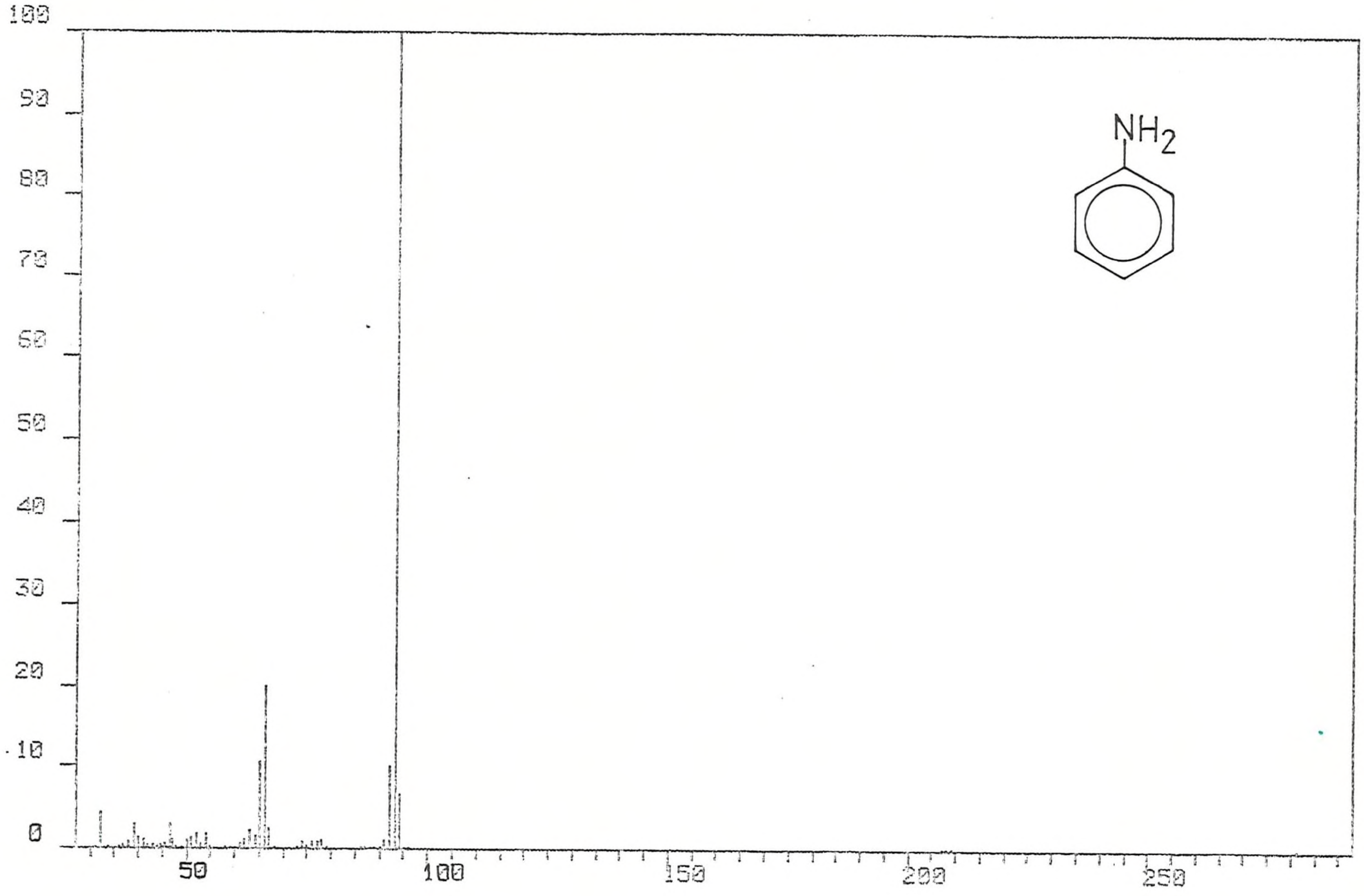
Chromatogram of the electrolysis of nitrobenzene in propanol-water, 3M H_2SO_4. Flow system $I = 200\ mA.cm^{-2}$. (a) = p-aminophenol

DS-50 MASS INTENSITY REPORT:
59JM2.17 [TIC=34341, 100%=14182] EI



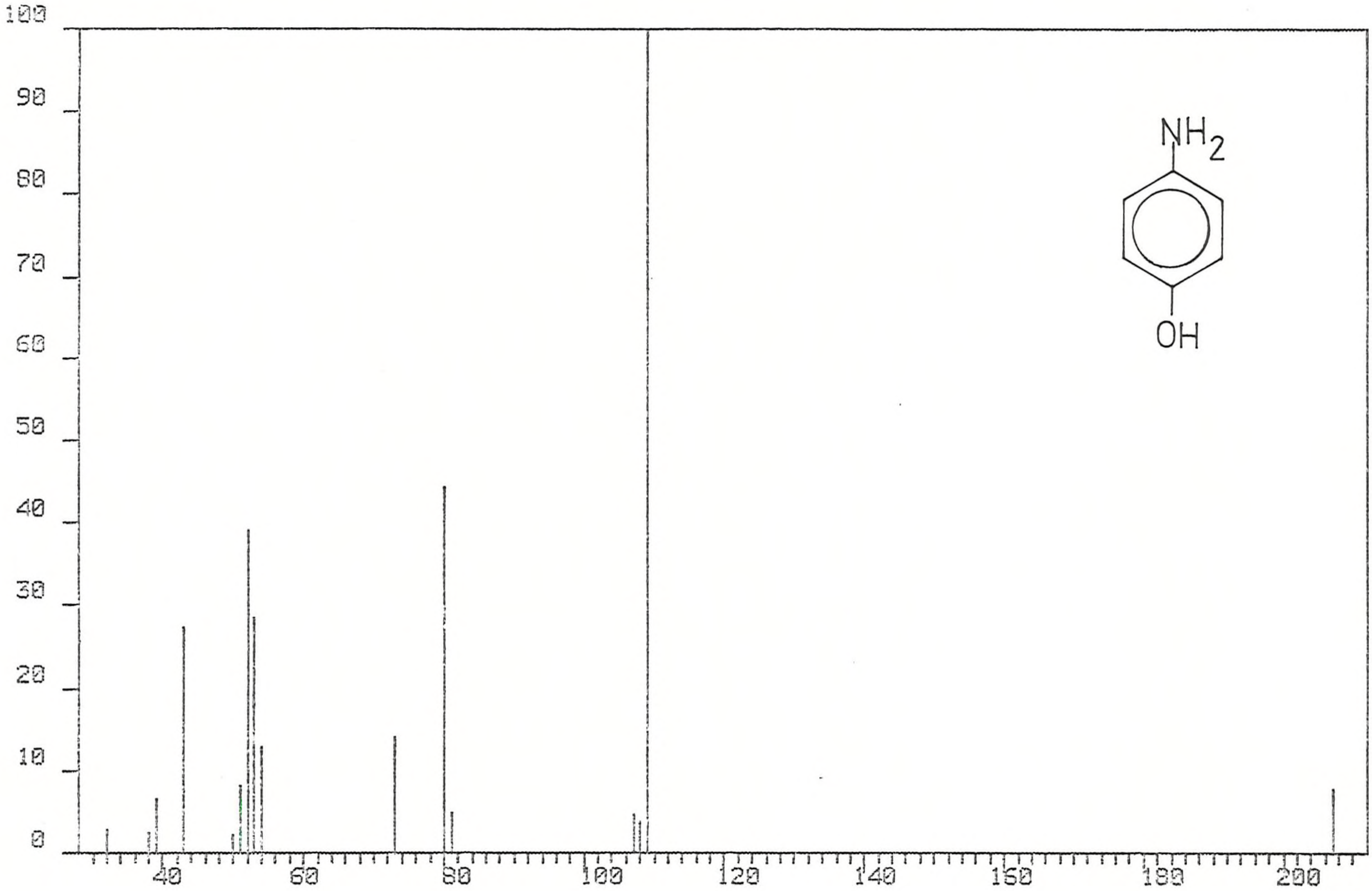
Mass Spectra of Sample (reduction of nitrobenzene at copper electrode). Aniline peak.

DS-50 MASS INTENSITY REPORT:
59JM1.35 [TIC=220673, 100%=112308] EI



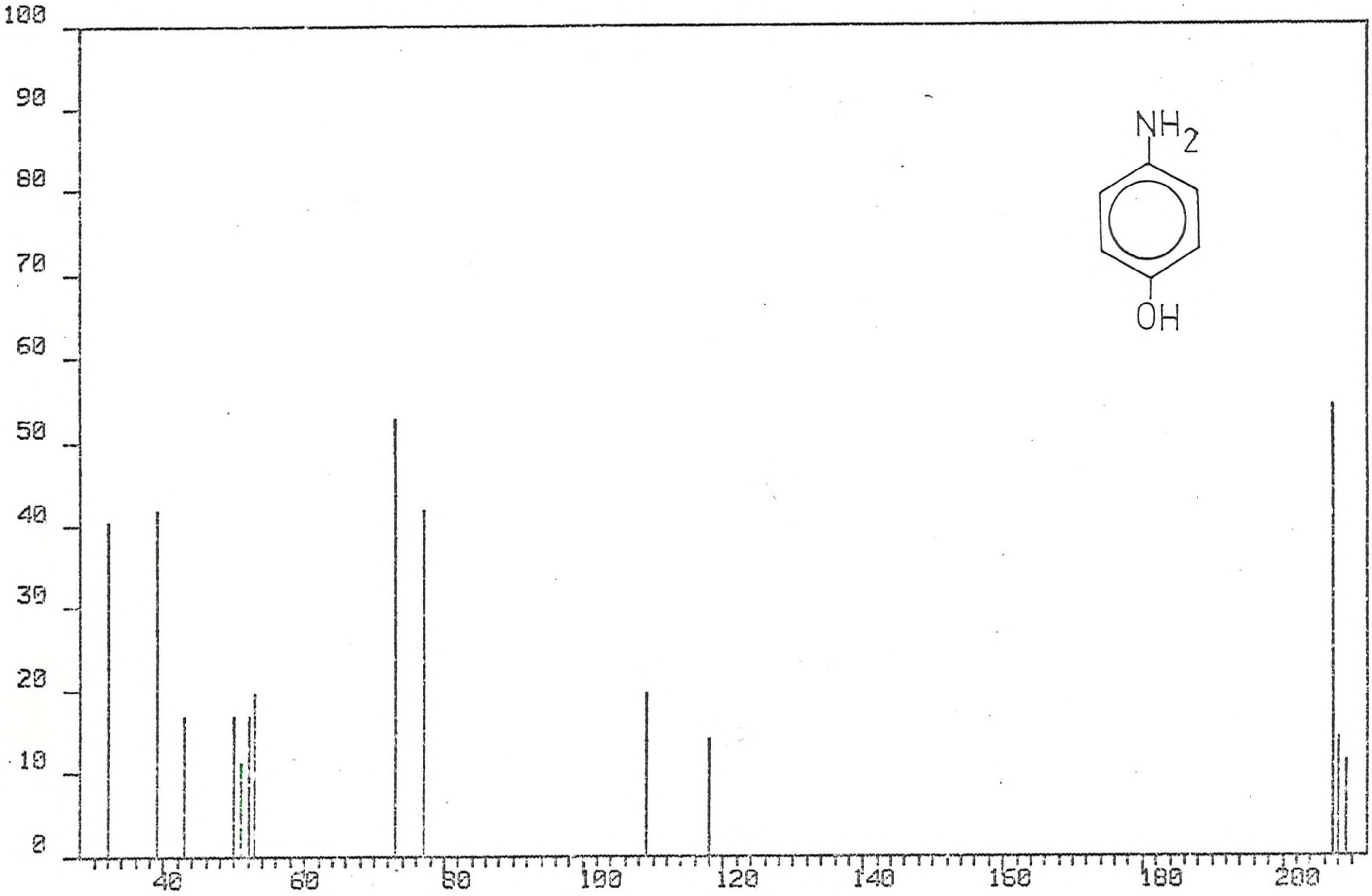
Mass Spectra of Standards. Aniline peak (2 mg/ml).

DS-50 MASS INTENSITY REPORT:
59JM7.9 [TIC=1352, 100%=359] EI

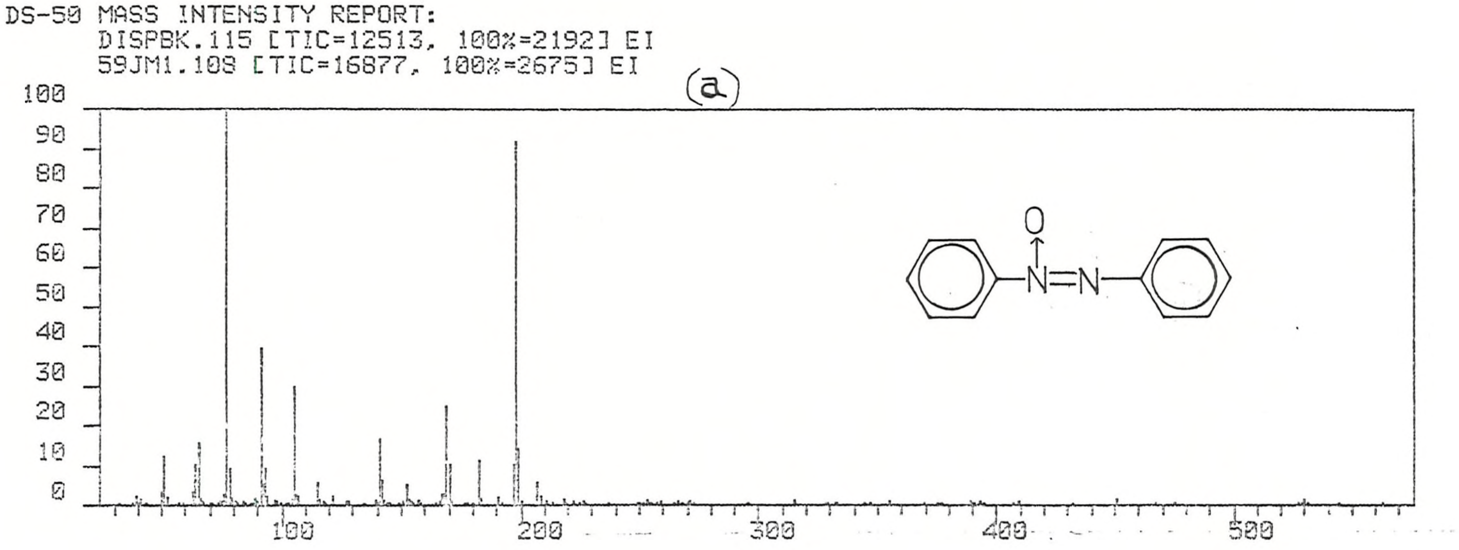


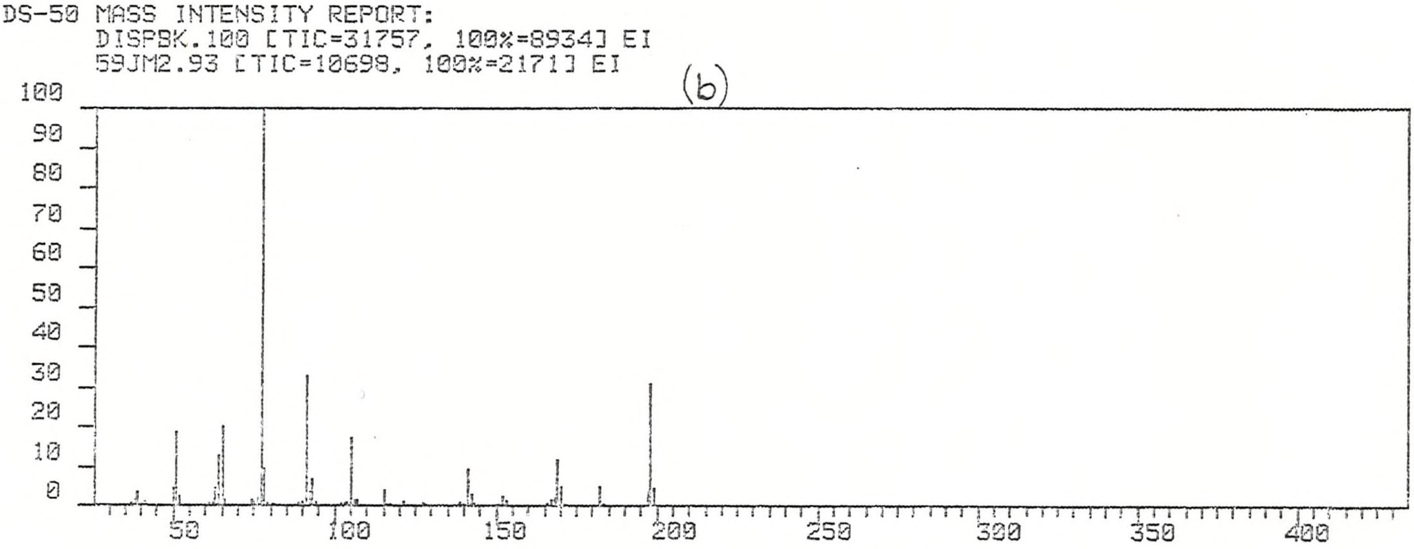
Mass Spectra of Standards. p-Aminophenol peak (2 mg/ml).

DS-50 MASS INTENSITY REPORT:
59JM6, 10 [TIC=372, 100%=72] EI



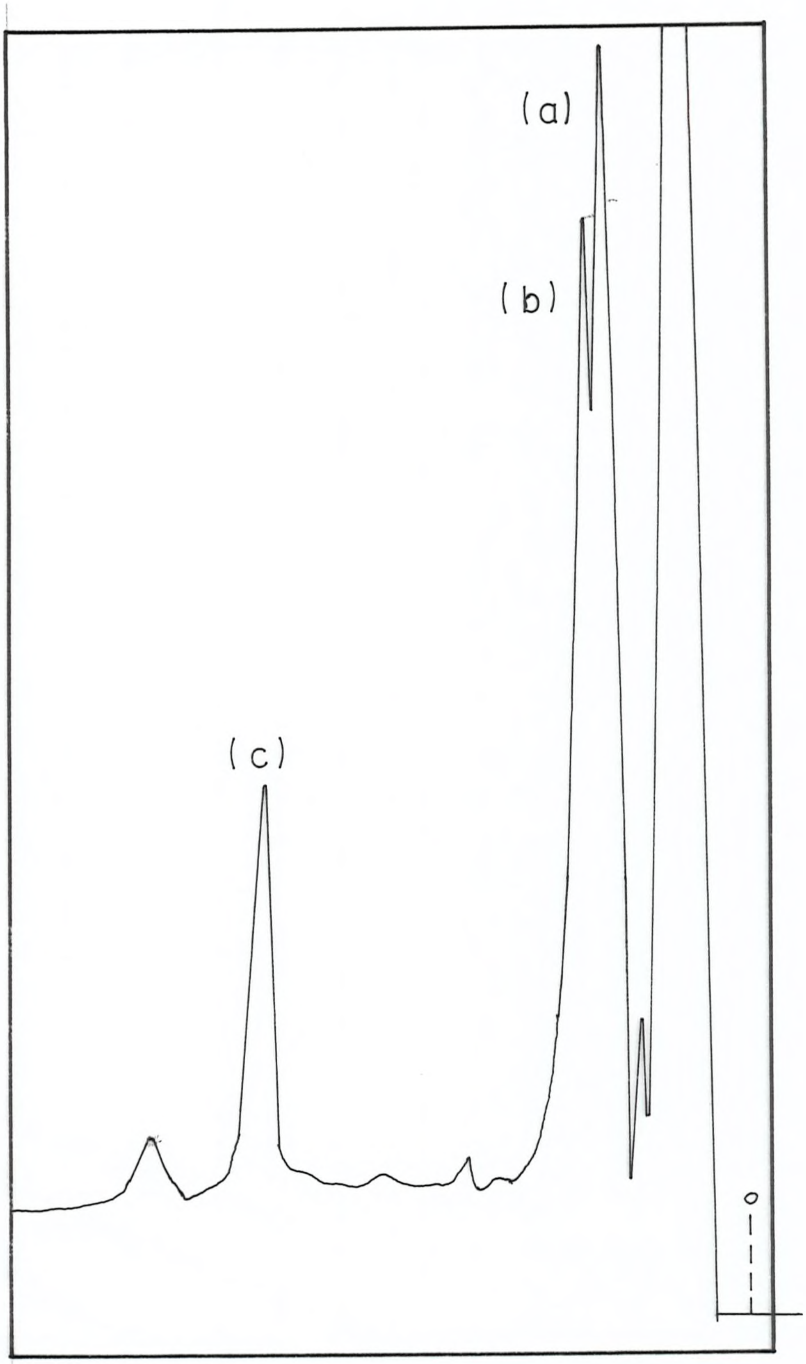
Mass Spectra of sample (reduction of nitrobenzene at copper electrode). p-Aminophenol peak.





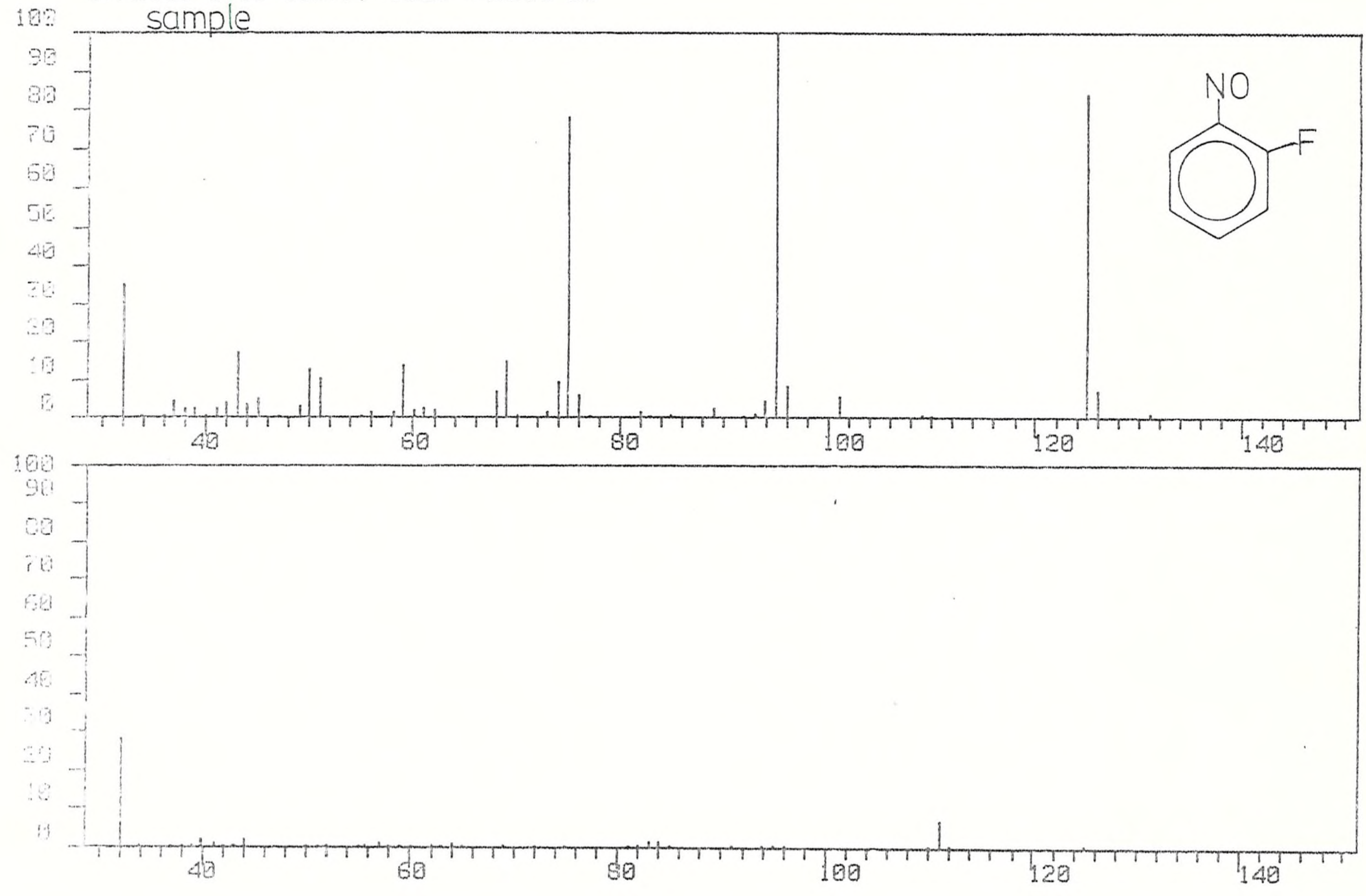
a).- Mass Spectra of Standards. Azoxybenzene peak (2 mg/ml)

b).- Mass Spectra of Sample (reduction of nitrobenzene at copper electrode). Azoxybenzene peak.

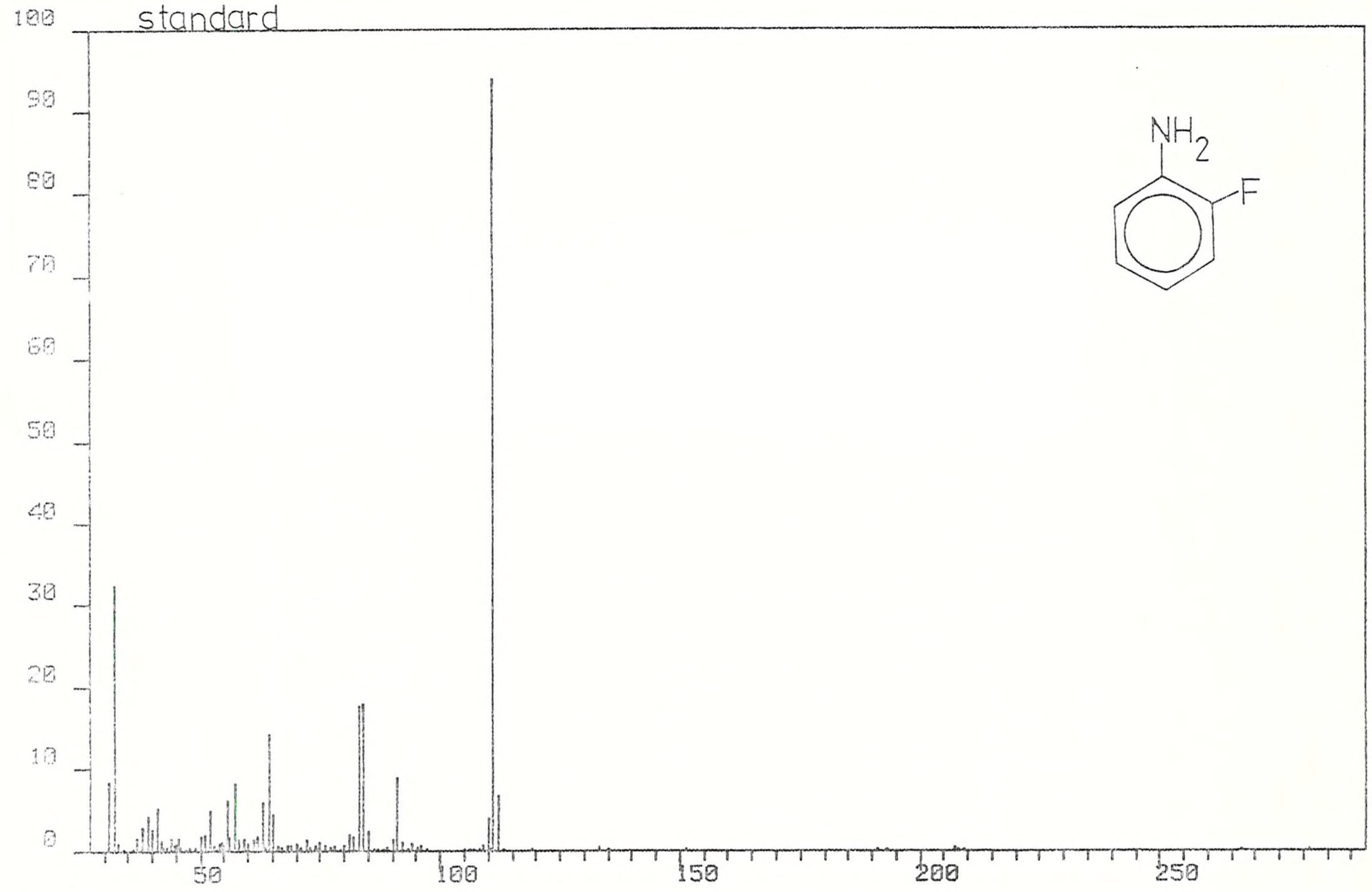


Chromatogram of the electrolysis of o-fluoronitrobenzene in propanol-water, 1M NH_4Cl on Hg. (a) = o-FC_6H_4NO, (b) = o-$FC_6H_4NH_2$ (c) = o,o'-difluoroazobenzene.

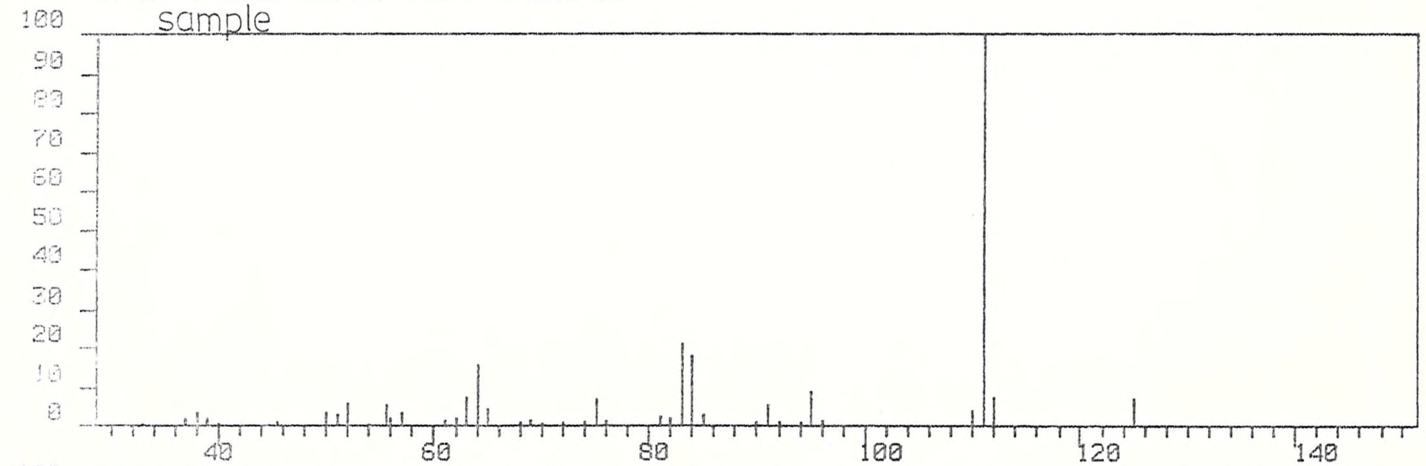
DS-50 MASS INTENSITY REPORT:
DISPBK.20 [TIC=15880, 100%=3097] EI
57M2.29 [TIC=83577, 100%=44091] EI



DS-50 MASS INTENSITY REPORT:
59JM1.11 [TIC=278070, 100%=52723] EI



DS-50 MASS INTENSITY REPORT:
DISPBK.25 [TIC=11456, 100%=4326] EI
57M2.13 [TIC=95038, 100%=48435] EI



100