

Electrochemical Studies of Organic Compounds
in Zinc Electrowinning Circuits

by

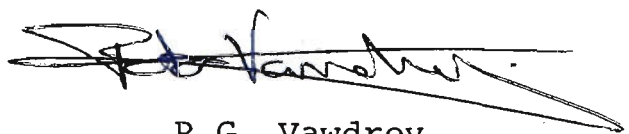
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This thesis is submitted to the Ballarat College of
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requirements for the degree of Master of Applied Science.

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A handwritten signature in black ink, appearing to read 'P.G. Vawdrey', with a long horizontal flourish extending to the right.

P.G. Vawdrey

July, 1986

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PROJECT AIM

The project was suggested to the author by Dr. T. Biegler, Division of Mineral Chemistry, CSIRO, following a background briefing by staff of the Electrolytic Zinc Company, Risdon, Tasmania.

The objective of the project was to determine the origin of organic impurities detected in the zinc electrowinning electrolytes, establish their electrochemical pathway, and determine their effects on zinc current efficiency at the Risdon plant.

SUMMARY

Most of Australia's zinc production is by the electrolytic zinc process, in which zinc is electrowon from an acid sulphate solution. The process is known to be exceptionally sensitive to the presence of trace impurities. At the Electrolytic Zinc plant (Risdon, Tasmania), isobenzofuranone (phthalide) has been detected in the electrowinning circuit, and found in higher concentrations during current efficiency slumps.

It was found that di-2-ethylhexylphthalate, (present in the liners and plastics used in the electrowinning circuit), is reduced to isobenzofuranone under the electrolysis conditions employed. In addition, an investigation involving a constant current electrolysis of a synthetic zinc electrolyte, has identified an additional pathway for the production of isobenzofuranone. 2-Naphthol, added to the electrolysis circuit for current efficiency purposes, is also a major precursor of isobenzofuranone. 2-Naphthol and possibly 1-nitroso-2-naphthol can be oxidized to phthalic acid, either at a lead anode or via anode oxidation products, and the phthalic acid produced can then be reduced to isobenzofuranone at a zinc cathode.

In addition, it was found that isobenzofuranone is further reduced at the potential of zinc deposition to ultimately yield 2-methylbenzaldehyde. This compound, which has also been detected in Risdon plant electrolytes, is also toxic in the zinc electrowinning circuit.

The compound 2-methylbenzyl alcohol has also been detected via a GLC examination of Risdon plant liquors. However, this compound was not detected in the present investigation, and thus no explanation can be offered for its presence in plant electrolytes.

The toxicity of zinc electrolyte impurities on current efficiency was determined by a cyclic voltammetric technique. The results of this investigation indicate that the presence of isobenzofuranone and 2-methylbenzaldehyde can significantly lower current efficiency, and the compounds phthalic acid and 2-methylbenzyl alcohol also lower efficiency.

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CHAPTER 1: INTRODUCTION

1.1 General Introduction

About 70% of the world's, and the majority of Australia's, zinc production is by the electrolytic zinc process, in which zinc is electrowon from an acid sulphate solution. The process is known to be exceptionally sensitive to the presence of traces of metallic impurities in the electrolyte and careful purification measures are employed. Impurities act by increasing the rate at which hydrogen is evolved at the surface of the deposited zinc or the under-lying aluminium cathode, thereby decreasing the current efficiency for zinc deposition and increasing the energy costs of the process.

Detailed understanding of the electrochemical basis for toxic metal impurity effects is lacking. Moreover, it has recently been recognized that various organic compounds, present either as adventitious impurities or as residues of materials intentionally added at other stages of the process can have a major effect on current efficiency. It is suspected that the worst effects of these compounds occur in combination with metallic impurities such as cobalt. Little is known about the sources of the adventitious organic impurities and nothing about their mode of action.

1.2 The Zinc Electrowinning Circuit

The zinc ore mainly zinc blende (spharlerite) ZnS , usually found in association with galena, PbS , is concentrated at or near the mine and then transported to the zinc plant.

The Electrolytic Zinc process at Risdon^(1,2) is a continuous cyclic one. The zinc concentrate is roasted to form zinc oxide ("calcine"), and the roaster gas subsequently used for the production of sulphuric acid. The roasted concentrate is then leached with dilute sulphuric acid (approximately 1 molar), freed from aluminium and iron by adding excess of calcined material, cadmium and copper by agitation with a little zinc dust, nickel by the addition of dimethylglyoxime and the cobalt by the addition of 1-nitroso-2-naphthol. The purified zinc sulphate/sulphuric acid solution is then electrolysed at about 35°C in rectangular, lead-lined or PVC laminated wooden cells, using lead sheet anodes and thin aluminium sheet cathodes. Lead is chosen because it is almost insoluble in the acid electrolyte solution. The metal is even more efficient if it is alloyed, as is common practice, with 0.5 and 0.75% silver. Aluminium is used because, besides being a very good conductor, it is a comparatively easy matter to strip the deposited zinc from the cathode after electrolysis. The addition of a little glue or gum arabic to the electrolyte aids the efficient deposition of zinc on the cathodes. Oxygen is evolved at the anode and, as more hydrogen ions are formed, the sulphuric acid is regenerated and recirculated. Cells operate in the range 3.2 to 3.6V and a high current density (Electrolytic Zinc, Risdon operate at 409Am^{-2}), metal more than 99.9% pure being obtained. The cathodic zinc is melted and cast into ingots and blocks, and used in the production of alloys.

1.3 Impurities in Zinc Electrowinning Circuits

Electrical efficiency is of paramount concern in any industrial electrolytic process. Marked reductions in current efficiency (by as much as 60%) can occur with impurity concentrations of the order of $0.1 \text{ ppm (mgdm}^{-3}\text{)}$ (3-5). Although the concentration of a particular impurity can be lowered, at some cost, by an appropriate purification of the leach solution, this does not necessarily lead to a corresponding increase in current efficiency, as synergistic effects may be operative (6). In addition, as the zinc electrowinning process constitutes a closed circuit, some impurities can accumulate and lead to detrimental effects.

The concentration at which a particular impurity results in current efficiency problems is a matter of some debate (6). Many of the studies are qualitative in nature and do not suggest any mechanism for the reduction in current efficiency. Thus it is not uncommon to find orders of magnitude differences in the concentration values reported at which various impurities have significant detrimental effects (6). Indeed, in view of the complexity of a zinc electrowinning solution, it is feasible that a particular impurity may have a detrimental effect on deposition efficiency, even though it cannot be detected in the electrolyte solution.

A reduction in sulphuric acid concentration, an increase in zinc concentration or an increase in current density can often improve the current efficiency of the process. However, these variables are usually pre-set by economic factors, such as the daily output of the plant and the physical arrangement of the tankhouse.

1.3.1 Sources of Impurities

The zinc electrolyte is exposed to possible contamination from a large number of organic and inorganic species.

Inorganic contaminants enter the process as impurities in the calcine, and are leached along with the zinc. The common metal impurities encountered are, cobalt, copper, iron, nickel, cadmium, lead, manganese, aluminium and antimony.

The electrolyte can leach the organic compounds from the organic based products in which it comes in contact. Adventitious organic compounds in the electrolyte can result from the polyester resins in the fibre glass tanks, pipes and open channels used for manipulating the electrolyte around the process, the plastic sealant edge strips used on the aluminium cathodes and the PVC paraliners used in the electrolysis tanks.

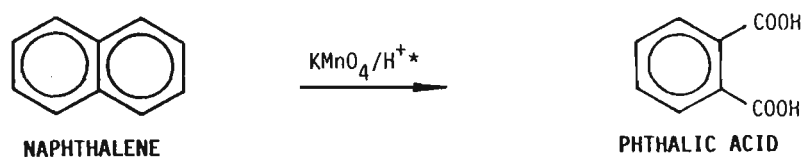
Sudden and unexplained falls in current efficiency at the Electrolytic Zinc plant led to a search for poisons present in the electrolyte. Gas-liquid chromatographic analysis of plant electrolytes at the time of current efficiency slumps indicated concentrations of isobenzofuranone higher than detected during normal plant operation. Thus, isobenzofuranone was strongly suspected of having a deleterious effect on the current efficiency for zinc reduction.

In this investigation the electrochemistry of isobenzofuranone and its precursors were studied in an attempt to determine its source and mode of action.

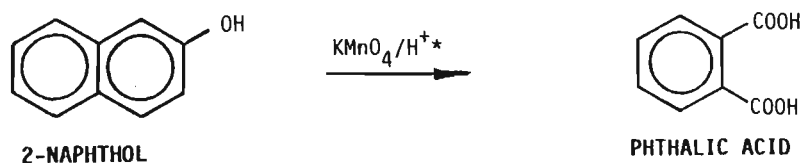
The zinc electrolyte toxic material, isobenzofuranone, IBF (phthalide)⁽⁷⁾, is a derivative of phthalic acid. Therefore the phthalic acid series of compounds is of considerable interest when studying the effect of organic impurities on the electrolysis of zinc.

1.3.1.1 Phthalic Acid

Naphthalene is a common impurity in 2-naphthol, which can be converted to phthalic acid by an oxidation process⁽⁸⁾. Within the zinc electrolysis cell the lead anode is held at a potential of + 2.07V (but as low as + 1.97V for high purity zinc) versus the SHE. The oxidative power of ozone expressed as a standard electrode potential is + 2.07V. Thus the oxidative power of the anode is considerable, and sufficient to oxidize naphthalene to phthalic acid.



Phthalic acid can also be produced by the direct oxidation of 2-naphthol under severe conditions.



(* Oxidation within the electrochemical cell can be via the anode or anode oxidation products).

Xylene, from oils and greases can undergo catalytic oxidation to produce phthalic acid and a small amount of isobenzofuranone.

Plastics are another source of phthalic acid, on account of phthalic anhydride being used in the manufacture of both alkyd resins and polyester resins.

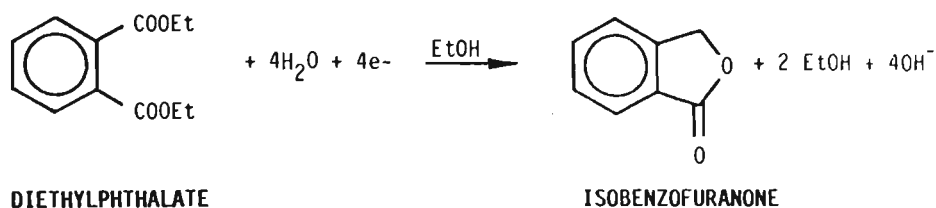
1.3.1.2 Phthalate Esters

Phthalates can enter the zinc electrolysis circuit leached as plasticisers (in PVC pipes, paraliners etc.), fibreglass resins (used as the accelerator vehicle), drying oils in paints, adhesives and synthetic rubber. However, the most likely source of phthalates is plasticisers in plastics, fibreglass resins and edge strip sealant.

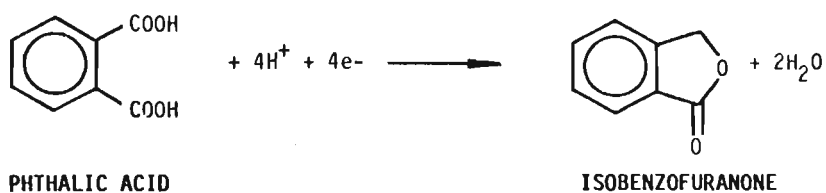
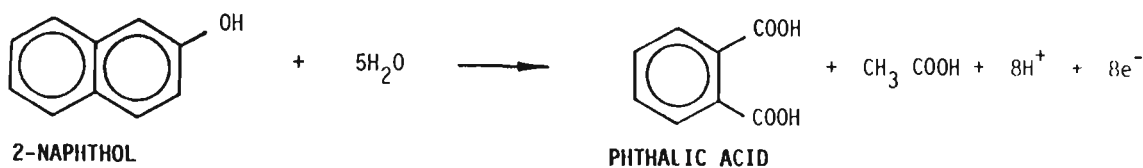
1.3.1.3 Isobenzofuranone

It is thought that isobenzofuranone has an extremely deleterious effect on the electrowinning of zinc⁽⁷⁾. Isobenzofuranone is found as an impurity in 2-naphthol, particularly that produced by the Cyanamid oxidation process. It is also used as an additive in lubricating oils⁽⁹⁾, and can be leached from high-impact polypropylene resins.

Diethylphthalate can be converted into isobenzofuranone via an electrochemical reduction⁽¹⁰⁾.



It has been suggested that the presence of isobenzofuranone in electrowinning liquors may be a result of the electrochemical reduction of phthalic acid produced from the oxidation of 2-naphthol⁽⁷⁾.



1.3.2 Effect of Impurities

The electrocrystallization of zinc is greatly affected by process conditions such as temperature, current density and chemical composition of the electrolyte.

Certain impurities (generally inorganic species) in the electrolyte are known to cause re-resolution of the deposited zinc⁽³⁾. The re-resolution usually takes place

after a period of zinc deposition, and the time required before the re-resolution can be looked upon as an incubation period. In some cases the effect of metallic impurities can be eliminated by the use of organic additives.

Dimethylglyoxime is used to precipitate nickel and 1-nitroso-2-naphthol to precipitate cobalt, the metals being removed from the electrolyte solution prior to electrolysis. As the reagents are used in excess, only unreacted precipitant is available for electrochemical modification within the electrolysis cell.

The effects of metallic impurities on the electrolysis of zinc sulphate solutions have been studied extensively⁽¹¹⁻²¹⁾. However, studies of the effects of organic impurities are limited. A study of the influence of combinations of impurities on the current efficiency of the electrolysis of zinc was carried out⁽²²⁾. In this study it was found that the influence of the combinations cobalt with antimony and cobalt with 2-naphthol are harmful, and that the combination cobalt, antimony and 2-naphthol is extremely unfavourable. In the latter case, the deposits were heavily corroded and showed a characteristic appearance of pinholes and of spherical voids. When 2-naphthol was present as the only impurity, tiny holes were observed in deposits. It has been shown that the discharge of zinc and other ions is inhibited by 2-naphthol⁽²³⁾. During electrolysis, hydrogen bubbles are probably attached to the 2-naphthol, thus making voids visible on the zinc surface.

1.3.3 Mechanisms of Impurity Action

Ordinarily, an impurity ion can codeposit with zinc if there is sufficient amount present in the bulk solution and it is more electropositive than zinc.

In practice, the bulk concentration of the impurity is very small compared to the zinc. Therefore, the deposition of the impurity on zinc may be controlled by diffusion so that only a small part of the electrode surface is covered by the impurity⁽¹⁴⁾. Whether the impurity forms a solid solution, a compound with zinc or deposit individually, the impurity coated part of the electrode evolves large amounts of hydrogen⁽¹⁴⁾. This can be either due to the impurity coated portion acting as a cathode for hydrogen ion reduction or as a cathode in the re-solution of zinc previously deposited. It is very hard to distinguish between the two unless the corrosion occurs to such a degree that a part of the deposit has been dissolved away.

The mechanism whereby the zinc current efficiency is decreased is dependent on the active impurity⁽⁶⁾. Three possible mechanisms can be postulated from the experimental data. Mechanism (a) involves the co-deposition of a low overpotential material with zinc and subsequent local cell corrosion of an auto-catalytic nature. Mechanism (b) assumes the active impurity to react with hydrogen in the double layer with subsequent decomposition in the electrolyte. This leaves the impurity free to react

again along a similar path. Mechanism (c) involves hydrogen deposition on impurities as a result of the lowering of hydrogen overpotential.

1.4 Additives in Zinc Electrowinning Circuits

The additives used in the zinc electrowinning process are essentially all organic in nature and hence must be considered as an important potential source of organic poisons for the process. Nickel is removed by the addition of dimethylglyoxime and cobalt by the addition of a calculated combination of 2-naphthol, sodium hydroxide and sodium nitrite to form 1-nitroso-2-naphthol.

2-Naphthol is also added to the electrolysis tanks along with a poorly characterized, high molecular weight, animal glue to give a good, smooth and massive deposit. Organic flocculants are also added to remove iron based precipitates such as jarosite in the early process steps. The complex salt potassium antimonytartrate is also added to the electrolyte for current efficiency reasons.

1.4.1 Effects of Additives

Organic additives also affect the nature of the zinc crystallization. As the additives can be adsorbed preferentially on certain crystal planes, it is possible to completely alter the growth of the deposit. The organic additives also make the grain size smaller by creation of additional nucleation sites during the electrodeposition. The organic addition agents are also susceptible to oxidation by MnO_2 or MnO_4^- , which are formed by

oxidation of Mn^{2+} at the anode surface. This in turn can cause still further alterations in the electrocrystallization.

Organic additives also are known to polarize the electrode to a greater extent than most inorganic additives, and shift the growth mode from lateral to outward⁽⁶⁾.

Turomshina and Stender⁽¹⁵⁾ have studied the effect of common impurities on hydrogen current yield and cathode potential at various temperatures and current densities. The combined effect of any two impurities is greater than the sum of their individual effects. Cases where the combined effect of the impurities is greater than their sum can be explained by the fact that in the three electrode microcells which are formed, one of the impurities serves as a microanode along with the zinc and yields ions in solution which can then be discharged on microcathodic portions. Where the combined effect of the impurities is less than the sum, it is thought that active hydrogen points on the zinc surface (gelatin is the additive) are blocked by deposition on them of metals having a higher hydrogen overpotential.

In a study of a combined additive consisting of antimony, 2-naphthol, and glue in acid zinc sulphate electrolytes, it was found that the favourable effect of 2-naphthol is due to the formation of complex compounds with cobalt cations, which are thereby removed from the reaction zone⁽²⁵⁾. It was also discovered that the adsorption processes depend both on the charge of the metal,

and on the nature of the surface-active substances and colloidal suspensions formed in the course of electrolysis in the acid zinc electrolyte. The combined colloidal system (antimony hydroxide and glue) has high dispersibility, and gives rise to a particularly thin, dense, and elastic film with a high contact area on the metal surface. This film not only has separating properties, but it also protects the aluminium and zinc against corrosion and favours the formation of more finely crystalline, dense, and smooth cathodic zinc deposits.

A cyclic voltammetric technique has been developed to provide a rapid, quantitative evaluation of the effectiveness of organic additives in controlling impurities in zinc electrowinning⁽²⁶⁻²⁸⁾. The technique involves measuring the relative increases in zinc activation overpotential on aluminium cathodes as a function of the concentration of additive. There is a range of overpotential within which the current efficiency reaches a maximum and which therefore indicates optimal conditions for electrowinning.

Animal glues were the most effective of the additives tested, which included several gums, enzymes and amino acids. The most effective animal glues had average molecular weights of 25,000 to 30,000. The effectiveness of the glues in controlling impurity effects appeared to be related to the protease content of the glues, whereas the requirement for good levelling properties was for the glues to have a molecular weight of at least 10,000.

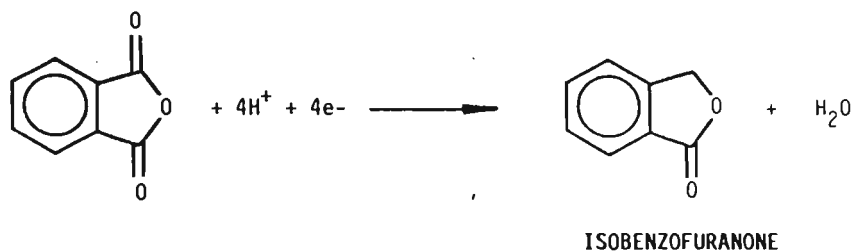
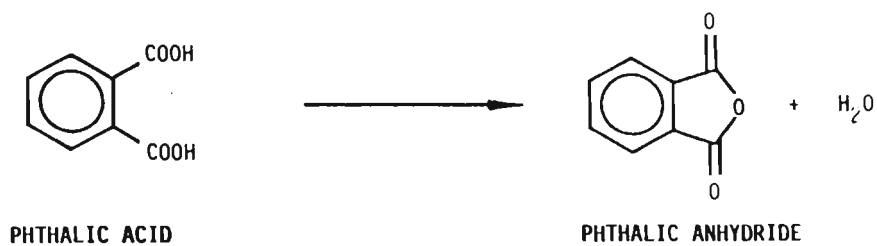
Saunders and Philips⁽²⁹⁾ have assessed the quality of zinc electrolytes by measuring the cathodic current efficiency during the electrodeposition of zinc. Efficiency measurements were carried out by a galvanostatic deposition and potentiometric dissolution of zinc onto and from a lead substrate. The results have been correlated with those obtained in commercial electrowinning operations.

1.5 Electrochemical Properties of Phthalic Acid and Related Compounds

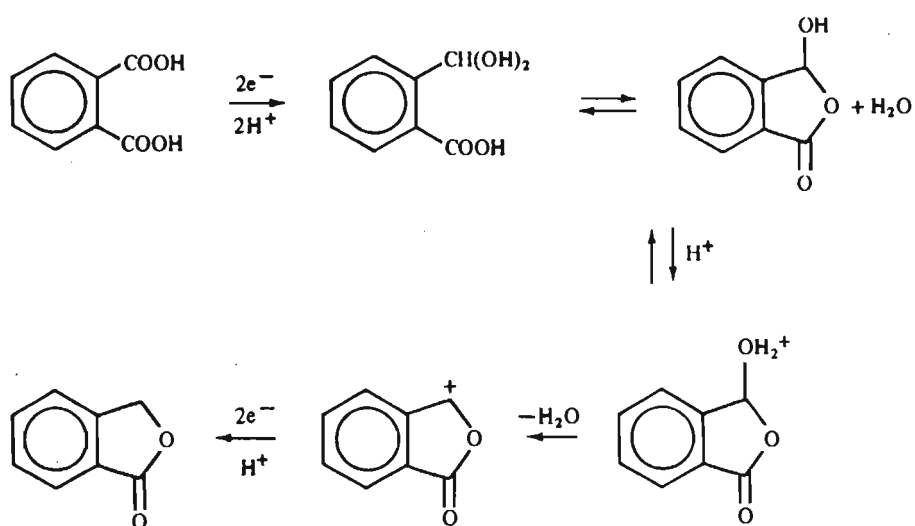
A number of electrochemical studies have been undertaken on phthalic acid and related compounds in solvents and supporting electrolytes quite different from the approximately one molar sulphuric acid encountered in the zinc electrowinning circuits⁽³⁰⁻⁴³⁾. However, it is necessary to study these compounds in suitable solvent systems to enable some understanding of their electrochemical behaviour to be obtained. This basic understanding is essential prior to the study of the effect of these compounds on the electrowinning of zinc.

1.5.1 Phthalic Acid

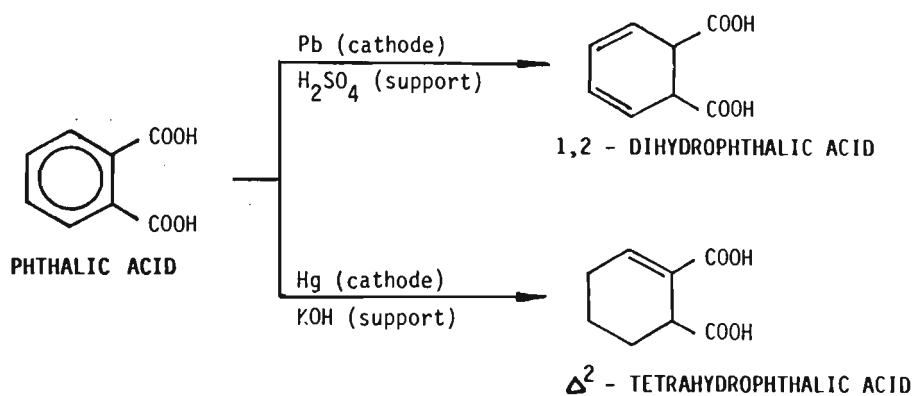
Aromatic dicarboxylic acids are reduced to the corresponding lactone, or dihydric alcohol, depending on the orientation on the ring of the carboxyl groups⁽⁴⁴⁾. Sakurai reports that o-phthalic acid when reduced at a lead cathode in neutral or weakly acidic media yields isobenzofuranone with phthalic anhydride as the intermediate product^(31,32).



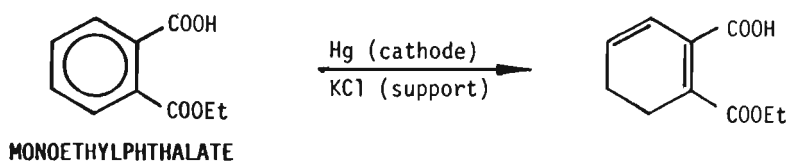
However, Jones⁽³³⁾ suggests a more probable mechanism in which phthaldehydic acid (in equilibrium with hydroxyphthalide) is the intermediate product, and that the hydroxyphthalide should be easily reducible after protonation and loss of a water molecule.



Reduction of the benzene ring of phthalic acid has also been reported⁽³⁴⁻³⁶⁾. Phthalic acid, has its ring structure attacked in both acidic and basic media. In the former medium, at a lead electrode the less highly reduced structure, 1,2-dihydrophthalic acid is obtained⁽³⁵⁾, whereas in the basic medium at a mercury cathode Δ^2 -tetrahydrophthalic acid is the main product⁽³⁶⁾.



If the monoethylester of phthalic acid in an aqueous KCl medium is similarly treated at a mercury cathode, the monoethylester of 3,4-dihydrophthalic acid is obtained⁽³⁷⁾.



Three reduction waves for phthalic acid can be observed by varying the pH of aqueous solutions. The first wave, observed in most acidic solutions, shows a kinetically limited pre-electrochemical solution reaction. Two interpretations have been proposed by independent workers^(38,39). Lack of proportionality between observed limiting current and the undissociated phthalic acid concentration led Furman and Bricker⁽³⁸⁾ to postulate a reduction mechanism involving a prior chemical reaction between biphthalate anions and hydrogen ions in the vicinity of the electrode surface, to produce the reducible species presumed to be un-dissociated phthalic acid, H_2Ph . Data of Ryvolova and Hanus⁽³⁹⁾ suggest that the electroreducible species is the protonated super acid H_3Ph^+ , whose formation at the electrode surface caused the apparent pre-electrochemical kinetic complication.

The above contradiction on the mechanism was resolved by a polarographic and chronopotentiometric study of phthalic acid solutions⁽⁴⁰⁾. The dependence of half-wave potentials on pH in the concentrated acid region to pH 4.0 was measured. Limiting currents as a function of pH and mercury column height were measured, and the slopes of waves analysed. Additional spectrophotometric data on the protonation of undissociated phthalic acid give further support to the mechanism of Ryvolova and Hanus⁽³⁹⁾. Using the approximate superacidity constant of H_3Ph^+ determined spectrophotometrically, the rate constant for the protonation reaction has been calculated by the Koutecky method, which relates the prior chemical reaction rate

constant to the observed kinetically-limited current and diffusion-limited current.

The products of the other reduction waves of phthalic acid have not been investigated.

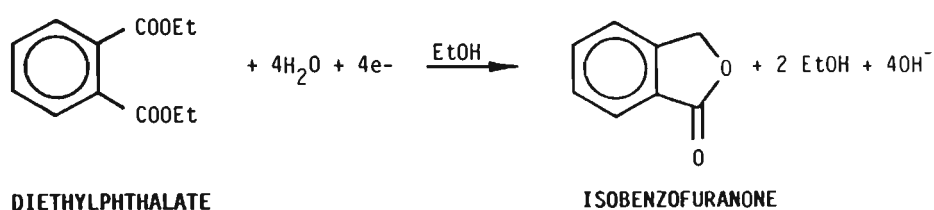
1.5.2 Phthalic Anhydride

Anhydrides have received very little attention as substrates for cathodic reductions. Polarography of cyclic anhydrides in aprotic media (acetonitrile, DMF) yields two one-electron waves for the most easily reduced anhydrides (pyromellitic, dibromopyromellitic and tetrachlorophthalic anhydride)^(45,46). Controlled potential electrolysis (CPE) of phthalic and pyromellitic anhydrides at the potential of the first wave gave highly coloured, oxygen-sensitive solutions, which later were shown to give well resolved ESR spectra of the corresponding radical ions⁽⁴⁵⁾. Phthalic anhydride has been reduced to isobenzofuranone on a preparative scale⁽³¹⁾, but the reaction conditions employed (ethanol-water-ammonium carbonate) indicates that monoethylphthalate must have been the actual substrate. Two waves separated by 0.86V, were observed in the reduction of phthalic anhydride in DMF containing tetraethylammonium iodide⁽⁴⁷⁾.

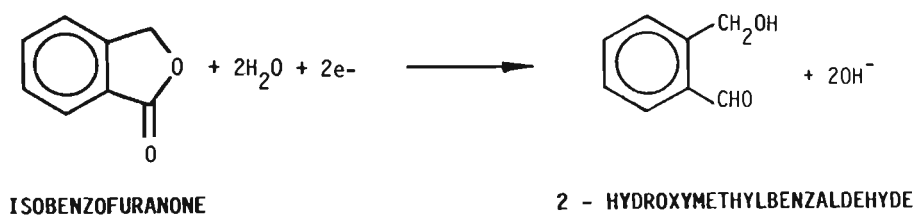
1.5.3 Phthalates

Polarographic data for ester reductions are scarce, but a few investigations on esters of aromatic acids have been reported^(10,48-50). Whitnack et al.⁽¹⁰⁾ have investigated the methy, ethyl, butyl, and octyl esters of phthalic acid at the dropping mercury electrode. In ethanolic solutions, containing quarternary ammonium salts

as supporting electrolytes, two well defined diffusion currents are observed. The reduction process was found to be diffusion-controlled and irreversible for each wave. Four electrons are involved in the first reduction and two in the second. Isobenzofuranone was established as the intermediate reduction product for the cathodic reduction of diethylphthalate by controlled potential electrolysis.



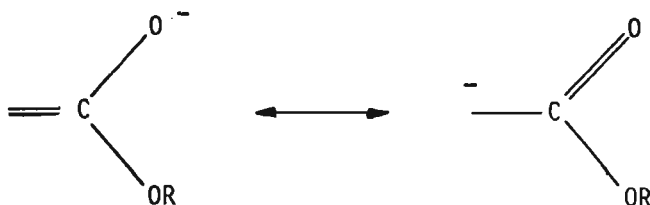
The end product in the electrode process is so far unknown. From the experiments of Whitnack et al., it seems likely that the second step in the polarographic reduction is the following:



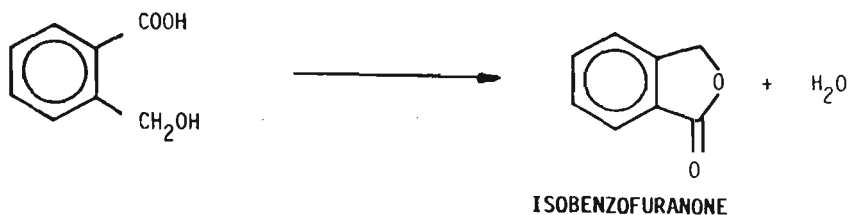
However, under the conditions of the large scale electrolysis experiments, the product is not stable and only a resinous material was recovered from the catholyte⁽¹⁰⁾. Neutral and alkaline solutions offer the best conditions for measurement of this wave, and the

diffusion currents in these media are a linear function of the concentration of phthalate ester.

A comparison of the half-wave potentials, of the first step in the reduction of derivatives of carboxylic acids has been reported⁽⁴⁷⁾. Phthalates were found to be more difficult to reduce than terephthalates, evidently due to steric hindrances as a result of conjugation. In addition, steric hindrances as a result of a co-planar arrangement of the two ester groups in the product of the two electron reduction of phthalate, (orthoquinoid structure) lower the degree of delocalization of the negative charge and the stability of the dianion, thus producing isobenzofuranone:



It has been established that the electrolysis of the half esters of phthalic acid takes another course than the electrolysis of potassium phthalate^(37,38). The half ester salts of trans-2,6-dihydrophthalic acid were isolated in good yield from the electrolyzed solution. Besides these dihydrogenated products, a considerable quantity of isobenzofuranone was isolated. Rodionov and Zvorykina⁽³⁷⁾ proposed that the formation of isobenzofuranone is explained by the reduction of the half ester salts with potassium amalgam according to the following reactions, although these are not a likely source of isobenzofuranone in zinc electrowinning electrolytes:



1.5.4 Isobenzofuranone

Few electrochemical studies involving isobenzofuranone have been reported. It has been identified as a reduction product of phthalic acid, phthalic anhydride and phthalate esters^(10,31-33,37-51), (see sections 1.4.1, 1.4.2 and 1.4.3). The final reduction product of isobenzofuranone has not been identified.

1.5.5 2-Naphthol

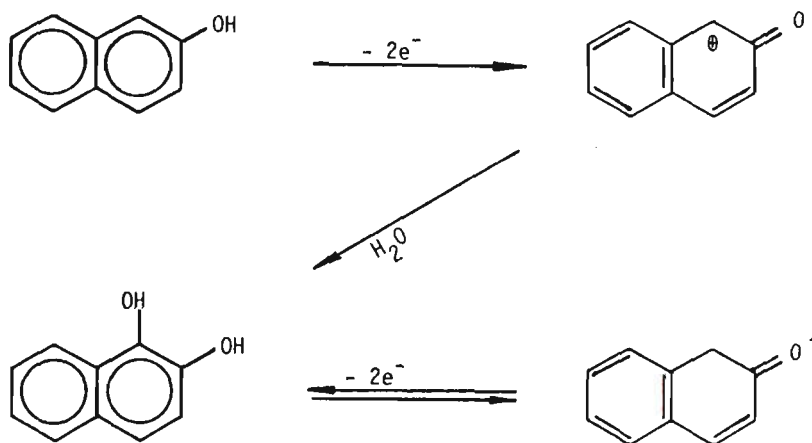
2-Naphthol can be oxidized chemically or electrochemically to phthalic acid⁽⁸⁾ (see section 1.3.1.1).

The electrochemical behaviour of 2-naphthol is similar to that of 1-naphthol⁽⁵²⁾. Although not reducible, the compound yields two oxidation peaks and one distinct follow-up couple. The couple was identified as 1,2-dihydroxynaphthalene/1,2-naphthaquinone and is produced from the second oxidation peak. There is no reversible

couple corresponding to the expected 1,1'-bi-2-naphthol, as ortho-dimers do not form stable quinones.

The hydroxylated product, 1,2-dihydroxynaphthalene, was identified by nuclear magnetic resonance spectroscopy. Attempts to separate and identify a dimer from a controlled potential electrolysis at the first oxidation peak by the same authors were unsuccessful.

A coulometric oxidation at +1.0V followed by a coulometric reduction at 0.0V, indicated that ca. 60% of the 2-naphthol was hydroxylated to 1,2-dihydroxynaphthalene. The hydroxylation pathway is shown below⁽⁵²⁾.



1.6 Summary

From the literature cited in this introduction, it is evident that little attention has been paid to the organic compounds of interest (isobenzofuranone, phthalic acid, phthalate esters and 2-naphthol). With the exception of 2-naphthol, no attention has been paid to the effect of these compounds on the electrowinning of zinc.

Once the electrochemical properties of these compounds have been fully investigated, the possible reaction pathways in an electrowinning cell can be assessed and the effects of the range of compounds on zinc electrowinning can be evaluated.

CHAPTER 2: FUNDAMENTAL TECHNIQUES

2.1 Voltammetry

2.1.1 Introduction

Voltammetry is the general term applied to the study of the current potential relationships obtained when a potential is applied to a working electrode. When the working electrode is a dropping mercury electrode (DME), the technique is known as polarography. Voltammetric experiments may be carried out in either stirred or unstirred solutions.

2.1.2 Cyclic Voltammetry

2.1.2.1 Introduction

In cyclic voltammetry, a triangular ramp potential function is applied to the working electrode, and the resulting current measured as a function of this potential (53-62).

The rate of potential sweep can be as slow as a few millivolts per second or as fast as many hundreds of volts per second. When the time interval between reverse sweeps is relatively short, the products of the forward sweep do not have sufficient time to diffuse into the bulk solution and thus are available for investigation on the reverse sweep.

The current is measured over the entire potential scan; i.e. both anodic and cathodic currents are measured, giving a complete record of a species' electrochemical behaviour.

Unlike steady-state techniques, where the limiting current becomes constant, the current in cyclic voltammetry increases to a maximum as the potential of the electrochemical reaction is approached, then decays as the concentration of the electroactive species in the vicinity of the electrode is depleted, as a result of the unstirred solution, yielding a peak shaped curve.

2.1.2.2 Reversibility and Cyclic Voltammetry

Cyclic voltammetry can be used to provide a rapid and rigorous method of electrochemical investigation. In particular, the reversibility of an electrode reaction can be evaluated.

The half wave potential, $E_{1/2}$, in polarography can be related to the peak potential, E_p of a voltammogram. At 25°C, for a reversible system the relationship is:

$$E_p = E_{1/2} - 0.029/n \text{ volts}$$

The peak potential is 0.029/n volts more cathodic or anodic than $E_{1/2}$ for a reduction or anodic process respectively. Thus, for an electrochemically reversible system, the anodic and cathodic current peaks are separated by approximately 0.058/n volts, and the peak separation is independent of scan rate. As the system becomes less reversible, the separation between the anodic and cathodic

peaks increases. For irreversible systems the peak separation is dependent on scan rate.

If the switching potential is less than 200-300mV past the peak potential, a greater peak separation than $0.058/n$ volts may be observed. This results because even at the peak potential, the concentration of the form (oxidized or reduced) undergoing the reaction at the electrode is not zero. Thus the conditions during the forward scan compared to the reverse scans will differ. The result is a shift in the peak potential.

The difference between the peak potential and the potential at which the current is one-half the maximum value, $E_p/2$, is useful in describing the shape of a peak. For a reversible system this is given by:

$$\left| E_p - E_{p/2} \right| = 0.058/n \text{ volts}$$

The peak of a reversible system is therefore quite sharp.

For a reversible system, E_p and $E_{p/2}$ are independent of potential sweep rate. However, for irreversible systems these values vary approximately $0.03/\alpha n$ per tenfold change in sweep rate (where α is the electron transfer coefficient).

The peak current of an irreversible system is smaller than that for a reversible system. This difference can, under certain conditions, be used to determine the reversibility of a system.

2.1.2.3 The Cell

The cyclic voltammetry cell consists of a vessel capable of containing the electrolyte, a reference, auxiliary and working electrode. In addition, facilities to deaerate and maintain the electrolyte under oxygen free conditions are necessary.

The potential of the working electrode is controlled with respect to a reference electrode, and the current flowing between the working and auxiliary electrode measured.

2.1.2.4 Electrodes

Voltammetry involves a three electrode system working, reference and auxiliary.

Stationary electrodes (e.g. platinum) and the hanging mercury drop electrode (HMDE) can be used as working electrodes. The HMDE has the advantage that a fresh surface can be achieved by merely replacing the drop. In contrast, stationary electrodes may require cleaning after each sweep.

The reference electrode provides a stable reproducible reference potential against which the working electrode can be maintained. The saturated calomel electrode is a common and practical reference electrode.

An auxiliary electrode (often platinum) is provided to complete the electrochemical circuit.

2.1.2.5 Experimental Instrumentation

In this investigation all cyclic voltammetric experiments were carried out using a Princeton Applied Research Model 170 Electrochemistry system, which is an all electronic multifunctional electrochemical instrument incorporating a built-in X-Y pen and ink recorder and a potentiostat with \pm 100 volt of compliance and current capabilities of 1 ampere at 100 volt or 5 ampere at 20 volt. It is capable of performing almost all known electrochemical techniques.

The hanging mercury drop electrode (HMDE) used was a Metrohm BM5-03 micrometer syringe type and the cell a water jacketed Metrohm EA876 at 298K. A Metrohm saturated calomel electrode (SCE) and a platinum cylinder were used as the reference and auxiliary electrodes respectively.

The mercury used in the hanging drop electrode was triply distilled (zur Analyse Merck).

2.2 Electrolysis

Constant potential and constant current are the two types of control available in electrolysis⁽⁶²⁾. The constant potential technique permits selection of the desired reaction to the exclusion of others. In contrast, the constant current technique does not permit potential control.

2.2.1 Constant Current Techniques

As discussed, the technique of constant current electrolysis precludes the possibility of electrode-potential control in dilute solutions of electroactive

species. As the concentration of the electroactive species in the solution is depleted, the desired electrode reaction can no longer sustain the current flow through the cell. For reduction processes the potential becomes more cathodic until an additional reaction, such as the reduction of another electroactive species (often the evolution of hydrogen), takes place to maintain the current flow. Once the cathode potential is sufficiently negative for the evolution of hydrogen, it will remain relatively stable at a level fixed by solution pH and the hydrogen overpotential. This situation would be intolerable if a metal was co-depositing, as the continual evolution of gas at the cathode is unsuitable for adherent deposits.

Electroactive species can be separated by pH control or by complexation to change their equilibrium potentials.

Platinum and mercury are commonly used electrode materials. Platinum is used as an anode for oxidation, as well as cathode for reduction of readily reduced species. As a result of platinum's low overvoltage, hydrogen evolution can interfere with other electrode reactions.

Mercury is frequently used as a cathode material because its extremely high hydrogen overvoltage permits most metals to be deposited and other electroactive species to be reduced without interference from hydrogen evolution. As an anode, however, mercury finds few uses because of the ease with which it can be oxidized.

2.2.2 Experimental Instrumentation

In this investigation all constant current electrolysis experiments were carried out using a constant current source designed and constructed within the Chemistry Department of the Ballarat College of Advanced Education.

2.3 Gas-Liquid Chromatography

2.3.1 Introduction

Gas-liquid chromatography (GLC) ^(62,63) achieves its separation by partitioning a sample between a mobile gas phase and a thin layer of non-volatile liquid held on a solid support.

The basis of all chromatographic separation is the partition of the sample components between two immiscible phases. In GLC the sample, after vapourization, is introduced to the top of the column by the carrier gas. The solutes are adsorbed at the head of the column by the stationary phase and desorbed by fresh carrier gas. This partitioning occurs repeatedly as the sample travels through the column, with the sample being separated into its various component bands. The components are eluted in order of their increasing partitioning ratio and swept into a detector attached to the column exit. The response of the detector is recorded on a chart as a plot of time versus composition of the carrier gas. The retention (residence) time of a peak identifies the component, while the area under the peak is proportional to concentration. The

limitations of GLC to volatile materials can be extended with columns capable of operating at temperatures up to 450°C, pyrolytic techniques and the production of volatile derivatives.

2.3.2 GLC Instrumentation

Instrumentation for GLC ranges from the very basic gas regulation, injector, oven, column and single detector system, to more elaborate systems which utilize double columns, temperature gradient apparatus, pre-columns and a variety of detection systems.

2.3.2.1 Injector

The sample must be introduced as a vapour in the smallest possible volume and in the minimum amount of time, so as not to disturb the equilibrium of the column conditions. The introduction must be in a reproducible manner with a high degree of precision.

Liquid samples are vaporized in a metal block which is heated to a temperature which exceeds the boiling point of all components present in the sample by a controlled resistance heater. These samples are injected into the metal block using a microsyringe through a self-sealing rubber septum.

Gas samples are better introduced using calibrated sample loops which can be switched in and out of the carrier gas flow.

Pyrolysis has become a widely accepted method for handling solids.

2.3.2.2 Chromatographic Columns

Packed and open (unpacked) columns are the two main types used in GLC. The main advantage of open columns is the low pressure drop and unrestricted flow along the column, thus long coiled columns up to 300m can be used. The separating ability of a coated wall open column is similar to that of a packed column, thus rapid separations of compounds that have small differences in physical properties can be achieved. Packed columns are tubes generally between 0.7 and 2m in length fitted with an inert support coated with a non-volatile liquid phase.

Diatomaceous earths which have been crushed and calcined above 900°C are commonly used for supports in packed columns.

A number of non-volatile materials have been used as partition liquids for many diverse separations. The general rule in selecting a liquid phase is that polar liquid phases are best for polar samples and, conversely, non-polar liquid phases are best for non-polar samples.

2.3.2.3 Detectors

A response from the detector is required on the arrival of the separated components at the column exit.

The flame ionization detector (FID) is currently the most widely used detector system. Other detectors using the

differences in thermal conductivity of a filament exposed to only the carrier gas and a similar filament exposed to sample components in carrier gas. Electron capture detectors are also used.

2.3.3 Experimental Instrumentation

In this investigation all gas chromatographic experiments were carried out using a Pye Unicam Series 104 Gas Chromatograph.

CHAPTER 3: THE ELECTROCHEMICAL BEHAVIOUR OF SOME
ORGANICS PRESENT IN ZINC ELECTROWINNING
CIRCUITS

3.1 Introduction

Organic compounds in the Electrolytic Zinc circuit enter the system as either adventitious impurities or additives⁽⁷⁾.

Adventitious organic compounds in the electrolyte can result from the polyester resins in the glass fibre tanks, pipes and open channels used for manipulating the electrolyte around the process, the plastic sealant edge strips used on the aluminium cathodes and the PVC paraliners used in the electrolysis tanks.

In addition, a number of organic additives are deliberately introduced in the Electrolytic Zinc circuit to improve current efficiency and deposit morphology. Nickel is removed by the addition of dimethylglyoxime and cobalt by the addition of a calculated combination of 2-naphthol, sodium hydroxide and sodium nitrite to form the 1-nitroso-2-naphthol cobalt complex. 2-Naphthol is also added to the electrolysis tanks along with a poorly characterized, high molecular weight, animal glue to give a good, smooth and massive deposit. An organic flocculating agent ("al-floc") is added to assist in removing the resulting precipitates. Potassium antimonytartrate is also added to the electrolyte for current efficiency reasons.

Isobenzofuranone has been detected in Electrolytic Zinc plant liquors and found to be deleterious to the

current efficiency of zinc electrowinning⁽⁷⁾. However, its mode of action is unknown. Phthalic acid is a precursor for isobenzofuranone and also has been detected in plant liquors. Thus, the electrochemistry of phthalic acid and its derivatives is of considerable interest in studying the effect of organic impurities on the electrolysis of zinc.

3.2 Electrochemical Properties of Phthalic Acid and Related Compounds

A number of electrochemical studies of phthalic acid and its derivatives has been carried out in solvents and supporting electrolytes quite different from the approximately one molar sulphuric acid used in the zinc electrowinning circuits. The potential of the hydrogen reduction wave for aqueous sulphuric acid solutions is less cathodic than the reduction potentials of some of the organic compounds to be studied. Thus, in the present investigation, the compounds were examined in a solvent system which eliminates interference from the solvent reduction wave. This preliminary study is essential to give an understanding of the various reactions in less complex systems prior to the study of the effect of these compounds on the electrowinning of zinc.

3.2.1 Chemicals and Reagents

(i) Phthalic acid: BDH, laboratory reagent (> 99% purity).

- (ii) Isobenzofuranone: Merck, zur Synthese reagent was recrystallized twice from water (m.p. 74°C).
- (iii) Sulphuric Acid: Ajax, analytical reagent (purity 95.0 - 98.0%).
- (iv) Di-2-ethylhexylphthalate: Merck, laboratory reagent (purity > 99%).
- (v) 2-Naphthol: May and Baker, laboratory reagent (purity > 99%).
- (vi) 2-Ethylhexan-1-ol: BDH, laboratory reagent (purity > 99%, b.p. $181 - 185^{\circ}\text{C}$).
- (vii) Diethylphthalate: May and Baker, laboratory reagent (purity > 99%, b.p. $292 - 299^{\circ}\text{C}$).
- (viii) Tetramethylammonium chloride: Aldrich, laboratory reagent (purity > 97%).
- (ix) Ethanol.. analytical reagent, ethanol.
- (x) Sodium Nitrite: BDH, analytical reagent (purity > 98%).

Deionised water was used throughout.

3.2.2 Phthalic Acid

A number of studies have been carried out on the reduction of phthalic acid⁽²⁸⁻³³⁾. Isobenzofuranone has been identified as the main product, while reduction of the benzene ring can occur under less severe conditions^(34,35,36). These studies are reported in detail in Chapter 1.

In the present investigation, phthalic acid was found to give an irreversible reduction wave at a potential slightly cathodic to the zinc reduction wave and anodic to the hydrogen reduction wave in 1.1 molar sulphuric acid at a mercury electrode. The electrolysis product produced at the potential of this wave was later identified (Chapter 5) as isobenzofuranone.

3.2.3 Phthalates

A number of phthalic acid esters have been investigated by Whitnack et al.⁽¹⁰⁾ at the dropping mercury electrode (see Chapter 1.5.3). The product of the first reduction wave was identified as isobenzofuranone.

In the present investigation, controlled potential electrolysis of isobenzofuranone at a potential corresponding to the second reduction wave (Fig. 3-1) produced a resinous product which could not be successfully isolated and identified. However, an infra red spectrum of the material exhibited alcohol and carbonyl functionalities on an aromatic skeleton.

In the present investigation, di-2-ethylhexylphthalate was electrolyzed at a potential corresponding to the first

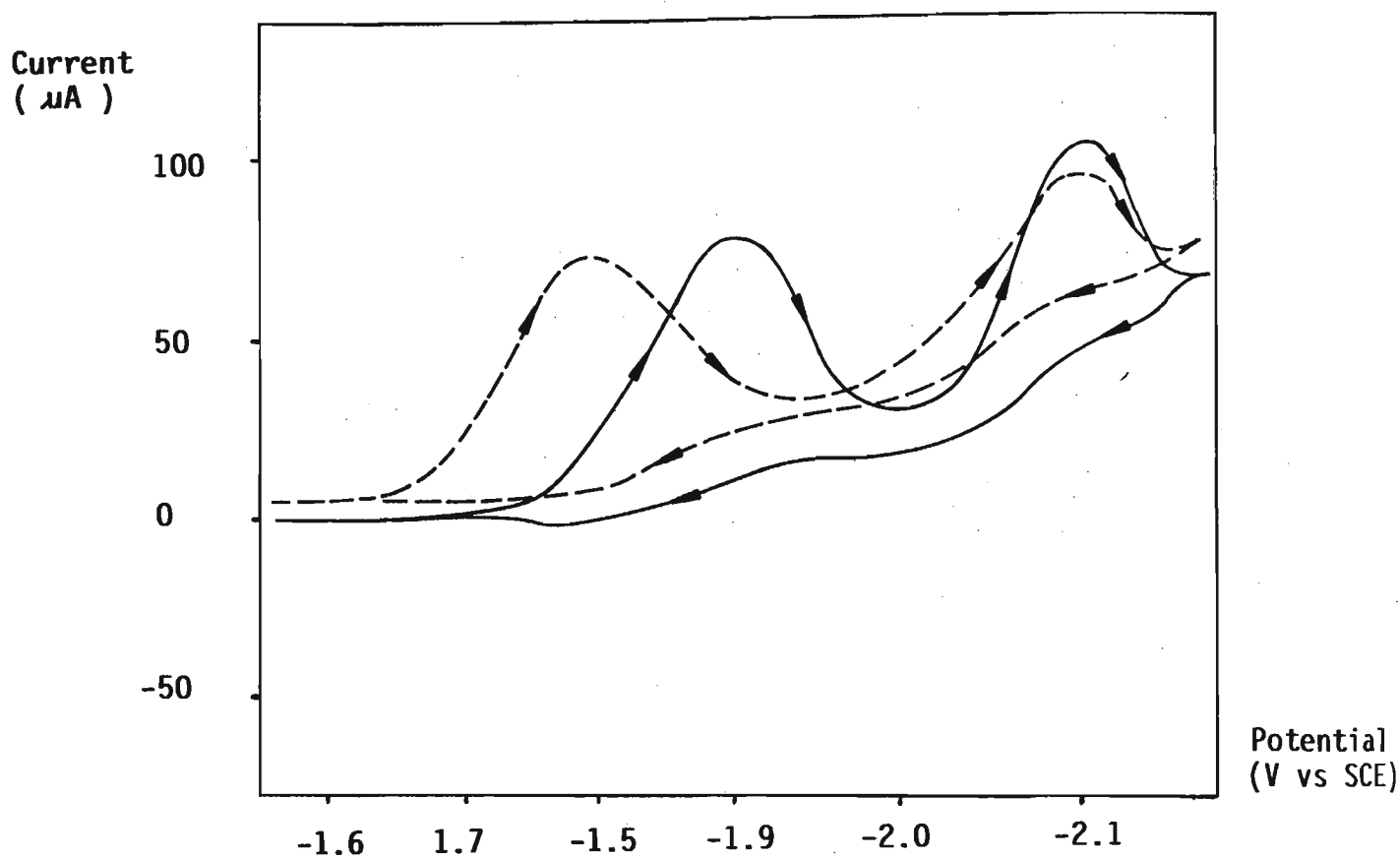
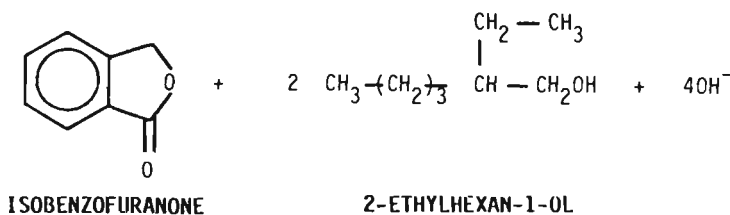
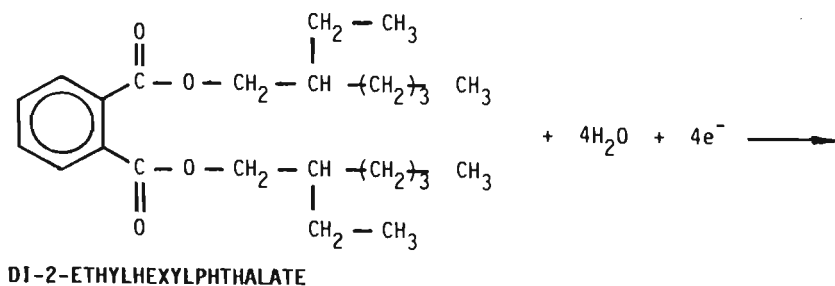


Fig.3-1. Cyclic voltammograms of diethylphthalate -----, and di-2-ethylhexylphthalate ———, in 75% ethanol solution with tetramethylammonium chloride support, HMDE, 100mVs^{-1} scan rate, 298K.

reduction wave (Fig. 3-1). The electrolysis products were identified as isobenzofuranone and 2-ethylhexan-1-ol using Gas-liquid Chromatography:



The first of the two reduction waves for di-2-ethylhexylphthalate occurs at a more cathodic potential than that for diethylphthalate (Fig. 3-1). The second reduction wave for both phthalates occurs at the same potential, corresponding to reduction of isobenzofuranone.

3.2.4 2-Naphthol

The electrochemical behaviour of 2-naphthol is similar to that of 1-naphthol⁽⁵²⁾, as reported in Chapter 1. Although not reducible (on platinum or mercury), the compound can undergo oxidation to 1,2-dihydroxynaphthalene⁽⁵²⁾. However, the complete oxidation of 2-naphthol to phthalic acid requires more severe oxidative conditions than can be provided at a platinum or mercury electrode.

electrode in a zinc sulphuric acid solution.

3.3 Conclusion

Of the compounds investigated, only phthalate esters and phthalic acid can directly produce isobenzofuranone when reduced at mercury or platinum cathodes.

However, mass balance studies carried out by Galbraith⁽⁶⁶⁾ indicate that there is insufficient phthalate ester entering the plant electrolyte to account for the concentration of isobenzofuranone found. Thus phthalate esters can be discounted as the sole precursor for isobenzofuranone in the Electrolytic Zinc circuit.

CHAPTER 4: THE EFFECT OF SOME ADDITIVES ON THE
CYCLIC VOLTAMMETRIC BEHAVIOUR OF
ZINC IN SULPHURIC ACID

4.1 Introduction

The effect of impurities on the hydrogen overpotential for zinc deposition on an aluminium substrate has been studied by O'Keefe et al. (26-28) using the technique of cyclic voltammetry. This technique is claimed to provide a rapid, quantitative evaluation of the effectiveness of organic additives in minimizing the deleterious effects that impurities have on zinc deposition. O'Keefe et al. found that animal glues having average molecular weights between 25,000 and 30,000 and high protease content exhibited the greatest overpotential effect. These glues were also most effective in controlling impurity effects in zinc electrowinning.

The purpose of this investigation was to use a cyclic voltammetric technique to study the effect of a number of additives on the zinc and hydrogen reduction waves resulting from the electrolysis of a zinc electrolyte.

The organic additives used in this investigation were selected following the results of a gas chromatographic study of plant electrolytes⁽⁶⁶⁾. The study detected the presence of a number of organic compounds including phthalic acid, isobenzofuranone, 2-methylbenzaldehyde and 2-methylbenzyl alcohol.

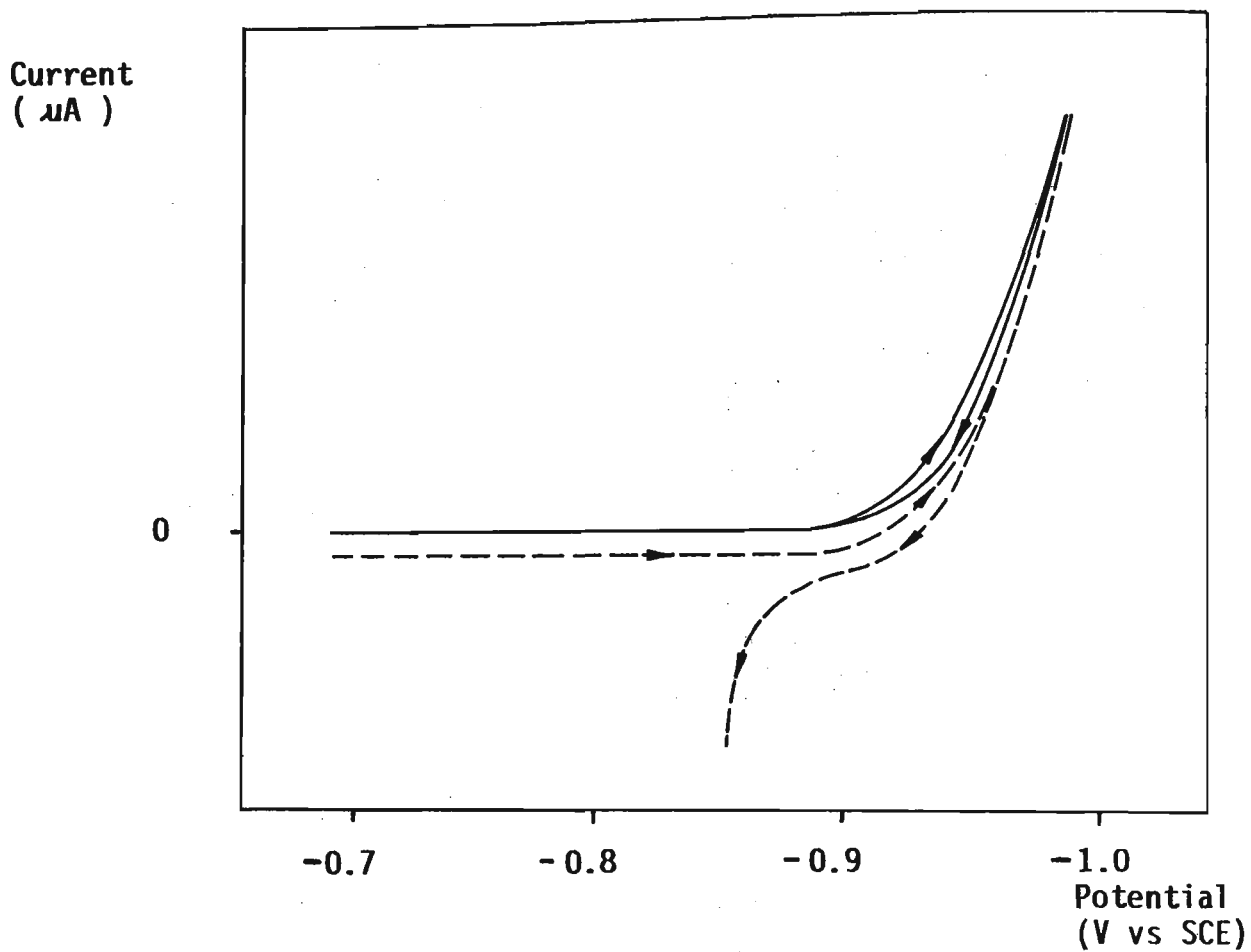


Fig.4-1. Cyclic voltammograms of a 5×10^{-3} M zinc sulphate in 1.1 M sulphuric acid solution at a zinc cathode ---- and aluminium cathode _____.

In a separate study carried out at the Electrolytic Zinc plant, it was found that cobalt exhibits a synergistic effect on zinc current efficiency when present in combination with isobenzofuranone⁽⁷⁾.

4.2 Chemicals and Reagents

- (i) Cobalt Sulphate: BDH, laboratory reagent (purity > 97%).

- (ii) 2-Methylbenzaldehyde: Aldrich, laboratory reagent (b.p. 199 - 200°C).

- (iii) 2-Methylbenzyl alcohol: Aldrich, laboratory reagent (purity > 98%, m.p. 36 - 39°C).

- (iv) Zinc sulphate: Ajax, analytical reagent (purity 99.5 - 100.5%).

Additional chemicals and reagents were as stated in Chapter 3 (section 3.2.1).

The zinc electrolyte used in this study was $5 \times 10^{-3} \text{M}$ in zinc sulphate and 1.1M in sulphuric acid.

4.3 Experimental

4.3.1 General

The effect of impurities on the zinc reduction wave cannot be studied using an aluminium or zinc cathode as the zinc and hydrogen waves overlap (Fig. 4-1). However,

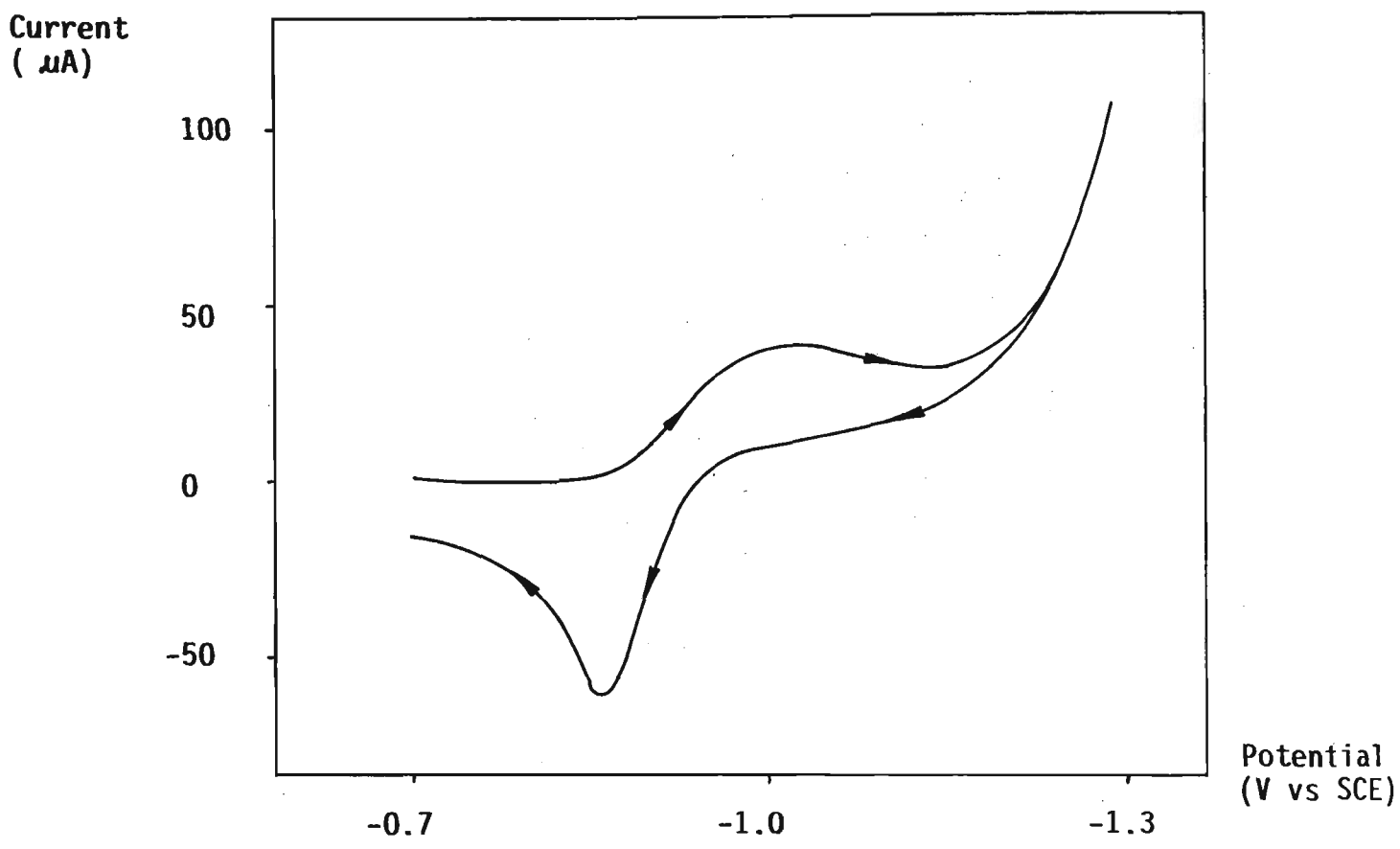


Fig.4-2. Cyclic voltammogram of 5×10^{-3} M zinc sulphate in 1.1 M sulphuric acid solution at a HMDE, 100mVs^{-1} scan rate and 298K.

Current
(μA)

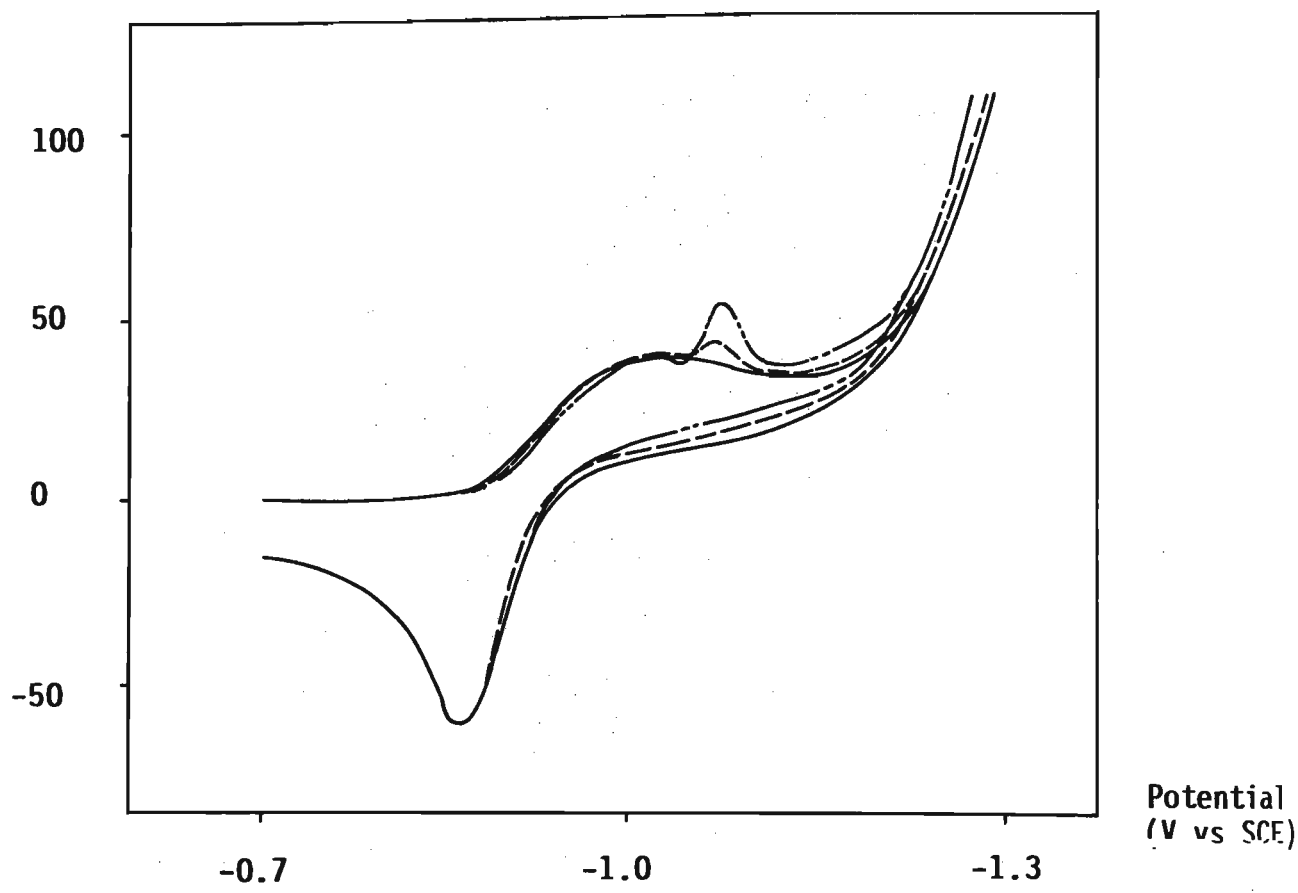


Fig.4-3. Cyclic Voltammograms of $5 \times 10^{-3}\text{M}$ zinc sulphate in 1.1 M sulphuric acid solution at a HMDE, 100mVs^{-1} scan rate, 298K with:

0 M	phthalic acid	————
$1.0 \times 10^{-3}\text{M}$	" "	-----
$2.0 \times 10^{-3}\text{M}$	" "	- . . . -

the waves are separated on a mercury cathode (Fig. 4-2) so that the effects of an impurity on each can be experimentally measured. Assuming that similar effects occur at other cathode materials, such measurements can be used to explain impurity effects on zinc current efficiency. For example, a decrease in current efficiency could be attributed to an anodic shift in the hydrogen wave, a cathodic shift in the zinc wave, or both.

In this investigation, a three electrode system was employed to record cyclic voltammograms. A hanging mercury drop electrode (HMDE), of surface area $(2.01 \pm 0.09) \times 10^{-2} \text{ cm}^2$, was used as working electrode and a cylindrical platinum foil electrode with a surface area of 0.66 cm^2 as auxiliary. The working electrode potential was recorded with respect to the saturated calomel electrode (SCE).

The potentials of the zinc and hydrogen reduction wave are expressed as their decomposition potentials (E_D), given by the intersection of extrapolations of the residual current and the straight line rising portion of the waves.

4.3.2 The Effect of Phthalic Acid

0.5 cm^3 increments of a $2.5 \times 10^{-2} \text{ M}$ solution of phthalic acid were added to 25.0 cm^3 of the zinc electrolyte solution and the cyclic voltammograms recorded. The range of phthalic acid concentrations was 0.5, 1.0, 1.5, 2.0 and $2.5 \times 10^{-3} \text{ M}$. Phthalic acid had no effect on the position of the zinc reduction wave, but caused a small anodic shift in the hydrogen wave (Figs. 4-3, 4-4).

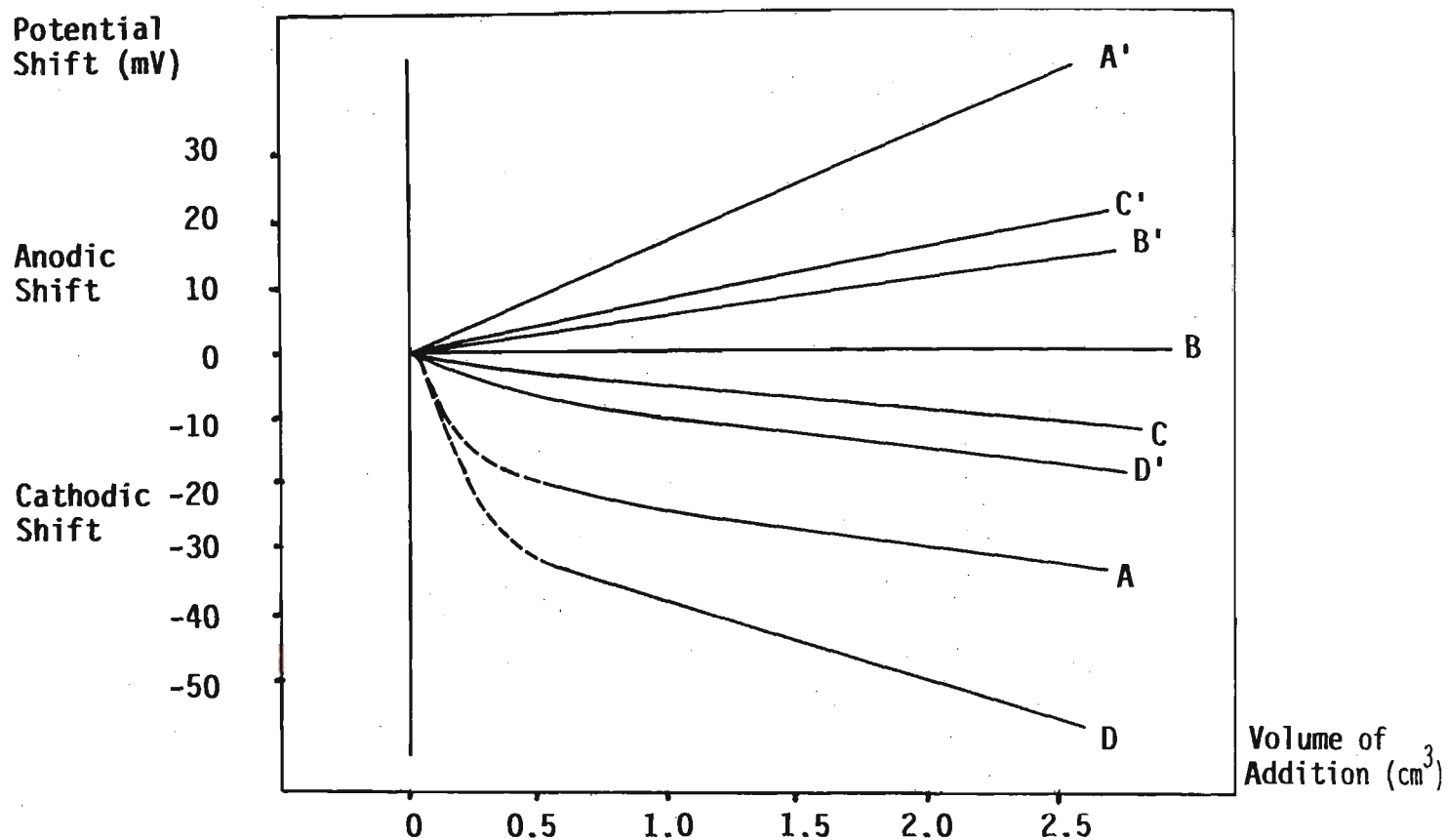


Fig.4-4. Plot of shift in decomposition potential of both hydrogen and zinc reduction waves versus volume of addition,
 isobenzofuranone zinc wave A hydrogen wave A'
 phthalic acid " " B " " B'
 2-methylbenzyl alcohol zinc wave C hydrogen wave C'
 2-methylbenzaldehyde " " D " " D'

Current
(μA)

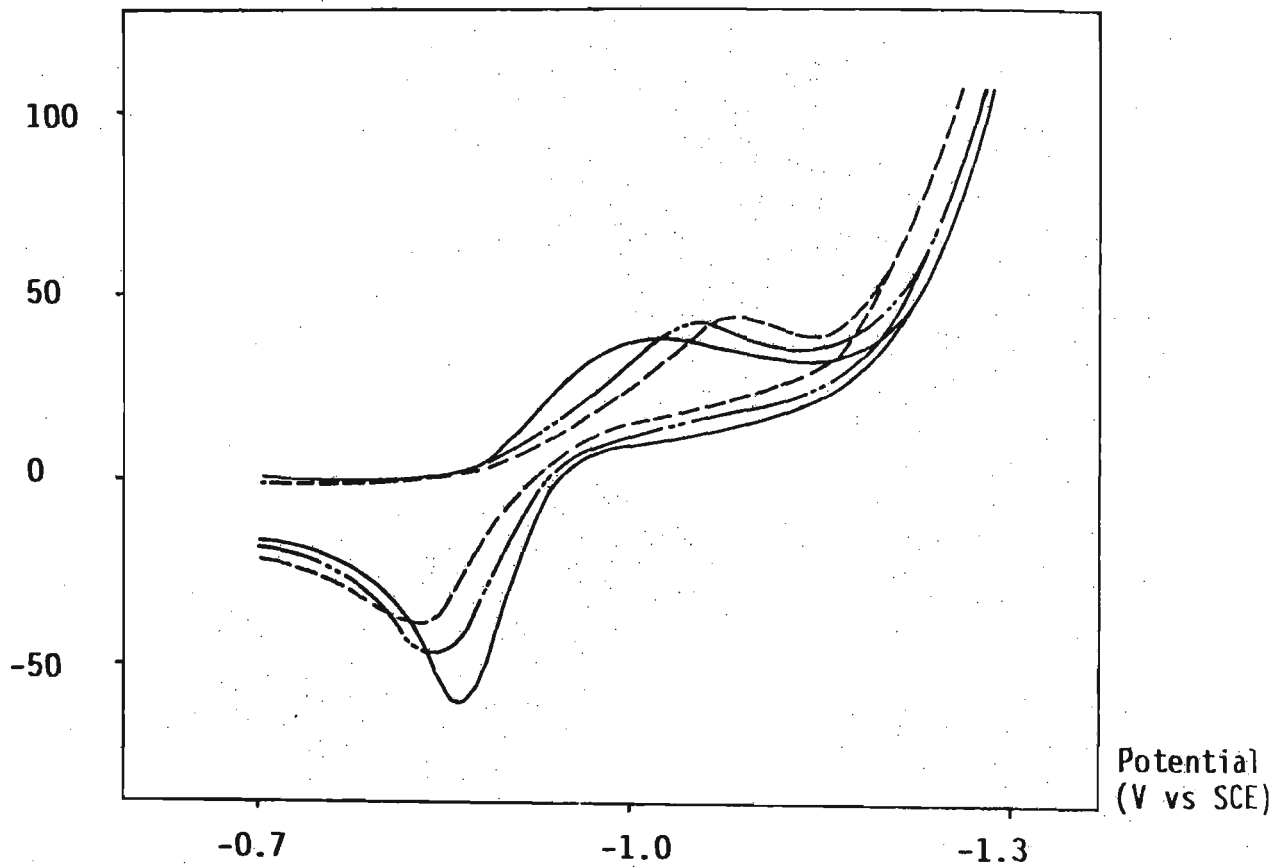


Fig.4-5. Cyclic voltammograms of 5×10^{-3} M zinc sulphate in 1.1 M sulphuric acid solution at a HMDE, 100mV scan rate, 298K, with:

0 M	Isobenzofuranone	—————
1.0×10^{-3} M	"	- - - - -
2.0×10^{-3} M	"	- · - · -

The phthalic acid reduction wave is cathodic to the zinc reduction wave (Fig. 4-3). This reduction product was subsequently identified as isobenzofuranone (Chapter 5) and is not reoxidized on the anodic sweep.

The results indicate that phthalic acid itself should not be deleterious in the zinc electrowinning circuit.

4.3.3 The Effect of Isobenzofuranone

0.5 cm³ increments of a 2.5 x 10⁻²M isobenzofuranone solution were used in this investigation, giving concentrations of 0.5, 1.0, 1.5, 2.0 and 2.5 x 10⁻³M. Isobenzofuranone produces a cathodic shift in the zinc reduction wave, along with a smaller anodic shift in the hydrogen reduction wave (Figs. 4-4, 4-5). In combination, these shifts suggest that isobenzofuranone will produce a significant drop in current efficiency.

On the reverse sweep there is an anodic shift in the position of the zinc oxidation wave. This shift is proportional to the isobenzofuranone concentration (Fig. 4-4). The shift in anodic and cathodic zinc waves indicates a decrease in reversibility with increasing organic concentration.

4.3.4 The Effect of 2-Methylbenzyl Alcohol

2-Methylbenzyl alcohol has been reported⁽⁶⁶⁾ as a reduction product of phthalic acid in the electrolysis of plant liquor electrolytes. The addition of 0.5 cm³ increments of a 2.5 x 10⁻²M 2-methylbenzyl alcohol solution to a pure zinc electrolyte giving concentrations of

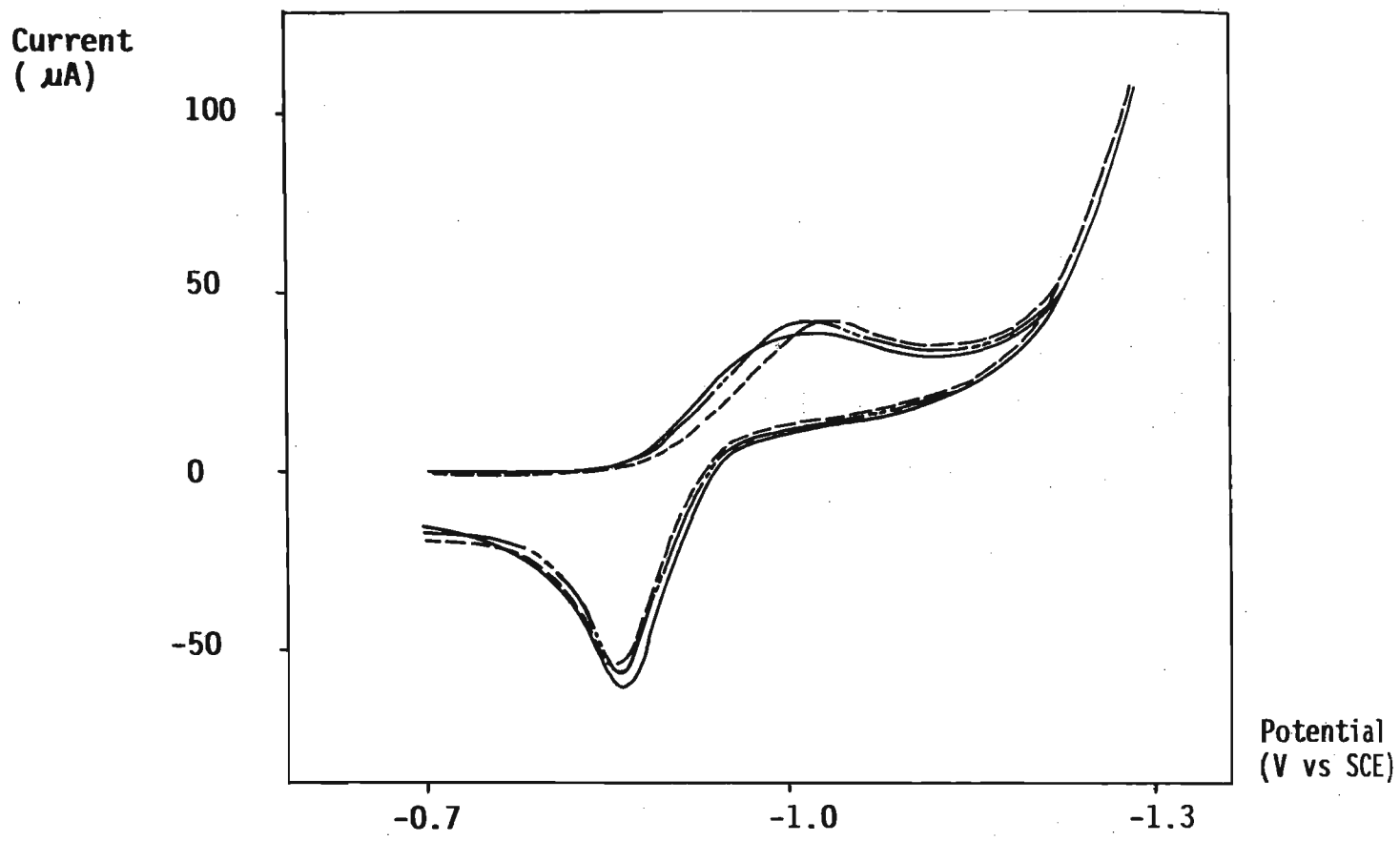


Fig.4-6. Cyclic voltammograms of 5×10^{-3} M zinc sulphate in 1.1 M sulphuric acid solution at a HMDE, 100 mVs^{-1} scan rate, 298K, with:

0 M	2-methylbenzyl alcohol	—————
1.0×10^{-3} M	"	- · - · - · -
2.0×10^{-3} M	"	- - - - -

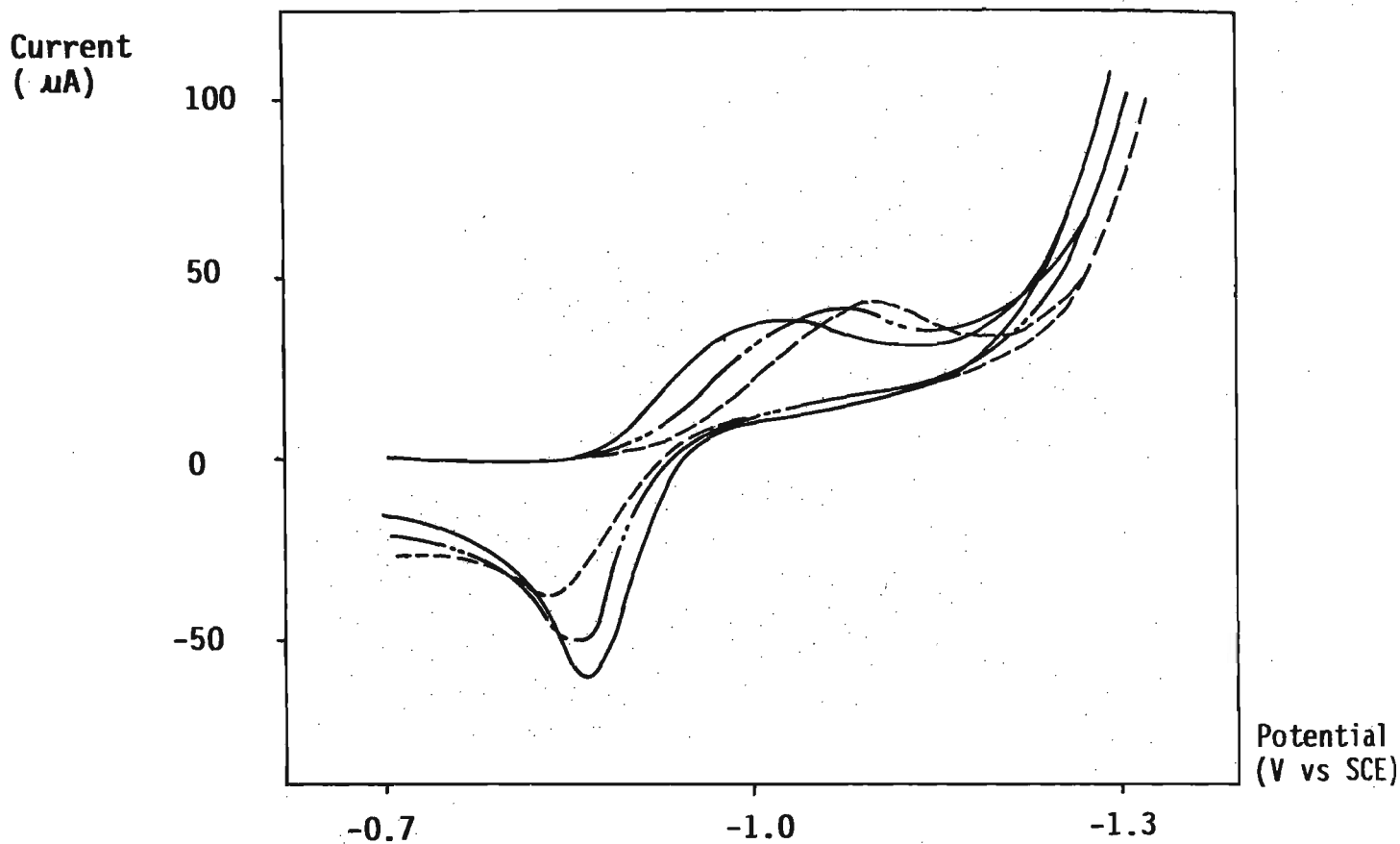


Fig.4-7. Cyclic Voltammograms of 5×10^{-3} M zinc sulphate in 1.1 M sulphuric acid solution at a HMDE, 100mVs^{-1} scan rate, 298K, with:

0 M	2-methylbenzaldehyde	—————
2.7×10^{-4} M	"	- · - · - · -
5.5×10^{-4} M	"	- - - - -

0.5, 1.0, 1.5, 2.0 and 2.5×10^{-3} M had a similar effect to that of isobenzofuranone (Figs. 4-4, 4-5, 4-6).

A comparison of Figs. 4-5 and 4-6 shows that 2-methylbenzyl alcohol should not be as toxic as isobenzofuranone with respect to the zinc reduction current efficiency.

On the anodic sweep, there is an anodic shift in the position of the zinc oxidation wave. This shift is proportional to the concentration of 2-methylbenzyl alcohol present (Fig. 4-4). The shift in anodic and cathodic zinc waves again indicates a decrease in reversibility with increasing organic concentration.

4.3.5 The Effect of 2-Methylbenzaldehyde

2-Methylbenzaldehyde is a major product of the electrolytic reduction of phthalic acid at constant current using a zinc cathode (refer Chapter 5).

0.5 cm³ increments of a saturated 2-methylbenzaldehyde solution (6.86×10^{-3} M in 1.1M sulphuric acid, as determined by gas chromatography) were used in this investigation giving concentrations of 1.37, 2.74, 4.12, 5.49 and 6.86×10^{-4} M. The effect of 2-methylbenzaldehyde differs to that of isobenzofuranone (Fig. 4-5) in that, instead of an anodic shift in the hydrogen wave, a small cathodic shift occurs (Figs. 4-7, 4-4). However, similarly to isobenzofuranone, a large cathodic shift in the zinc reduction wave occurs which considerably outweighs the small cathodic shift in the hydrogen reduction wave.

Change in the Separation between Decomposition potentials, E_D (mV).

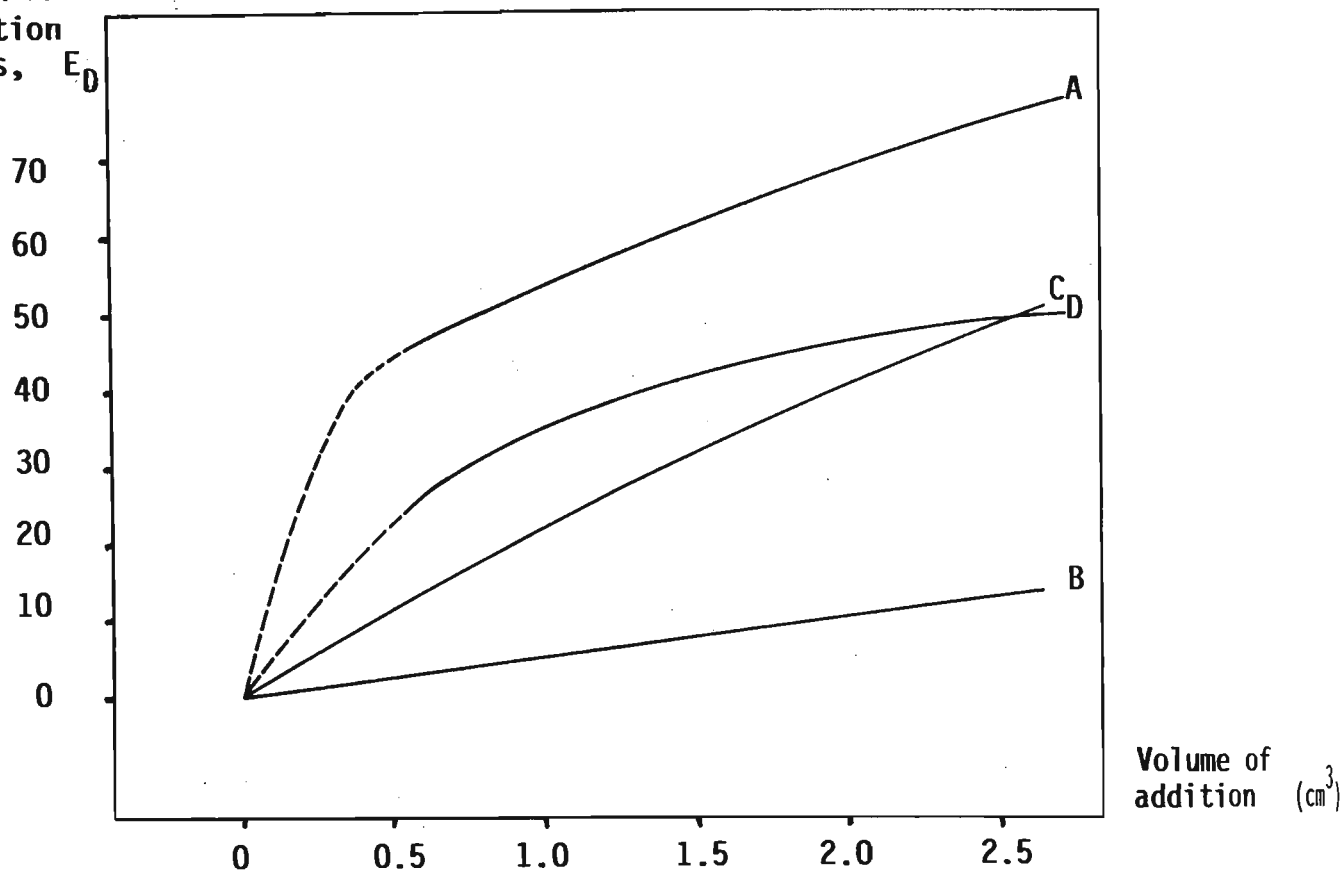


Fig.4-9. Plot of the change in separation between decomposition potentials (zinc and hydrogen reduction waves) versus volume of addition.

isobenzofuranone	A
phthalic acid	B
2-methylbenzyl alcohol	C
2-methylbenzaldehyde	D

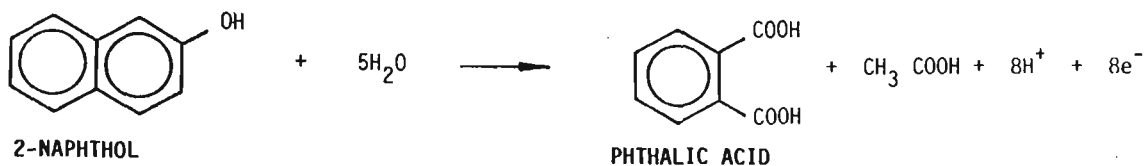
The results obtained in this investigation using a mercury cathode do not therefore offer any explanation for the reported synergistic effect of cobalt and isobenzofuranone on the current efficiency of zinc reduction in plant liquors⁽⁷⁾.

4.4 Conclusion

The results of the effects of these additives on the separation between the zinc and hydrogen reduction waves may be useful in predicting their effects on current efficiency. The larger the separation, the higher the expected current efficiency, while a smaller separation should correlate with a lower current efficiency. Thus the relative toxicity of the various compounds toward the reduction of zinc can be compared.

Phthalic acid and cobalt as individual additives have little effect on the separation and thus can be considered to have minimal effect on the current efficiency (Fig. 4-9). In increasing order of toxicity with respect to concentration, these are followed by 2-methylbenzyl alcohol, isobenzofuranone and 2-methylbenzaldehyde.

In Electrolytic Zinc plant electrolytes, 2-naphthol is added to the electrolysis cell to improve current efficiency and promote formation of a smooth, massive and easily stripped deposit⁽⁷⁾. Oxidation of 2-naphthol to phthalic acid within the electrolysis cell can occur via the anode or anode oxidation products.



Phthalic acid is then reduced at the zinc cathode to isobenzofuranone. The isobenzofuranone formed is then reduced to 2-methylbenzaldehyde and ultimately to 2-methylbenzyl alcohol. Isobenzofuranone is known to be toxic and another unidentified organic is thought to be very toxic to the current efficiency of zinc reduction⁽⁷⁾. These results suggest that the toxic unidentified organic may be 2-methylbenzaldehyde which is a reduction product of isobenzofuranone.

Analysis of plant electrolytes at the time of current efficiency slumps have shown much higher levels of isobenzofuranone than detected during normal plant operation. The results obtained for isobenzofuranone indicate that a decrease in current efficiency is expected with increasing isobenzofuranone concentration, this is consistent with the above plant observations. Thus this technique appears to provide a useful indication of how various factors affect current efficiency for zinc reduction.

CHAPTER 5: A GAS CHROMATOGRAPHIC INVESTIGATION
 OF PHTHALIC ACID ELECTROLYSIS PRODUCTS

5.1 Introduction

Aromatic dicarboxylic acids are reduced to the corresponding lactone or dihydric alcohol, depending on the orientation on the ring of the carboxyl groups⁽⁴⁴⁾.

Alternate pathways for the reduction of o-phthalic acid have been proposed by Sakurai^(31,32) and Jones⁽³³⁾ as described in Chapter 1. Isobenzofuranone has been identified as the main reduction product, while reduction of the benzene ring can occur under less severe conditions⁽³⁴⁻³⁶⁾.

Phthalic acid was selected for study as it is known to be an oxidation product of 2-naphthol and has been detected in plant electrolytes. Oxidation of residual additive 2-naphthol is expected to occur within the zinc electrowinning cell.

In the present investigation gas chromatography was used to monitor the products and reactant of electrolysis of phthalic acid at constant current in a synthetic zinc electrolyte. The gas chromatographic technique was developed from a technique used by Galbraith⁽⁶⁶⁾.

Zinc and aluminium cathodes were used in this investigation. These materials were selected as they are the two cathode materials appearing in zinc electrowinning circuits. Aluminium is used as a substrate for the electrodeposition of zinc.

5.2 Chemicals and Reagents

(i) o-Xylene: Ajax, laboratory reagent

(purity > 95%, b.p. 142 - 145°C).

(ii) Dimethylphthalate: BDH, laboratory reagent

(purity > 99%, b.p. 280 - 285°C).

(iii) Boron trifluoride-methanol complex: BDH,

reagent for methylating acid groups for GLC analysis

(approximately 14% boron trifluoride in absolute methanol).

Additional chemicals and reagents were as stated in Chapter 3 (section 3.2.1) and Chapter 4 (section 4.2).

5.3 Experimental

5.3.1 General

The electrolysis of phthalic acid was carried out in a 400 cm³ electrolysis cell using zinc and aluminium as cathodes and a lead electrode as anode with neither isolated. The area of each electrode was approximately 5.2 cm², and a constant current of 210 mA was applied, resulting in a current density of 40.4 mA cm⁻² (404 Am⁻²) which is comparable to the current density used in Electrolytic Zinc's zinc electrowinning circuits (around 400 Am⁻²). The electrolysis cell was thermostated at 35°C, once again in the operating range of practical zinc electrowinning.

The gas chromatographic investigation was carried out using a 5% OV-17 column thermostated at 195°C with flame ionization detectors operating at 250°C and a carrier gas of nitrogen flowing at 1.5 cm³s⁻¹.

5.3.2 Phthalic Acid Electrolysis

This study involved the constant current electrolysis of 300 cm³ of 3 x 10⁻²M phthalic acid solution in 1.1M sulphuric acid for a period of twenty four hours, cathode and anode potentials were measured and a 5.0 cm³ aliquot of electrolyte solution removed for subsequent analysis.

The methylating agent requires a non-aqueous environment due to the boron trifluoride decomposing on contact with water. To achieve this a technique was developed in which each electrolyte sample was extracted with 5.0 cm³ of diethyl ether, evaporated to dryness and finally dried in a vacuum desiccator for two hours. The dried extract was then dissolved in 1.0 cm³ of methylating reagent (boron trifluoride-methanol complex (14%)) and heated on a steam bath for ten minutes to effect methylation^(67,68). The resulting solution was then swamped with 4.5 cm³ of water to decompose unreacted boron trifluoride (avoids contamination of chromatographic column), and extracted with 5.0 cm³ of diethylether. Five microlitre aliquots of the ether extract were then injected onto the gas chromatographic column.

A blank determination using the methylating agent and phthalic acid yielded a single chromatographic peak due to the formation of dimethylphthalate. A similar test

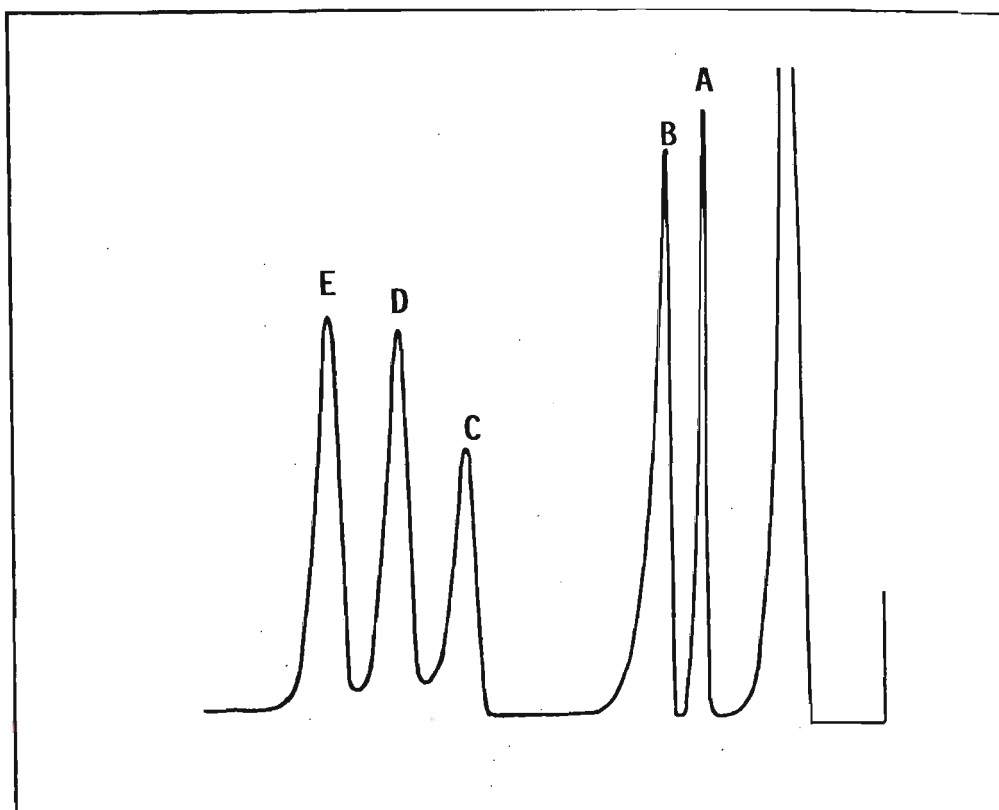


Fig.5-1. Chromatograms of phthalic acid derivatives.
 A - 2-Methylbenzaldehyde ($1.241 \times 10^{-2}M$)
 B - 2-Methylbenzyl Alcohol ($0.866 \times 10^{-2}M$)
 C - Phthalic anhydride ($1.076 \times 10^{-2}M$)
 D - Isobenzofuranone ($0.996 \times 10^{-2}M$)
 E - Dimethylphthalate (methylated phthalic acid)
 ($1.039 \times 10^{-2}M$)

COMPOUND	R_F VALUE
2-Methylbenzaldehyde	0.447
2-Methylbenzyl Alcohol	0.359
Phthalic Anhydride	0.191
Isobenzofuranone	0.163
Dimethylphthalate	0.142

Table 5-1. R_F Values for phthalic acid derivatives.

using the methylating agent and each of the phthalic acid derivatives of interest yielded single chromatographic peaks for 2-methylbenzaldehyde, 2-methylbenzyl alcohol, phthalic anhydride and isobenzofuranone.

5.3.2.1 The Gas Chromatographic Technique

A chromatographic technique was investigated in accord with the work of Galbraith⁽⁶⁶⁾ utilizing a 5% OV-17 column. For phthalic acid and its derivatives, good separation with a minimum analysis time was achieved by optimizing the oven temperature and carrier gas flow rates as shown in Figure 5-1.

Phthalic acid required methylation prior to analysis. The methylation was achieved by the use of a commercial reagent, boron trifluoride-methanol complex. To avoid deterioration of column performance residual boron trifluoride must be removed prior to sample injection. This was performed by decomposing the residual boron trifluoride with water and extracting the sample with diethyl ether.

Calibration of the detector response for each of the phthalic acid derivatives were performed.

The ratio of the retention times of each of the phthalic acid derivatives to the retention time of the unimpeded gas gives R_F values which are listed in Table 5-1.

5.3.2.2 Using Zinc as Cathode

Analysis of the resulting gas chromatograms allowed both the identification and concentration of the electrolysis products to be determined. The retention characteristics and standard addition techniques were

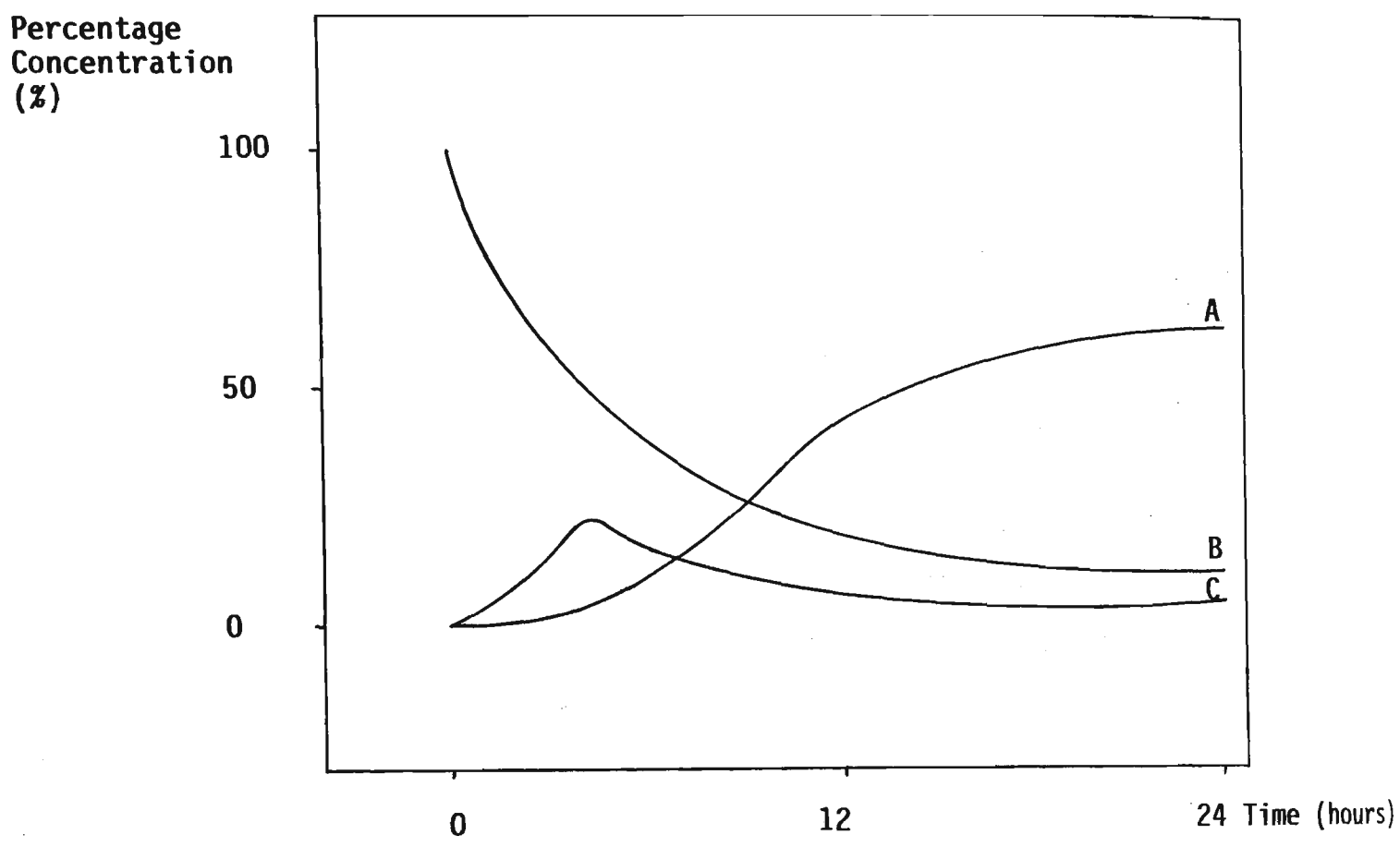
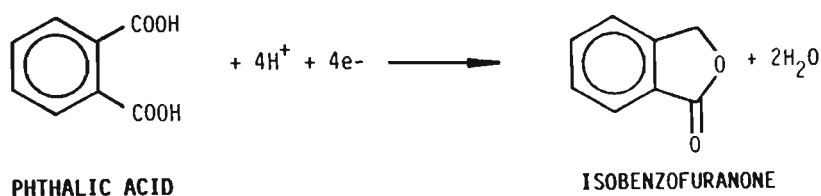


Fig.5-2. Time dependence plot of the percentage concentration of 2-methylbenzaldehyde 'A', phthalic acid 'B', and isobenzofuranone 'C', (determined as dimethylphthalate) during constant current electrolytic reduction of 3×10^{-2} M, phthalic acid in 1.1 M sulphuric acid solution, zinc cathode, lead anode, 308K, 40mAcm^{-2} current density. Mass balance calculations involving replicate determinations account for approximately 75% of the phthalic acid electrolysed.

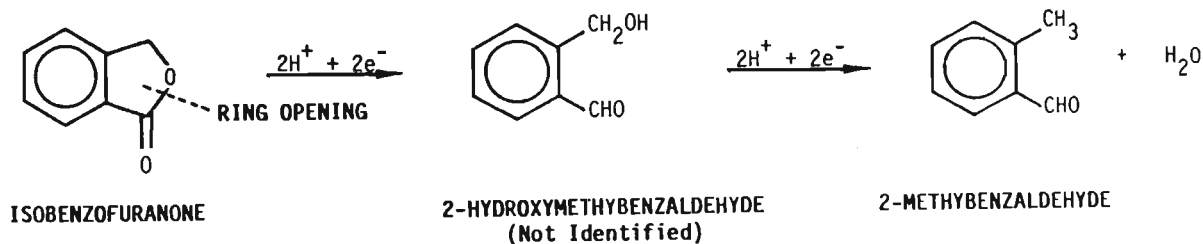
used to identify the electrolysis products. The individual concentration of these products were determined by integration of the area under the peaks with respect to their individual response characteristics. The resulting time-dependence plot is shown in Figure 5-2.

The results of the gas chromatographic study support the following pathway for phthalic acid reduction on a zinc cathode.

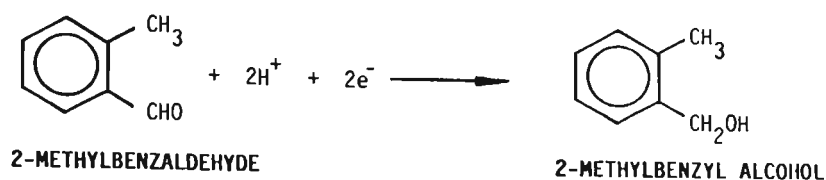
Phthalic acid is first reduced to isobenzofuranone as proposed by Jones (33) :



The isobenzofuranone formed is then further reduced to 2-methylbenzaldehyde, presumably through at least one intermediate, as follows:



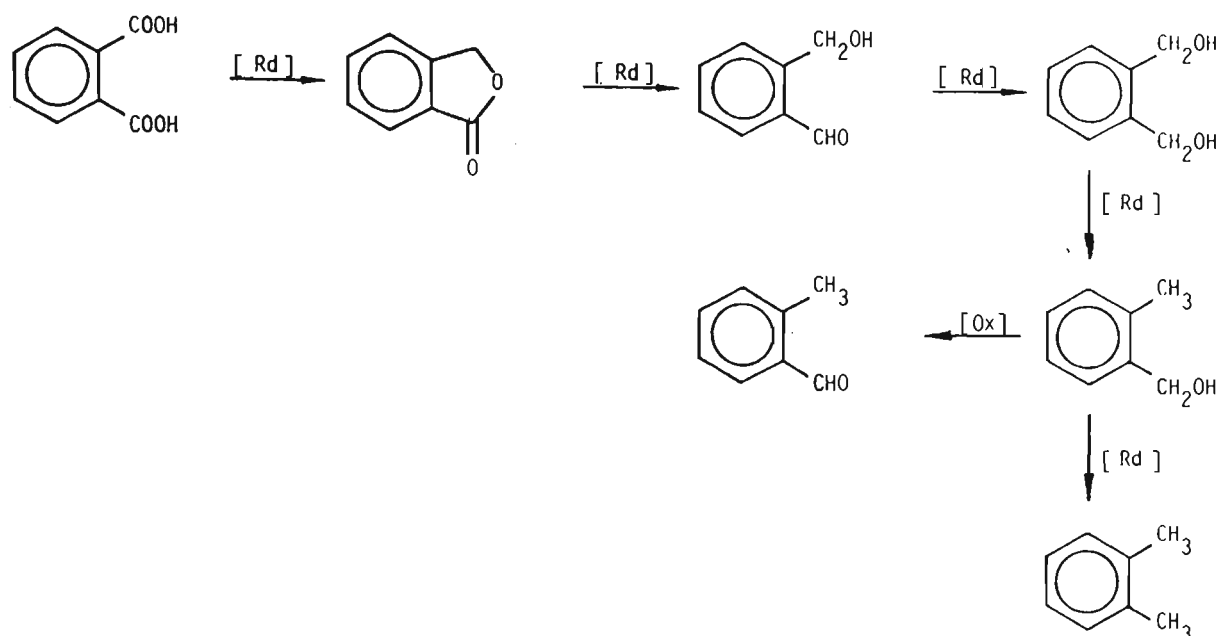
It has been reported⁽⁶⁹⁾ that 2-methylbenzaldehyde can be further reduced to 2-methylbenzyl alcohol:



However, 2-methylbenzyl alcohol was not detected in the present gas chromatographic study using zinc or aluminium cathodes, and it is not known by which mechanism it is formed within EZ plant electrolytes.

The proposed reduction scheme is in agreement with other reports. Whitnack et al.⁽¹⁰⁾ and Rodd⁽⁷⁰⁾ state that 2-hydroxymethylbenzaldehyde is the reduction product of isobenzofuranone. Hessert⁽⁷¹⁾ also reports that 2-hydroxymethylbenzaldehyde can be oxidized to phthalic acid using alkaline potassium permanganate.

The following reduction scheme which was suggested by Ault⁽⁶⁹⁾ to account for the presence of isobenzofuranone and 2-methylbenzyl alcohol in zinc electrowinning cells can also be discounted, as o-xylene was analysed for and not detected in the electrolysis extracts.



5.3.2.3 Using Aluminium as Cathode

Analysis of the resulting gas chromatograms indicated that no isobenzofuranone, 2-methylbenzaldehyde or 2-methylbenzyl alcohol was detected. After 24 hours of electrolysis, approximately 70% of the original phthalic acid remained and an extremely small quantity of o-xylene was detected. An aluminium cathode operating at the current density of the zinc electrowinning cell is thus not capable of reaching a sufficiently negative potential to facilitate the reduction of phthalic acid, as aluminium possesses a lower hydrogen overpotential than zinc. A zinc cathode allows the electrode to gain sufficiently negative potential (- 1.1 to - 1.2V vs SCE) to reduce phthalic acid.

In contrast, a potential of between - 0.9 and - 1.0V vs SCE was measured for an aluminium cathode operating in an experimental electrolysis cell.

The results of the gas chromatographic investigation indicate that the pathway proposed for the reduction of phthalic acid on a zinc cathode does not apply for an aluminium cathode.

5.4 Conclusion

The reduction of phthalic acid in a sulphuric acid electrolyte initially yields isobenzofuranone. Isobenzofuranone is then reduced to 2-methylbenzaldehyde, possibly through the intermediate product 2-hydroxymethylbenzaldehyde.

A number of the steps in this reduction scheme is supported by earlier workers^(31-33, 70, 71) and by the results of the present gas chromatographic investigation.

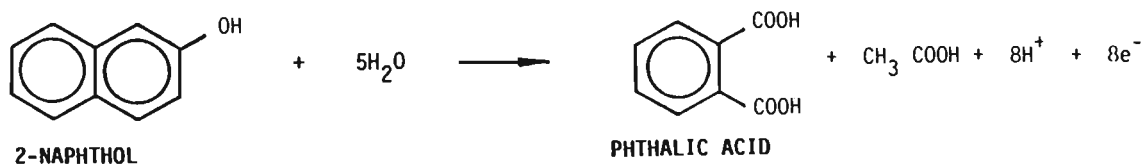
The zinc cathode is considered to play an important role as the electrode surface at which the reduction takes place, as none of the formentioned reduction products were detected when an aluminium cathode was used. Zinc is capable of acquiring a sufficiently negative potential due to its larger hydrogen overpotential, hence facilitating the reduction of phthalic acid.

CHAPTER 6: A GAS CHROMATOGRAPHIC INVESTIGATION
OF 2-NAPHTHOL ELECTROLYSIS PRODUCTS

6.1 Introduction

The electrochemical behaviour of 2-naphthol has been reported to be similar to that of 1-naphthol⁽⁵²⁾ as described in Chapter 1.

Phthalic acid can be produced by direct chemical or electrochemical oxidation of 2-naphthol under severe conditions ($\text{MnO}_4^-/\text{H}^+$ or O_3)⁽⁸⁾. The potential of the lead anode in the experimental electrolysis cell operates between +1.8 and +2.0V vs SCE. The oxidative power of ozone expressed as a standard electrode potential is +2.07V vs SHE (+1.83V vs SCE). Thus, the oxidative power of the anode (and anode oxidation products) is considerable, sufficient to oxidise 2-naphthol to phthalic acid:



In this investigation, gas chromatography was used to monitor the electrolysis of 2-naphthol at constant current in a synthetic zinc electrolyte (as described in Chapter 5).

A lead electrode was used in this investigation as working electrode, as this is the anode material used in electrowinning zinc.

6.2 Chemicals and Reagents

Chemicals and reagents were as stated in Chapter 3 (section 3.2.1), Chapter 4 (section 4.2) and Chapter 5 (section 5.2).

6.3 Experimental

6.3.1 General

The electrolysis of 2-naphthol was carried out in a 400 cm³ electrolysis cell using an aluminium cathode and lead anode (zinc cannot be used as cathode as any phthalic acid produced would be further reduced to isobenzofuranone). The electrolysis and gas chromatographic parameters were as described in section 5.3.1.

A blank determination was also carried out to allow for the effect of the methylating agent on 2-naphthol.

6.3.2 2-Naphthol Electrolysis

This study involved the constant current electrolytic oxidation of 300 cm³ of 3×10^{-2} M 2-naphthol solution in 1.1M sulphuric acid for a period of twenty four hours.

At hourly intervals for the first eight hours and then at twenty four hours, cathode and anode potentials were measured and a 5.0 cm³ aliquot of electrolyte solution removed for subsequent analysis.

Each electrolyte sample was analysed as described in section 5.3.2. Analysis of the resulting gas chromatograms allowed both the identity and concentration of the electrolytic oxidation product to be determined. The

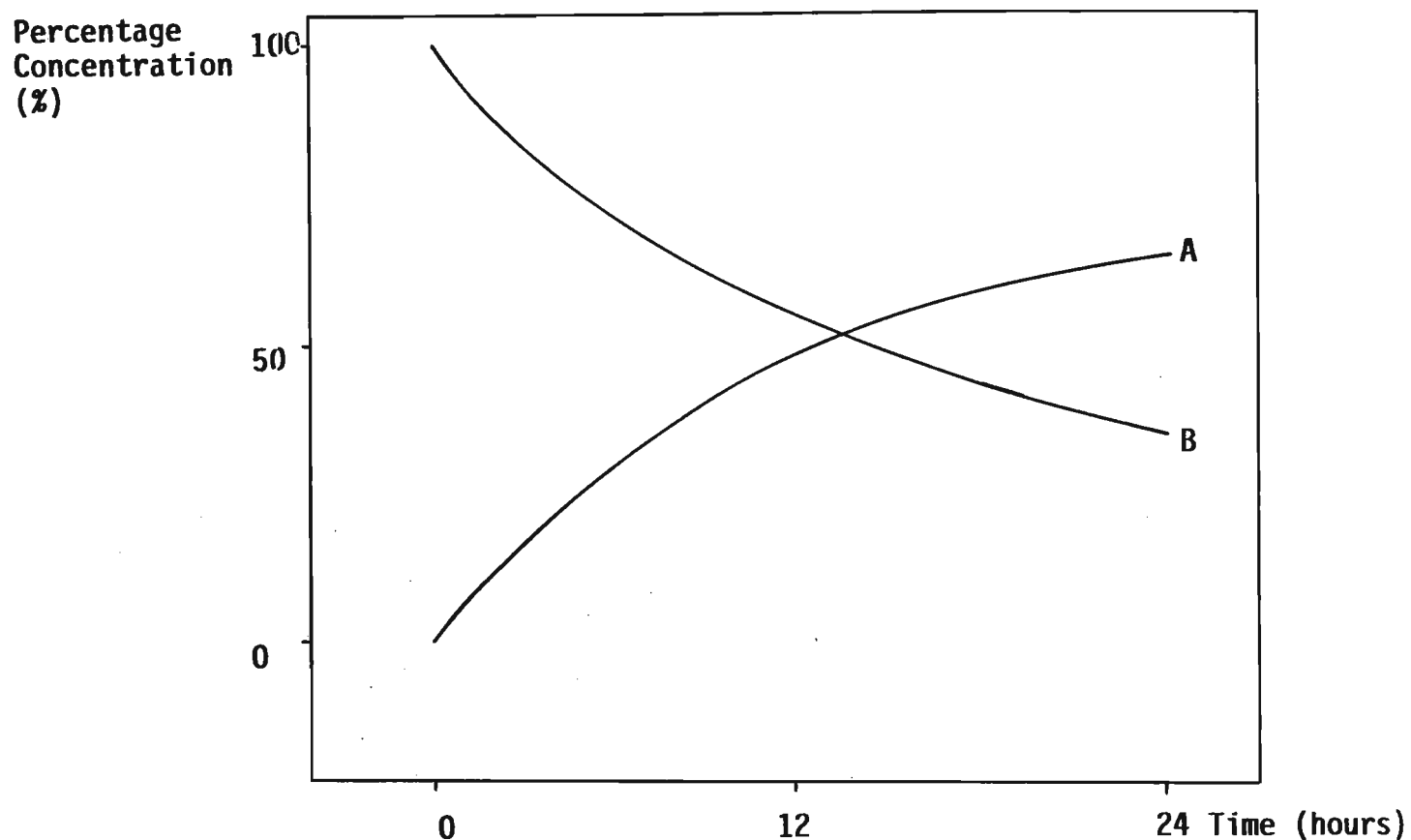
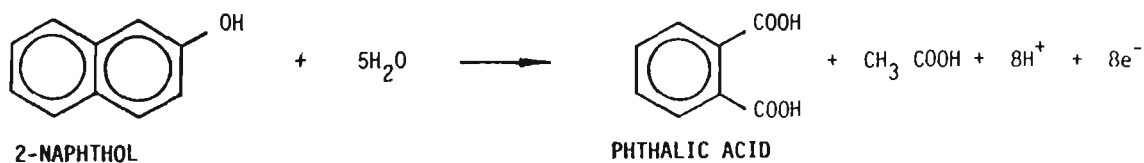


Fig.6-1. Time-dependence plot of the percentage concentrations of phthalic acid, 'A' and 2-naphthol, 'B', during the constant current electrolytic oxidation of 3×10^{-2} M 2-naphthol in 1.1 M sulphuric acid, lead anode, aluminium cathode, 308K, 40mAcm^{-2} current density. Mass balance calculations involving replicate determinations account for approximately 70% of the 2-naphthol electrolysed.

retention characteristics and standard addition techniques were used to identify the electrolysis products. The individual concentration of these products were determined by integration of the area under the peaks with respect to their individual response characteristics. The resulting time-dependence plot of the concentrations of phthalic acid and 2-naphthol is shown in Figure 6-1.

From these results it can be concluded that 2-naphthol is oxidized to phthalic acid, presumably through a number of intermediates:



6.4 Conclusion

The oxidation of 2-naphthol at a lead anode in a sulphuric acid solution of concentration similar to that used in zinc electrowinning yields phthalic acid. This indicates that a source of phthalic acid in the Risdon electrolyte is the 2-naphthol which is used as an addition reagent to control the deposition of zinc.

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