APPLICATIONS OF POLAROGRAPHY AND RELATED TECHNIQUES IN ORGANIC ANALYSIS

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Abstract

The polarographic behaviour of cinnamic acid and a series of substituted cinnamic acids (4-cyano, 3- and 4- chloro, 4-bromo, 3- and 4- methoxy, 4-methyl) has been investigated. With the exception of 4-cyano cinnamic acid, each acid was reduced via a protonated complex of the anion to the saturated acid. The course of reduction of 4-cyano cinnamic acid was pH dependent. In acid solution the nitrilo group was reduced to a primary amine while in neutral and alkaline solutions the olefinic group was reduced both in a protonated complex of the anion and in the unprotonated anion.

A comparison has been made of the polarographic behaviour of some derivatives of dithiocarbamic acid which are used as fungicides, i.e. alkyl dithiocarbamates, ethylene bis dithiocarbamates and thiuram disulphides.

The application of a.c. polarography to the determination of these compounds was considered. Linear potential sweep chronoamperometry was applied to the determination of alkyl dithiocarbamates at a dropping mercury electrode. The use of cathodic potential sweeps gave a greater sensitivity than did anodic sweeps; this effect was due to formation of an insoluble salt at the electrode surface during the delay period before the potential sweep was applied.

The pre-concentration of dithiocarbamates at a mercury electrode was used as a basis of a method for their determination by cathodic stripping voltammetry. The method was applied to all three types of dithiocarbamate with a lower sensitivity limit of 10^{-8} M.

Finally, an operational amplifier instrument for controlled alternating current oscilloscopic polarography was designed and constructed. The instrument was evaluated for the application of sine, triangular and square wave currents at variable frequencies.

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Contents

I. Introduction

1.1 The Polarographic Method

Polarography is a well established technique which has found application in analytical chemistry, electrochemistry, the study of the kinetics of reactions in solutions and the structural analysis of organic compounds and inorganic complexes. The principles of the method were first described by Heyrovský[1] in 1922; the term 'polarography' was introduced three years later[2].

Polarography is based on the special properties of an electrochemical cell consisting of a dropping mercury electrode (DME) and a reference electrode inserted in the studied solution. The current flowing through this cell is measured as a function of the electrical potential applied to the electrodes, producing a current-voltage curve or polarogram. The potential applied to the cell is equal to the potential of the DME plus the reference electrode potential

$$E_{CELL} = E_{DME} + E_{REF} \qquad (1)$$

This is true only if (i) the potential drop arising from the passage of a small current through the cell resistance is negligibly small and (ii) the potential of the reference electrode does not alter when a small current is passed through it. Under these conditions the DME potential is equal to the applied cell potential, with respect to the reference electrode and varying the applied potential effectively varies the potential of the DME. Analytical selectivity in polarography arises from the fact that different electrode reactions occur at different electrode potentials. The essential conditions that the cell resistance is low and that the reference electrode potential remains constant are usually achieved by using solutions of high conductance and large surface area reference electrodes.

Recent improvements in polarographic instrumentation[3] have allowed the method to be applied to solutions of low conductance and require only negligible currents to flow through the reference electrode.

The potential range available at the DME is limited in both positive and negative directions. At positive, anodic potentials mercury is oxidised to mercury(I) or (II) ions; the potential at which this occurs depends on the stability of the complex between the mercury ions and the anions present in solution. Weakly complexing anions such as perchlorate allow potentials as positive as + 0.4 V vs. saturated calomel electrode (SCE) to be reached. The cathodic potential is limited by reduction of the cations present in solution, or the solvent itself. In aqueous acid solutions reduction of hydrated protons occurs at about - 1.0 V vs. SCE while in neutral or alkaline solutions containing tetra-alkylammonium ions reduction of the solvent occurs at about - 2.7 V vs. SCE which is the most negative potential attainable at a mercury electrode. The greater range of cathodic potentials available at the DME is reflected in the fact that most observed electrode reactions are reductions

The cell current has two components, a capacitative current and a Faradaic current. Capacitative currents arise through changes in the capacity of the electrical double layer at the electrode solution interface. Such changes result from the periodic variation in the surface area of the DME and from adsorption-desorption processes. Faradaic currents result from electrolytic oxidation and reduction reactions at the electrodes corresponding to charge transfer across the electrode solution interface. The Faradaic process is equivalent to a complex RC impedance; in d.c. polarography only the resistive term is important. Analytically, only the Faradaic current is significant as this can be related to the concentration of the substance undergoing the electrode reaction. The limit of sensitivity in polarographic analysis is reached when the Faradaic current becomes small in comparison with the capacitative current.

As a simple example of a d.c. polarographic experiment consider the measurement of a polarogram of a pure aqueous solution 1.0 M in potassium chloride. The potential applied to the polarographic cell is varied linearly slowly so that the rate of change of current with time never approaches the response time of the current recorder.

The recorder time constant itself must not be greater than about twice the drop time of the DME. When the DME potential is more positive than 0.0 V vs. SCE an anodic current flows through the cell due to the electrode reaction

$$Hg^{0} + Cl^{-} \longrightarrow \frac{1}{2} Hg_2Cl_2$$

When the electrode is more negative than 0.0 V, a small capacitative current flows through the cell, but no charge transfer occurs until a potential of - 1.8 V is reached when the electrode reaction

$$K^{+} + e \longrightarrow K^{0}(Hg)$$

takes place producing a large cathodic current. In the potential range 0 to -1.8 V vs. SCE where no charge transfer occurs, the DME is said to be ideally polarised.

Suppose now a small amount of a thallium(I) salt is added to the potassium chloride solution so that it becomes 10^{-4} M in thallium(I) ions. A polarogram of this solution shows that a current begins to flow at about - 0.4 V due to reduction of thallium(I) ions,

$$Tl^{+} + e \longrightarrow Tl^{0}(Hg)$$

As the electrode potential becomes more negative the rate of reduction of thallium(I) increases and therefore the current increases.

The fraction of total cell current carried by the thallium(I) ion is given by the transport number of that ion

$$t_{Tl} = \frac{i_{Tl}}{i} = \frac{c_{Tl}\,\lambda_{Tl}}{\sum_n c_n\,\lambda_n} \qquad (2)$$

where i is current, c concentration, and λ equivalent ionic conductance. Thus in the presence of a large excess of potassium and chloride ions, the transport number of the thallium(I) ion becomes very nearly zero; the major part of the current is carried through the solution by migration of potassium and chloride ions. Reduction of thallium ions at the DME decreases their concentration in the vicinity of the electrode and a mass transport process operates to maintain a uniform concentration in solution. As only a small fraction of the thallium ions move under electrostatic forces, the mechanism of this mass transport process is largely diffusion. Eventually a potential will be reached on the polarogram where the rate of reduction of thallium ions is equal to their rate of diffusion to the electrode from the bulk of the solution. When this condition obtains, the cell current can increase no further and is termed a limiting diffusion current. The cell current will remain at this limiting value until the reduction potential of potassium ions is reached when the current will again increase. Once the reduction potential of thallium has been reached charge transfer occurs and the electrode is no longer ideally polarised; the thallium ion is called a depolariser and the potassium chloride a supporting electrolyte. Because of its characteristic shape, the current-voltage curve is called a polarographic wave. Two properties of the wave are of interest, (i) the wave height, which can be related to concentration and (ii) the potential at half the wave height, the half-wave potential ($E_{1/2}$) which is a thermodynamic constant characteristic of the depolariser.

The polarographic method is not restricted to the study of the reduction of simple metal ions. Because migration of the depolariser under an electric field is of little importance in the presence of a sufficient concentration of supporting electrolyte, reduction of neutral molecules and anions is possible. Early recognition of the fact that many organic compounds are polarographically active has resulted in a wide interest in this subject, with an impressive literature[4] which continues to grow rapidly[5].

1.2 Polarographic Limiting Currents

The limiting current which flows at the plateau of a polarographic wave includes contributions from a number of different processes. The current which would be obtained from the supporting electrolyte alone, without the presence of the depolariser, is termed the residual current. This itself has two components, the capacitative current arising from charging the double layer capacity at each mercury drop and a current due to Faradaic reduction of impurities in the solution. The most probable impurity is oxygen, which is polarographically reducible and must be removed from solution, usually by purging with an indifferent gas such as nitrogen or hydrogen. If the depolariser is ionic the limiting current will contain a contribution from the migration of its ions in the electrical field existing between the cell electrodes. This migration current is usually made negligibly small by the presence of a large concentration of supporting electrolyte.

The most important contribution to the limiting current is made by the Faradaic electrode process. According to Faraday's Law the electrolysis current is given by

$$i = nF \frac{dN}{dt} \qquad (3)$$

where i is the current, n the number of electrons transferred in a unit molecular electrode reaction, F the Faraday, and dN/dt the rate at which the depolariser reaches the electrode surface. This rate may depend only on the mass transport process by which the depolariser reaches the vicinity of the electrode from the bulk of the solution, or it may be influenced by other processes. Under normal polarographic conditions the mass transport process is mainly diffusion. However, in some related voltammetric techniques (i.e. techniques involving measurement of the current-potential-time relationships at an electrode) the mass transport process may be influenced by stirring the solution or rotating the electrode.

Although diffusion controlled currents are most frequently used in analytical chemistry, other processes may be involved in determining the rate at which the depolariser reaches the electrode surface and hence in limiting the height of the polarographic wave. When the depolariser is formed in solution as the product of a chemical reaction, the rate of the electrode reaction may be determined by the kinetics of the chemical reaction. Where either the depolariser or its electrode reaction product is strongly adsorbed on the electrode the polarographic wave height may be limited by the extent of adsorption. Catalysis may also be involved in limiting the rate of an electrode reaction. These effects allow the limiting currents of polarographic waves to be classified as (i) diffusion, (ii) kinetic, (iii) adsorption, and (iv) catalytic currents.

(i) Diffusion currents

The occurence of the reaction

$$A + ne \longrightarrow B$$

at the surface of an electrode decreases the concentration of A in the vicinity of the electrode. A concentration difference then exists between the bulk of the solution and a thin shell of solution surrounding the electrode which results in diffusion of A towards the electrode surface. The problem of calculating the concentration gradient towards a growing mercury drop electrode was first solved by Ilkovič[6] who assumed that linear diffusion occured towards a plane electrode with area equal to that of the surface of the drop. Application of Fick's Laws of diffusion gave the Ilkovic equation for the mean limiting diffusion current,

$$i = 607 \ nCD^{1/2}m^{2/3}t^{1/6} \qquad (4)$$

where n is the number of electrons transferred, c the concentration, D the diffusion coefficient, m the rate of mass flow of mercury through the capillary and t the drop time. Subsequently other derivations have been given by several workers who have introduced various corrections to the Ilkovič equation. The best known of these is the Koutecký[7] equation which is based on a rigorous treatment of spherical diffusion towards a specific electrode. Certain differences exist between the results given by the Ilkovič and Koutecký treatments. Thus the Ilkovič equation predicts that the diffusion current constant

$$I = \frac{i}{cm^{2/3}t^{1/6}} \qquad (5)$$

is a constant independent of the capillary characteristics m and t, whereas the Koutecky equation predicts that I varies with m and t. However such differences are of smaller magnitude than experimental errors and are insignificant in analysis.

Under a given set of experimental conditions the Ilkovič equation reduces to

$$i = kc \tag{6}$$

where k is a constant. This linear relationship between limiting current and concentration is the basis of most analytical polarographic methods. Because the diffusion coefficient is unknown, k is also unknown, and thus polarography, in common with other instrumental methods of analysis, is not an absolute method.

(ii) Kinetic Currents

When a compound undergoes a slow chemical reaction to form an electroactive species

$$A \longrightarrow B + ne \longrightarrow C$$

in the vicinity of the electrode and the chemical reaction is slow enough to be the rate determining step in the process the limiting current is called a kinetic current[8]. A very common chemical reaction in aqueous solutions is that of protonation; this occurs with carboxylic acids and a range of non-ionic compounds which show weak acid-base properties. An equilibrium will exist between the two forms

$$A \quad + \quad H^{+} \rightleftharpoons AH^{+}$$

and in the most general case both the acid and its conjugate base will be polarographically reducible. The acid will be reduced at more positive potentials. The polarographic dissociation constant of the system, pK', i.e. the pH at which the waves due to acid and base forms are of equal height, will be several pH units higher than the dissociation constant pK. This effect has been explained[9] by the removal of the more easily reduced acid from the equilibrium, followed by recombination of the base with a proton. The polarographic wave height is limited by the rate of the recombination process, and the disturbance of the equilibrium is observed as a shift in pK value. More recently, Mairanovskii[10] has suggested that under the influence of the electric field, the pH of the solution at the electrode surface is lower than in the bulk of the solution. Thus the value of pK' would correspond to the pH in the bulk solution at which the surface pH was equal to pK.

For quantitative analytical measurements diffusion currents are preferred to kinetic currents, because of the latters marked dependence on pH and temperature.

(iii) Adsorption Currents

Adsorption effects which influence polarographic waves can be due to surface activity of the depolariser or its reaction products, or to some component of the supporting electrolyte. The adsorption of electroinactive species at the electrode surface can accelerate or inhibit the reaction and the use of such compounds must be treated with caution in polarographic analysis. Adsorption of the depolariser is assumed to occur to some extent in almost all organic electrode reactions, and is thought to produce a significant increase in the concentration of reactant at the electrode surface[10,11]. In the extreme case a separate wave may be observed due to reduction of the adsorbed depolariser. Because the reduction of the adsorbed molecules requires a greater energy than does the reduction of free molecules, the adsorption wave is observed at a more negative potential. Similarly where the reaction product is strongly adsorbed, the reaction process requires less energy and the adsorption wave is observed at more positive potentials[12].

Analytically, currents limited by adsorption effects are of little application. The wave height is governed by the extent of adsorption and for most processes this reaches a limiting value over most of the concentration range which is polarographically accessible.

(iv) Catalytic Currents

Two types of catalytic current may be distinguished. In the first type the limiting current of a polarographic wave is increased in the presence of an electroinactive catalyst. The second type of catalytic wave involves a shift to more positive potentials of a polarographic wave, usually due to reduction of hydrogen, by an electroinactive catalyst. Analytically catalytic waves are attractive because the limiting currents are large and high sensitivity can be achieved. However few examples involving organic species are known. The first reported example of a catalytic process catalysed by another reagent was the increase in current observed for the oxidation of an indigosulphonate dye in the presence of hydrogen adsorbed on palladium particles[13]. Perhaps the most famous example of a catalytic process is the Brdička serum filtrate reaction[14] which can be used in the diagnosis and investigation of cancer and other pathological conditions.

1.3 The Organic Electrode Process

The electrochemical reduction of organic compounds is almost invariably a more complicated process than the simple charge transfer reactions involved in the reduction of inorganic ions. Mairanovskii[15] considers the major differences arise from:

(i) the adsorption of organic species at the electrode surface which accelerates the reaction by increasing the depolariser concentration at the electrode and by polarising the depolariser molecule in the high electric field of the double layer[16],

(ii) the participation of hydrogen ions in the potential determining step (in aqueous or semi-aqueous solvents),

(iii) the inhibition of the process by the reaction products if their surface activity is greater than that of the depolariser,

(iv) the formation of hydrogen bonds or other interactions of the depolariser with solution components.

The simplest organic electrode processes are observed in non-aqueous aprotic solvents[17,18] the commonest of which are acetonitrile, N, N' dimethylformamide, and dimethylsulphoxide. In such solvents electron transfer to the depolariser results in the formation of a stable radical anion, which is observed as a characteristic one-electron thermodynamically reversible polarographic wave. Stable radicals can be formed in this way from compounds (e.g. aromatic hydrocarbons[19]) which are electroinactive in other solvent systems. Additional advantages to the use of these solvents are better solvent properties than aqueous solvents, the greater range of oxidising potentials available (at solid electrodes) and their inertness towards hydrolysable compounds. However, to be weighed against these advantages is the fact that the solvents almost invariably contain electroactive impurities and therefore require extensive purification procedures. This limitation has so far restricted their use mainly to studies of electrode reaction mechanisms but it may be anticipated that they will find an increasing number of analytical applications.

Most analytical applications of organic polarography are based on the electrode reactions observed in proton donating solvents, among which water is by far the most common example. The range of organic compounds soluble in water can be extended by addition of a water miscible organic solvent (an alcohol, dioxane, etc.) . The appearance of a one electron wave corresponding to the formation of a free radical is rare in aqueous solvents, although it is not unknown and is observed, for example, in the reduction of cinnamaldehyde[20].

More usually the reaction involves the participation of protons and may be formulated

$$\mathrm{Ox} + ne + pH^{+} \longrightarrow \mathrm{Red}$$

Because protons are consumed in the reaction, the solution must be adequately buffered to prevent a change of pH in the vicinity of the electrode. Such changes can influence not only the reduction potential and the reaction rate but also the course of the reaction itself.

In general the electrode process will involve bond fission or reduction of an unsaturated site in the molecule and has led to the principle that organic polarography is a method of functional group analysis. Although it is the properties of the molecule as a whole which determines the energy necessary for reduction, it is rare to be able to distinguish polarographically between two structurally similar compounds containing the same electroactive centre. However, examples are known where such distinctions can be made, for instance it is possible to analyse mixtures of benzaldehyde with an alkyl aryl ketone[21].

A description of the overall reaction occuring at the electrode can be obtained by determination of the number of electrons transferred to the depolariser, n, and by identification of the electrode reaction product. Under diffusion controlled conditions a value of n may be obtained by solution of the Ilkovič equation, using an estimated value for the diffusion coefficient. Experimentally, this is done by comparing the polarographic wave height for the depolariser with that for an equimolar concentration of a similar compound with known n, under the same instrumental conditions. This method is very convenient, despite its obvious uncertainty, because the value of n is integral and is most probably small. More accurate determinations of n, based on Faraday's Law, can be made by coulometric studies at a DME (micro or millicoulometry). A constant current coulometric method has been described[22], but most determinations have been made by controlled potential coulometry. Integration of current with time can be achieved by following the decrease in polarographic limiting current with time[23] or by electronic integration.[24]

Once the value of n is known, possible products of the electrode reaction can be postulated. Unequivocal distinction between these possibilities can only be made by isolation and identification of the electrolysis products. Because only minute amounts of the product are formed at the DME attempts have been made to scale up the electrolysis using a stirred mercury pool electrode. Results obtained by this method are not always reliable as the different conditions obtaining at the electrode surface can alter the course of the reaction. In general, it is preferable to collect the products of exhaustive electrolysis at a DME, and identify them by a suitably sensitive analytical technique[25].

The mechanism of an organic electrode reaction is extremely complex and requires a complete description of mass transfer, charge transfer, chemical reactions, adsorption, desorption and possible reaction intermediates. Comprehensive descriptions of this type are not available at present, for instance there is no agreement as to the mechanism of charge transfer or indeed whether it occurs at all.

However partial descriptions of electrode reactions can be given in chemical, electrochemical, and thermodynamic terms.

Chemical mechanisms for electrode reactions can be given in terms of ionic and radical intermediates. The latter approach is usually preferred as there is some experimental evidence, e.g. based on ESR measurements[26], for the formation of radicals in aqueous solution. The fission of a chemical bond requires the addition of two electrons and two protons

$$\text{--A---B--} + 2\,e + 2\,H^{+} \longrightarrow \text{--AH} \quad \text{HB--}$$

Although compounds are known which yield polarographic waves corresponding to more than two electron additions, it is probable that such reactions occur in two stages, the second of which is rate determining. Thus in the reduction of semicarbazones ($n=4$) it has been shown[27] that the N-N bond is reduced in a two electron step, followed by reduction of the azomethine intermediate to a primary amine. Possible schemes for the two electron fission of a bond can be divided into two types. In the first type, the two electrons are added consecutively and protonation takes place subsequently (the EEC mechanism). In the second type protonation occurs between the addition of the two electrons (the ECE mechanism). Protonation of the molecule prior to electron addition is not precluded in either case. A two electron polarographic wave will result when the rate determining step is the addition of the second electron, or occurs subsequently. When the radical formed by addition of the first electron is stable, two one electron waves will be observed (the second of which may be obscured by reduction of the supporting electrolyte).

Electrochemically, it is not postulated that the depolariser need come into contact with the electrode surface before the reaction can take place.

In the absence of any species specifically adsorbed on the electrode surface the plane of closest approach is often assumed to be the outer Helmholtz layer[28]. The situation is much more complicated in the presence of specific adsorption and there is little which can be said in this case. In the very high potential gradient existing at the electrode solution interface[16], the depolariser is polarised and takes up the correct orientation to allow the addition of one or more electrons to the electroactive centre. It is apparent therefore, that the structure of the electrical double layer will exert a considerable influence on the mechanism of the electrode reaction. In addition to determining the hydrogen ion concentration at the electrode surface and the extent of adsorption of the depolariser, the double layer structure determines the potential difference between the electrode and the depolariser molecule.[11] Because the molecule need only approach the electrode to a point where the potential is sufficient for the reaction to occur, when the potential gradient is lower, the reduction potential will be lower. Thus when an alkali metal ion in the supporting electrolyte is replaced with a bulky, specifically adsorbed tetra-alkyl ammonium ion, the $E_{1/2}$ shifts to more positive potentials.

The most rigorous treatment of electrode processes is obtained by a kinetic and thermodynamic approach. The kinetics of a redox reaction

$$\mathrm{Ox} + ne \underset{k_{b,h}}{\overset{k_{f,h}}{\rightleftharpoons}} \mathrm{Red}$$

can be described by the potential dependent heterogeneous rate constants $k_{f,h}$ and $k_{b,h}$ for the forward and backward reactions,

$$k_{f,h} = k_{f,h^o} \exp\left[-\frac{\alpha nF}{RT}(E - E^o)\right] \qquad (7)$$

and

$$k_{b,h} = k_{b,h^o} \exp\left[-\frac{(1-\alpha)nF}{RT} - (E - E^o)\right] \qquad (8)$$

where E is the electrode potential, E^o a standard potential which determines k_{f,h^o} and k_{b,h^o}, and α is the electron transfer coefficient.

When the redox couple is thermodynamically reversible the electrode potential is related to the concentrations of oxidised and reduced species at the electrode surface by the Nernst equation

$$E = E^{o} - \frac{RT}{nF} \ln \frac{[Red]_{o}}{[Ox]_{o}} \qquad (9)$$

Substitution of concentrations under diffusion controlled conditions from the Ilkovič equation leads to the equation for a reversible polarographic wave

$$E = E^{o} - \frac{RT}{nF} \ln \left[\frac{i}{i_{LIM} - i} \sqrt{\frac{D_{Ox}}{D_{Red}}} \right] \qquad (10)$$

Assuming that the diffusion coefficients of the oxidised and reduced species are nearly equal, and introducing $E = E_{1/2}$ when $i = i_{LIM}/2$, (10) reduces to the well known equation

$$E = E_{1/2} - \frac{RT}{nF} \ln \frac{i}{i_{LIM} - i} \qquad (11)$$

Few organic compounds are known which are polarographically reduced in aqueous solution to give reversible waves, in most cases a slow electrode reaction gives an irreversible wave. The current at any point on an irreversible wave reflects not the position of a rapidly established equilibrium, but the rate of the half reaction concerned. The cathodic current corresponding to a reduction is given by

$$i \;=\; n_{\alpha}\; FA\;\; c_{Ox^{\circ}}\, k_{f,h^{\circ}}\; \exp\left[-\frac{\alpha nF}{RT}(E - E^{\circ})\right] \qquad (12)$$

from which it is apparent that a plot of ln i against E has a slope equal to $-\alpha n_{\alpha}$ F/RT and providing $c_{Ox^{\circ}}$ is a constant $k_{f,h^{\circ}}$ can be calculated. This condition is only approximately true at the foot of a polarographic wave. A rigorous treatment[29] of an irreversible wave gives

$$E \;=\; E_{1/2} - \frac{RT}{\alpha n_{\alpha}\, F}\;\ln\frac{i}{i_{LIM} - i} \qquad (13)$$

where

$$E_{1/2} \;=\; E^{\circ} + \frac{RT}{\alpha n_{\alpha}\, F}\;\ln 0.886\, k_{f,h^{\circ}}\sqrt{\frac{t}{D_{Ox}}} \qquad (14)$$

from which the kinetic parameters α and $k_{f,h^{\circ}}$ can be calculated. The value of n_{α} in this equation is not the total number of electrons transferred but the number in the rate determining step. Where the reaction mechanism is unknown it is possible to obtain values of $n_{\alpha}\,\alpha$ only.

In many organic electrode reactions protonation precedes the redox reaction proper

$$Ox \;+\; p\,H^{+} \rightleftharpoons HpOx^{p+} \;+\; ne \longrightarrow HpRed$$

where the protonation has a dissociation constant

$$K = \frac{[Ox]_o\,[H^+]^p}{[HpOx^{p+}]_o} \qquad (15)$$

The current is given by (cf. 12)

$$i = nFA\;k_{f,h}\,[HpOx^{p^+}]_o \qquad (16)$$

$$= nFA\;k_{f,h}\,\frac{[Ox]_o\,[H^+]^p}{K} \qquad (17)$$

Substituting for $k_{f,h}$ from (7) and for $[Ox]_o$ from the Ilkovič equation, the rigorous treatment[29] gives

$$E_{1/2} = \text{const} - 2.3\,\frac{p\,RT}{\alpha\,n_\alpha\,F}\;pH \qquad (18)$$

or

$$\frac{\partial E_{1/2}}{\partial pH} = -\;2.3\,\frac{p\,RT}{\alpha\,n_\alpha\,F} \qquad (19)$$

Thus protonation before electron addition requires that $E_{1/2}$ is pH dependent and (19) allows the number of protons to be calculated. However because of uncertainties in the value of α it is rarely possible to obtain a reliable value for p.

If two structurally related compounds have the same values of D_{Ox} and $\alpha\,n_\alpha$, and their $E_{1/2}$ values are measured under identical conditions, from (14)

$$(E_{1/2})_1 - (E_{1/2})_2 = \frac{2.3\ RT}{\alpha n_\alpha\ F} \log \frac{(k_{f,h^\circ})_1}{(k_{f,h^\circ})_2} \qquad (20)$$

If the two compounds are meta or para substituted benzene derivatives, they will obey the Hammett equation[30]

$$\log \frac{k}{k_0} = \sigma\rho \qquad (21)$$

where σ is a substituent constant and ρ a constant for a given reaction. Combining (20) and (21),

$$\Delta E_{1/2} = \frac{2.3\ RT}{\alpha n_\alpha\ F} \rho\ \sigma \qquad (22)$$

or

$$E_{1/2} = \rho'\sigma \qquad (23)$$

which is Zuman's[31] modification of the Hammett equation. Extensions of this equation are available which apply to ortho substituents, aliphatic, alicyclic, and heterocyclic systems[32]. Despite the fact that the theoretical basis of the equation has been questioned repeatedly[33,34,35], in the very great majority of cases investigated a linear relationship has been found to exist between $\Delta E_{1/2}$ and σ. Studies of this kind have been used in elucidating reaction mechanisms, for example in distinguishing between two possible mechanisms.[36]

1.4 Techniques Related to Polarography

While d.c. polarography remains the most widely used electroanalytical technique a number of related methods have been developed with the aim of increasing the sensitivity and selectivity of the d.c. method. Techniques which have been developed primarily for the study of electrode reaction mechanisms, e.g. coulostatic analysis[37], chronocoulometry[38] and radio-frequency polarography[39], but which have not yet been applied in analytical chemistry to any extent are beyond the scope of this account.

(i) Linear Potential Sweep Chronoamperometry

D.c. polarography is a special case of a more general voltammetric technique known as linear potential sweep chronoamperometry. As its name implies this involves the measurement of the current-time curve at an electrode during the application of a linearly changing potential. The mass transport process may be diffusion or can involve convection due to stirring the solution or rotating the electrode. The behaviour observed for a stationary electrode in a quiet solution is quite different from that observed where convection is involved. In the latter case the depolariser concentration at the electrode surface is continuously renewed, as with a DME, and the current time curve resembles a d.c. polarogram. For a stationary electrode once the reduction potential of the depolariser has been reached, its concentration decreases rapidly at the electrode surface and the current decreases, producing a peak shaped current-time curve. The peak current in this case is described by the Randles-Ševčík equation[40,41],

$$i \;=\; 2.687 \times 10^{5} \; n^{2/3} \; AD^{1/2} \; c \; v^{1/2} \qquad (24)$$

where v is the potential sweep rate. The numerical constant is that given by Nicholson and Shain[42]. The dependence of i on $v^{1/2}$ suggests that for maximum sensitivity a large potential sweep rate should be used. However the capacitative current is directly proportional to v, and so at high sweep rates the Faradaic current is completely masked.

A recent development of linear potential sweep methods has been to apply not a single or repetitive potential ramp to the electrode but to use instead a triangular wave. This technique, cyclic voltammetry, allows observation of the oxidation of the products of a chemically reversible reduction. For a thermodynamically reversible reaction the $E_{1/2}$ values of the forward and backward reactions will be identical. In linear potential sweep methods, for slow sweep rates it can be shown[42]

$$Ep = E_{1/2} + \frac{0.028}{n} \qquad (25)$$

where Ep is the peak potential. On a cyclic voltammogram of a reversible couple the cathodic and anodic peak potentials will be separated by 56/n mV. This condition will no longer obtain where the process is influenced by the kinetics[42-45] of the reaction or by adsorption[46]. Cyclic voltammetry might be expected to have some analytical applications, e.g. for determination of an irreversible species in the presence of a reversible species having the same reduction potential. However, at the present time few applications have been reported and the technique is used mainly in the study of electrode reaction mechanisms.

(ii) A.C. Polarography

The technique of a.c. polarography[47,48] involves measuring the a.c. current which flows through a polarographic cell when a small a.c. potential (about 10 mV) is applied. An a.c. polarogram is obtained by plotting a.c. current as a function of the d.c. potential of the DME while the amplitude of the a.c. potential remains constant. In the presence of a thermodynamically reversible couple a symmetrical peak shaped curve is obtained, the height of which is linearly dependent on concentration.

The behaviour of a polarographic cell under these conditions is frequently described in terms of its equivalent electrical circuit. Randles[49] has given an equivalent circuit for an electrode (i.e. a metal and the solution in contact with it) a simplified version of which is shown (Figure 1.1)

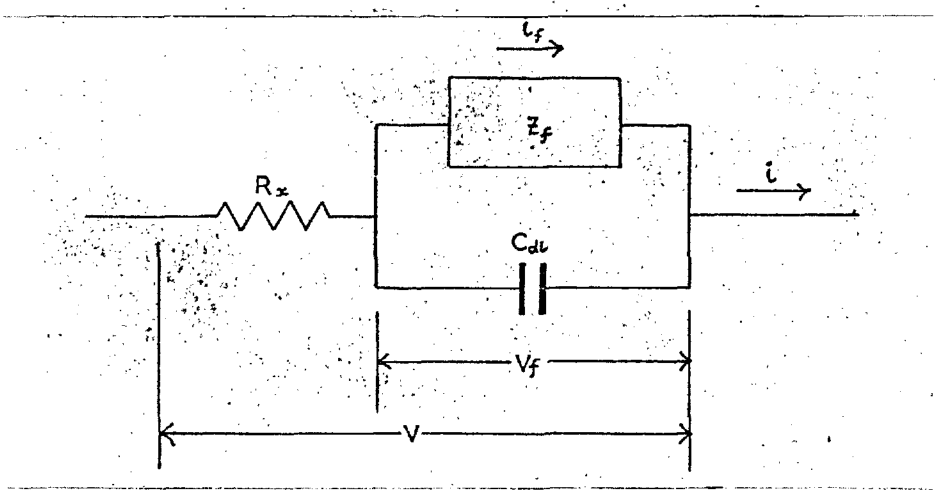


Figure 1.1 Equivalent Circuit of an Electrode

Here the complex RC impedance, Z_f, of the Faradaic process is shunted by the capacitance of the double layer, C_{dl}, in series with which is the electrode resistance R_x. The application of an a.c. potential V across this circuit results in an a.c. current i passing through it, with a phase angle ϕ between the current and potential. The current can be resolved into two components, the phase component and the quadrature component (Figure 1.2) which have phase angles of 0° and 90° with the applied potential.

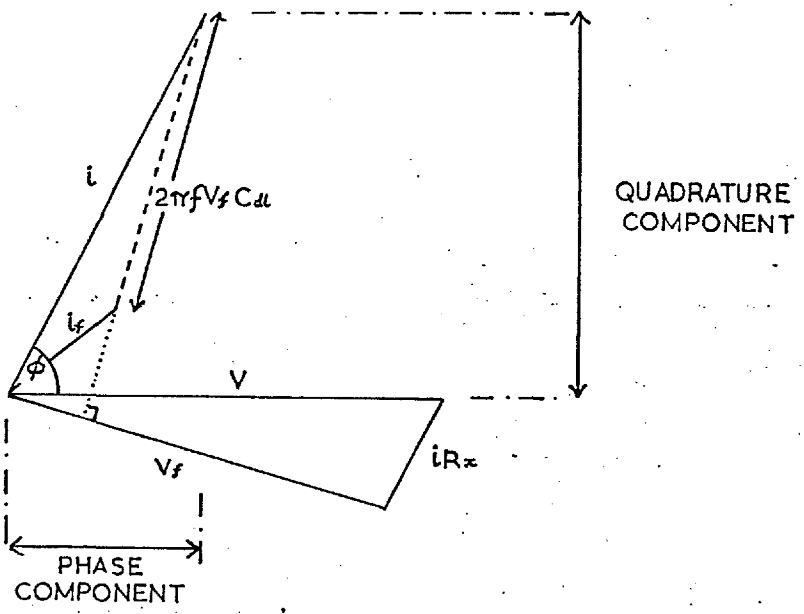


Figure 1.2 Vector Diagram of I-V Relationships

The potential IR_x across the series resistance is in phase with the current i and on the vector diagram are drawn parallel. The potential V_f across Z_f then completes the vector triangle $V-IR_x-V_f$. The potential V_f across the double layer capacity is 90° out of phase with the current, $2\pi fV_fC_{dl}$, through it, where f is the a.c. frequency. The current through the Faradaic impedance, i_f, then completes the current vector triangle $i - i_f - 2\pi f V_f C_{dl}$. From this vector diagram it is apparent that the phase component of the current contains contributions from the Faradaic impedance and the double layer capacity. The capacitative component is decreased if the series resistance R_x is made small. Thus phase selective a.c. polarography provides a simple means of separating the Faradaic and capacitative currents, providing the cell resistance can be made small. Measurement of the phase component is used for the determination of species undergoing redox reactions, while the quadrature current can be used in the determination of surface active agents which alter the capacity of the double layer.

(iii) Controlled Current Methods

The measurement of current voltage curves is usually achieved by varying the potential applied to an electrode with simultaneous recording of the current. The converse technique in which the potential is measured as a function of applied current has been advocated in both d.c.[50] and a.c.[51] polarography. Greater interest is shown at the present time in those techniques in which a controlled constant current is passed through a cell, with measurement of the potential-time curve. When a d.c. current is used the technique is known as chronopotentiometry, while the a.c. analogue has been called oscillopolarography.

Chronopotentiometry is performed under diffusion controlled conditions at a stationary electrode in a quiet solution. When a constant current is applied the surface concentration of a reacting species reaches zero in a finite time, the transition time, which is observed as a change of electrode potential. Sand showed that the transition time is given by

$$\tau^{1/2} = \frac{\pi^{1/2} n\ F\ A\ D^{1/2}\ c^{o}}{2\ i} \qquad (26)$$

Paunovic[53] has reviewed recent developments in chronopotentiometry, while Davis[54] has reviewed the analytical applications of the technique. The square root relationship between the measured variable and concentration, although unusual, is equally as effective in analysis as more direct relationships. The sensitivity of chronopotentiometry is limited by the difficulty of making proper correction for the current necessary to charge the double layer capacity.

The technique of oscilloscopic polarography at controlled alternating current was introduced by Heyrovský and Forejt[55,56] as a method of studying electrode processes. A large amplitude constant a.c. current is passed through the cell and the working electrode potential, which varies between its positive and negative limits, is displayed on an oscilloscope. A recent review of the technique has been given by Heyrovský and Micka[57] while Kalvoda[58] has given a detailed survey of practical applications. The method has not found wide acceptance in quantitative analytical measurements, but it is recognized as a test of polarographic reversibility.

1.5 Instrumentation

It is inevitable that as more exacting demands are made on analytical methods the instruments necessary to implement them have become more complex. Thus modern electroanalytical instruments reflect increasingly the growth in electronics which has been one of the features of the present century. There is little point in giving here an account of commercially available polarographs as reviews are available in the various monographs[47,59] and serve mainly as a guide to prospective customers. Instead, a single instrumental method which has been introduced during the previous ten years will be discussed. This method, based on the use of operational amplifiers, is essentially an analogue approach to chemical instrumentation. In an analogue system some chemical parameter is converted by a suitable transducer to an electrical current or voltage which is then operated on by the instrument to produce a convenient read out signal. Operational amplifier methods have been applied in many branches of analytical chemistry although up to the present time most applications have been in electroanalytical instruments. A more recent development has been to use digital instrumentation for data analysis[60-63] and waveform generation[62]. These methods always involve the use of analogue to digital (or digital to analogue, in the latter case) converters because an electrochemical cell itself is an analogue device. Operational amplifier instrumentation now has an extensive literature[64,65] which has not yet been adequately reviewed. Smith[48] has given a comprehensive review of methods applicable to a.c. polarography.

Operational amplifiers are now made in a number of different types so it is difficult to generalise their properties. The basic amplifier may be considered as a differential input, wideband (d.c. to 1 M Hz) high gain (10^4 to 10^8) electronic amplifier. Because it is a differential input device, its response is described by

$$e_o = A (e_A - e_B) \qquad (27)$$

where e_o is the output signal, e_A and e_B the signals at the two inputs and A the open loop gain. In all commercially available amplifiers the output is referred to earth. In many circuits, input A (the positive input) is held at earth potential, when the response of the amplifier is described by

$$e_o = - A e_B \qquad (28)$$

Input B (the negative input) is therefore known as the inverting input, because it changes the sign of the input signal, and thus provides for the use of a stable negative feedback loop. The positive input is non inverting.

An account of the different modifications of this basic amplifier, e.g. chopper stabilisation, FET input, varactor bridge circuits, cannot be given here; suffice it to say that the amplifiers are now available with nearly ideal properties. Most of the important and useful functions of the amplifier are achieved by use of suitable negative feedback circuits and input impedances. Operational amplifiers were originally designed for use in analogue computers where they perform such mathematical operations as addition, subtraction, multiplication and division by constants, integration, differentiation and transformation into logarithms. Many of these circuits have been successfully used in chemical instruments. A great many additional operational amplifier circuits have been devised which have purely instrumental functions. This approach to instrumentation in electrochemistry is largely due to the work of Booman[66], DeFord[67], and Kelley[3].

Operational amplifier circuits have been developed to instrument most of the established electroanalytical techniques e.g. d.c.[3], a.c.[48], square wave[68] and pulse polarography[69]. These circuits are almost invariably more reliable, cheaper and physically smaller than their 'classical' equivalents. Electroanalytical instrument circuits can be divided into three sections, (i) the circuit necessary to control the electrode potential (or current), termed a potentiostat (or galvanostat), (ii) the circuits which produce the waveforms to be applied to the electrode, i.e. function generators, and (iii) the circuits which measure the cell current (or electrode potential) and modify it to give a suitable output signal.

Schwarz and Shain[70] have classified the different configurations of operational amplifier potentiostats and galvanostats. There are two possible types of simple single amplifier potentiostats in which the working electrode (Figure 1.3a) and the counter electrode (Figure 1.3b) are held at earth potential

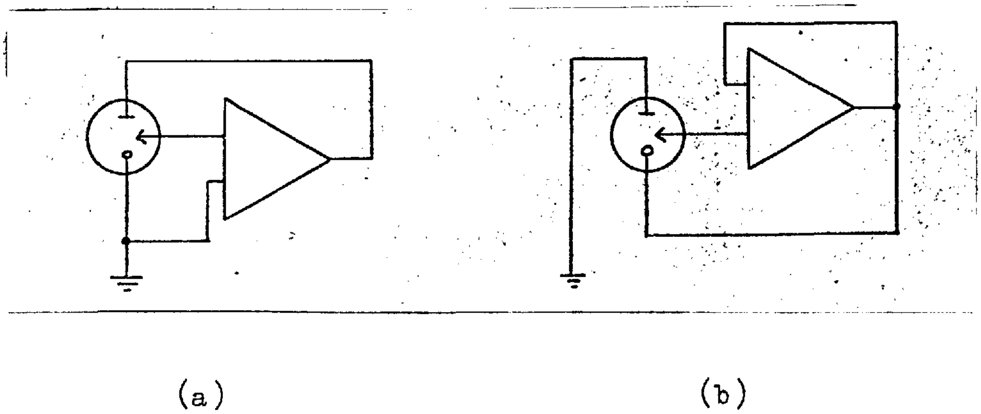

(a) (b)

Figure 1.3 Single amplifier potentiostats

Consideration of the possible positions in these circuits for the signal generator and the current measuring device shows that eighteen different circuits exist. Single amplifier potentiostats are very convenient where a fast response time is required but impose limitations on the other circuits involved. Where a composite signal source is required a multi-amplifier potentiostat is preferred, the most common configuration of which is shown (Figure 1.4)

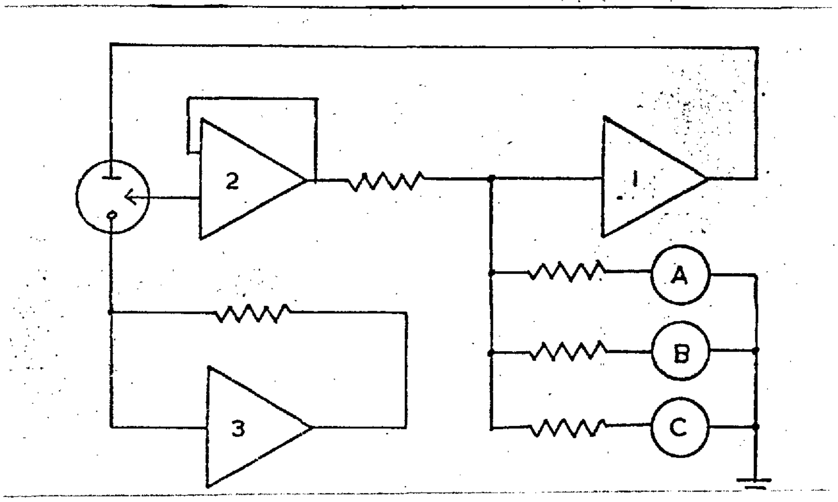


Figure 1.4 Summing Potentiostat

In this bridge circuit, the potential control amplifier, 1, maintains the reference electrode potential equal and opposite to the sum of the potentials from the signal sources A, B, and C. Amplifier 2 is a high input impedance, unity gain follower which prevents significant currents being drawn through the reference electrode. Amplifier

3, through its negative feedback resistor maintains the working electrode at earth potential (a virtual earth point).

The main advantage to the use of potentiostatic circuits is that the working electrode potential is measured against the reference electrode under zero current conditions. This not only allows a high impedance reference electrode to be used but also compensates for the internal resistance of the cell. It is now recognised that resistance compensation is never complete, the resistance of the working electrode and the solution between the working and reference electrodes remains uncompensated. This effect has been demonstrated both theoretically[71] and experimentally[72]. Because the cell current density is greatest in the vicinity of a micro working electrode most of the iR drop occurs within a short distance of the electrode surface. Thus attempts to overcome the uncompensated resistance by placing the reference electrode close to the working electrode are never completely successful. A different approach has been to estimate a value for the uncompensated resistance and then to use positive feedback to overcome it[73].

A wide variety of different signals and waveforms have been used in electroanalytical instruments. The simplest possible signal, a d.c. potential, may be obtained from a battery or stabilised power supply. Where a very low output impedance source is required, the primary source may be placed in the negative feedback loop of an operational amplifier[64]. A d.c. ramp function is also always required in a polarographic instrument and is obtained by integration of a constant potential[3]. Other types of signal, e.g. sine, square and triangular waves, pulse trains, etc., which may be required can be instrumented in several different ways[74].

Measuring circuits are required for the cell current in potentiostatic experiments and for electrode potential in galvanostatic methods. The first stage in current measurement is almost invariably a current to voltage converter (Amplifier 3 in Figure 1.4) which provides an output potential proportional to the cell current. This stage may then be followed by filters, rectifiers, demodulators, etc., to obtain the desired component of the cell current. In controlled potential coulometric experiments an integrator may complete the read out circuit, while differentiator circuits are often used to separate a small signal from a large but almost constant background. The measurement of electrode potential always requires the use of very high input impedance circuits, the unity gain voltage follower is frequently applied.

2. Polarographic Reduction of cis and trans Cinnamic Acids and Substituted Cinnamic Acids

2.1 Introduction

Analytical methods for the determination of organic compounds by polarography can be classified as direct methods, where the compound itself is electroactive, or indirect methods in which the compound is chemically converted to an electroactive species. In practice, direct methods are more useful because of their greater simplicity. Thus the development of such methods is no more complicated than selecting a suitable supporting electrolyte. However it is now recognised that trial and error solutions to this problem are unsatisfactory and a more systematic investigation is required. Reliable analytical methods must always be based on an experimental and theoretical treatment of the polarographic behaviour of the compound.

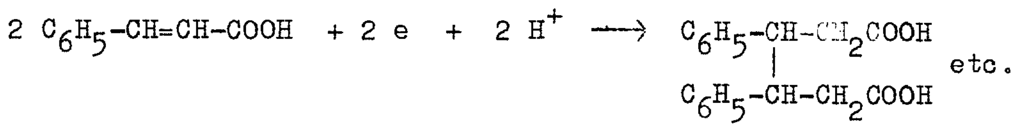
There are, of course, a large number of organic functional groups which are polarographically active and extensive studies have been made of the electrode reactions shown by some of them. As an introduction to the techniques of polarography it was decided to investigate the behaviour of the olefinic C-C double bond. Isolated olefinic groups are rarely polarographically active but become so when they form part of a conjugated system. Cinnamic acid was therefore chosen as a model substance.

The polarographic behaviour of cinnamic acid and substituted cinnamic acids has been studied by several workers. In some of these investigations the importance of having an adequately buffered supporting electrolyte was not realised[75-79]. The results of other studies have not always been in complete agreement[80-83].

In aqueous media, the most probable course of the electrode process would be a 2-electron reduction to the dihydro derivative,

$$C_6H_5\text{-}CH{=}CH\text{-}COOH \quad + \quad 2\ e \quad + \quad 2\ H^+ \longrightarrow C_6H_5\text{-}CH_2\text{-}CH_2\text{-}COOH$$

This would be observed as a single polarographic wave unless a stable radical intermediate was formed, when two 1-electron waves would result. It would also be possible for this free radical to terminate the reduction process by dimerisation



$$2\ C_6H_5\text{-}CH{=}CH\text{-}COOH \quad + 2\ e \quad + \quad 2\ H^+ \quad \longrightarrow \quad \begin{array}{l} C_6H_5\text{-}CH\text{-}CH_2COOH \\ \qquad\quad | \\ C_6H_5\text{-}CH\text{-}CH_2COOH \end{array} \quad \text{etc.}$$

This latter possibility would result in a mixed electrode process with an overall value of n, the number of electrons transferred, lying between 1 and 2. The extent of dimerisation would increase with increasing stability of the radical; it would also be promoted by increasing the concentration of the depolariser.

Ono and Uehara[80] have studied the problem and suggest a 2-electron reduction to the dihydro derivative. Their attempts to prove this by isolating the products of the controlled potential electroreduction of cinnamic acid at a mercury pool cathode were unsuccessful as a mixture of dihydrocinnamic acid and dimer (24% and 53%, respectively) was obtained. In this case the conditions existing at a mercury pool electrode would favour the dimerisation at the expense of the competing monomeric reaction. It is clear that preparative scale electrolysis is an unreliable method for establishing the course of the polarographic reduction of cinnamic acid.

Subsequently, Uehara and Ono[82] showed that the polarographic behaviour of four substituted cinnamic acids (4-hydroxy, 4-methoxy, 4-chloro and 4-bromo) was very similar to that shown by cinnamic acid. Markman and Zinkova[81] have compared the behaviour of the *cis* and *trans* isomers of cinnamic acid and reported a wide variation in the values of the limiting diffusion current and the transfer coefficient α for the two isomers.

In this investigation the polarographic reduction of a range of substituted cinnamic acids and three esters of cinnamic acid has been studied. A comparison has also been made of the polarographic behaviour of the *cis* and *trans* isomers of cinnamic acid and 3-chlorocinnamic acid.

2.2 General Polarographic Behaviour

In an aqueous ethanolic buffered solution the C-C double bond in cinnamic acid and substituted cinnamic acids was reduced in a single polarographic wave, the height of which was dependent on pH (Table 1)

Table 1

Polarographic Limiting Currents in μA for 5.10^{-4} M 50% Ethanolic Solutions of Compounds of the Type $X-C_6H_4CH=CHCOOH$

Compound	pH						
X	4.4	5.1	5.6	6.1	6.7	7.3	7.8
H			1.97	1.90	1.78	1.22	0.75
4-CH_3				1.60	1.68	0.90	0.67
3-Cl	1.34	1.52	1.84	1.82	1.79	1.15	0.82
4-Cl	1.38	1.57	1.70	1.70	1.55	0.77	0.50
4-Br	1.26	1.47	1.45	1.47	1.47	0.94	0.67
3-OCH_3			1.71	1.62	1.60	1.07	0.72
4-OCH_3				1.74	1.82	1.23	

On increasing the pH, the height of the wave decreased in the form of a dissociation curve (Figure 2.1)

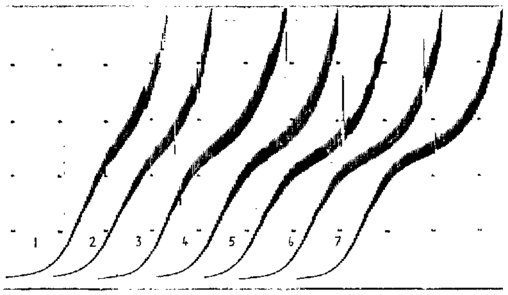


Figure 2.1 pH dependence of waves of 5.10^{-4} M cinnamic acid in 50% ethanol. pH: (1) 5.6; (2) 6.1; (3) 6.7; (4) 7.3; (5) 7.8. Starting potentials: (1 and 2) -1.3; (3) -1.35; (4) -1.4; (5) -1.45 V vs. SCE. Sensitivity: 4 μA f.s.d.; 100 mV/absc.

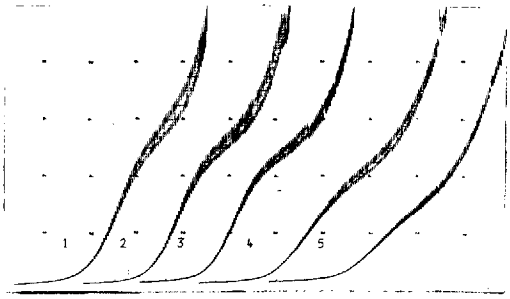


Figure 2.3 Polarographic waves of 5.10^{-4} M substituted cinnamic acids in 50% ethanolic acetate buffer pH 6.7. Substituents: (1) 4-OCH_3; (2) 4-CH_3; (3) H; (4) 3-OCH_3; (5) 4-Cl; (6) 4-Br; (7) 3-Cl. Starting potentials (1 and 2) -1.5; (3 and 4) -1.475; (5) -1.45; (6 and 7) -1.4 V vs. SCE. Sensitivity: 4 μA f.s.d.; 100 mV/absc.

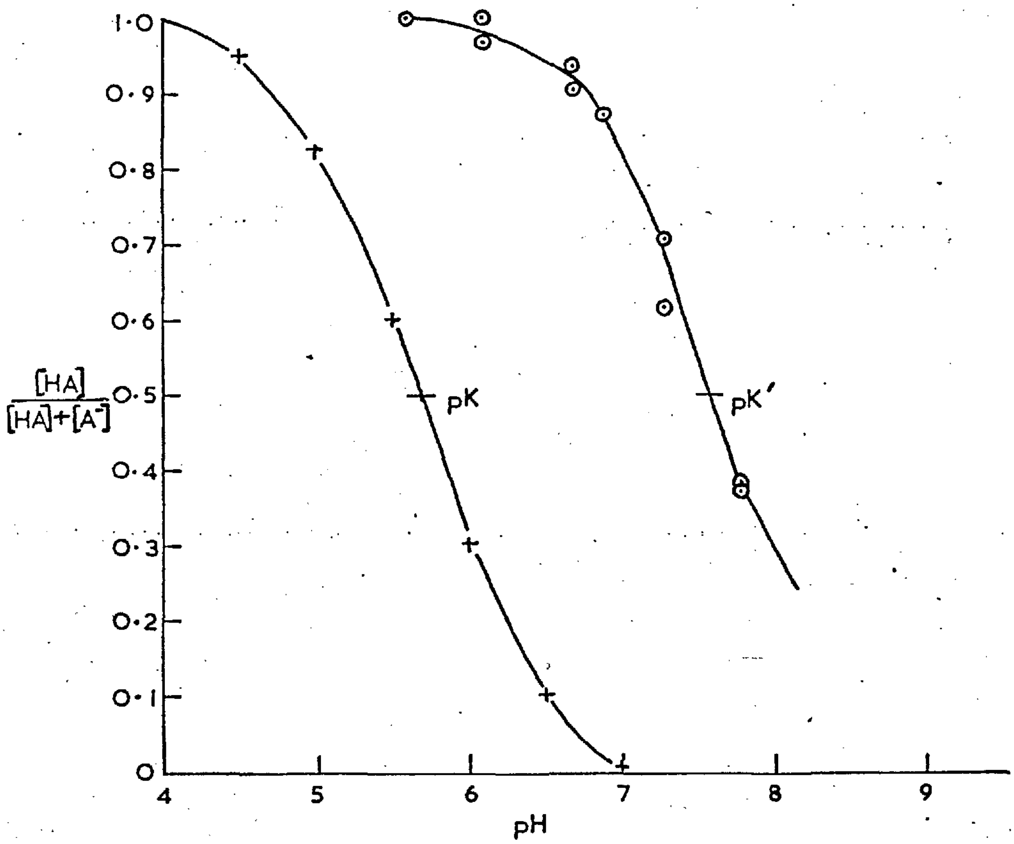


Figure 2.2 Dissociation curves of cinnamic acid in 50% ethanol determined potentiometrically (+) and polarographically (⊙).

The polarographic dissociation curve showed that the wave reached its limiting height at pH 6, and a comparison with the equilibrium dissociation curve, obtained by potentiometric titration, showed pK' to be 2 pH units higher than pK (Figure 2.2).

The polarographic dissociation constants of each of the acids were found to be similar though not identical (Table 2).

Table 2

Polarographic Data for 50% Ethanolic Solutions of Compounds of the Type $X\text{-}C_6H_4CH{=}CHCOOH$

X	pK'	α[a,b]	$dE_{1/2}/dpH$[c] (mV/pH)	$i_d/cm^{2/3}t^{1/6}$[a]
H	7.6	0.57	75	2.21
$4\text{-}CH_3$	7.3	0.52	87	1.86
3-Cl	7.6	0.60	88	2.11
4-Cl	7.25	0.53	85	1.97
4-Br	7.65	0.57	91	1.71
$3\text{-}OCH_3$	7.65	0.57	83	1.88
$4\text{-}OCH_3$	7.6[d]	0.43[d]	60[d]	2.02[d]

[a] Measured at pH 6.1

[b] Mean $\alpha = 0.54 \pm 0.02$

[c] Mean $dE_{1/2}/dpH = 81 \pm 4$ mV/pH unit

[d] A very poorly defined wave makes these results approximate only.

All the compounds studied were reduced in a not-too-well defined wave because the reduction occurred at very negative potentials where the wave was obscured by the current due to the reduction of the cation of the supporting electrolyte. Below pH 4 , the reduction of the C-C double bond was completely masked by hydrogen ion reduction. The presence of substituents on the benzene ring had a marked effect on the definition of the wave (Figure 2.3)

Electron withdrawing substituents (-I effect) caused the wave to be shifted to more positive potentials and hence improved the shape of the wave. Substituents having a +I effect, however, caused $E_{1/2}$ to be shifted to more negative values with the result that the wave became less clearly defined and the pH range over which the wave was measurable became even more limited.

The effect of varying the composition of the supporting electrolyte was studied in an attempt to improve the shape of the wave.

(i) The effect of varying the ethanol concentration over the range 0 to 75% was studied. No significant improvement in the shape of the wave was observed.

(ii) The concentration of the acetate buffer (with respect to acetate ion) was varied over the range 0.1 to 0.5 M. On decreasing the buffer concentration, the reduction of the cation of the supporting electrolyte was shifted to more negative potentials and hence the wave became better defined.

(iii) The influence of several cations was studied. Potassium, lithium, ammonium and calcium ions (0.1 M as chlorides) had no effect while in the presence of magnesium and lanthanum, no wave was observed. Tetra-alkylammonium ions (Et_4N^+, Bu_4N^+) caused a considerable improvement in the shape of the wave as $E_{1/2}$ was shifted some 50 mV more positive (Figure 2.4)

Figure 2.4 Effect of cations on the polarographic wave of 5.10^{-4}M cinnamic acid in 50% ethanolic acetate buffer pH 6.1. Cations: (1) 0.01 M Na^+; (2) 0.01 M Et_4N^+. Starting potentials - 1.35 V vs. SCE. Sensitivity 4 μA f.s.d.; 100 mV/ absc.

The optimum conditions for the direct analytical determination of cinnamic acid were found to be 50% ethanol containing 0.1 M buffer (pH 6) and 0.01 M tetra-alkylammonium ion. However, when quantitative measurements were obtained from the polarographic waves tetra-alkylammonium salts were not used because of their uncertain influence on the electrode reaction.

2.3 Electrode Reaction

The number of electrons transferred in the electrode reaction was estimated by comparing the wave height of cinnamic acid with the wave for equimolar solutions of

(a)	benzaldehyde semicarbazone	($n = 4$)
(b)	1,4 naphthoquinone	($n = 2$)
(c)	benzaldehyde	($n = 1$)

the three standards being measured in an acetate buffer, pH 4.2, containing 50% ethanol. The results indicated that $n = 2$.

This was confirmed by microcoulometric determination of the number of electrons transferred. The values obtained for cinnamic acid and 3- chlorocinnamic acid confirmed that $n = 2$ within the experimental accuracy of the method (Table 3)

Table 3

Microcoulometrically Determined Number of Electrons Transferred in the Reduction of Compounds of the Type X-$C_6H_4CH=CHCOOH$

X	Medium	n
H	50% ethanolic acetate buffer, pH 6.1	1.90; 2.01
3-Cl	50% ethanolic acetate buffer, pH 6.1	1.97; 1.91; 1.94

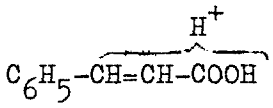
The identification of the products obtained from microcoulometric analysis was attempted to confirm the course of the electrode reaction. The object was to prove that the residual solution after constant potential electrolysis at the DME contained only α,β dihydrocinnamic acid together with residual cinnamic acid. The UV spectrum of cinnamic acid showed an absorption band (λ_{max} = 273 nm) corresponding to the conjugated C-C double bond, which was not present in the spectrum of the dihydro-derivative. The decrease in absorbance of the solution after electrolysis confirmed that the C-C double bond was polarographically reduced. After extraction with ether the electrolysis products were separated by thin layer chromatography. Owing to the difference in R_F values, the separation was difficult but it was found that, using a range of solvents recommended for the chromatographic separation of carboxylic acids[84], no spots corresponding to the presence of dimer were observed. An attempt to detect the molecular ions corresponding to the dimer by mass spectroscopy of the electrolysis products was unsuccessful as the products were found to decarboxylate. In the absence of any technique sensitive and selective enough to detect the formation of dimeric products, there is little evidence to support the contention that $\alpha\beta$ dihydrocinnamic acid is the sole product of the reduction. Microcoulometry gave a mean value for n less than 2 (1.94) but this technique is notoriously liable to systematic errors. However, this result did confirm that the dihydro derivative was the major product of the reaction.

2.4 Electrode Reaction Mechanism

Diffusion control of the electrode process at pH values below 6.5 was demonstrated by the dependence of the wave height on the height of the mercury reservoir. The wave height was directly proportional to concentration over the range $1.1\bar{0}^{4}$ to $1.1\bar{0}^{3}$ M. The polarographic dissociation curve (Figure 2.2) indicated that at pH values greater than 6.5, the wave became kinetically controlled.

The electroactive species involved in the reduction of cinnamic acid may be one or more of the following:

(i) the protonated complex

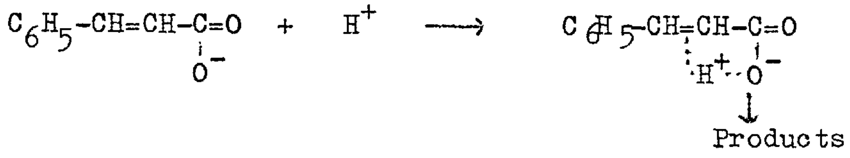


$C_6H_5\text{-}\overbrace{\text{CH=CH-COOH}}^{H^+}$

(ii) the undissociated acid

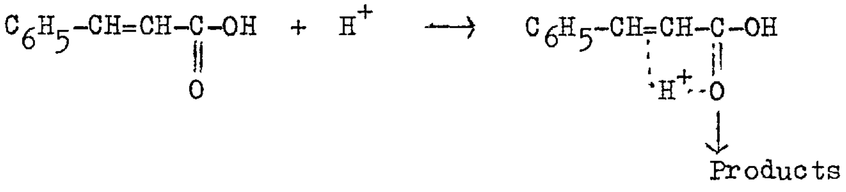
(iii) the cinnamate anion

The linear dependence of half-wave potential on pH (Figure 2.5) indicated that protonation was the first, rate determining, step in the reaction. Above pH 6.5, where the polarographic wave was kinetically controlled, potentiometric titration (Figure 2.2) indicated that the anion predominated in solution. It was therefore concluded that the electroactive species was a protonated form of the anion:



$$C_6H_5\text{-CH=CH-}\underset{O^-}{C}\text{=O} + H^+ \longrightarrow C_6H_5\text{-CH=CH-}\underset{H^+\cdots O^-}{C}\text{=O} \rightarrow \text{Products}$$

It was not possible to say with certainty whether one or two protons were involved in the pre-protonation. Thus a second protonation, following the recombination of the anion with a proton, is not precluded:



$$C_6H_5\text{-CH=CH-}\underset{\underset{O}{\|}}{C}\text{-OH} + H^+ \longrightarrow C_6H_5\text{-CH=CH-}\underset{\underset{H^+\cdots O}{\|}}{C}\text{-OH} \rightarrow \text{Products}$$

Theoretically, it would be expected that at low pH values reduction of the undissociated acid would occur without pre-protonation. The half-wave potential of this process would be independent of pH. Experimentally the region where this process would occur was not accessible. Although the wave was observed at pH values as low as 4, it was too close to the hydrogen ion reduction current to be

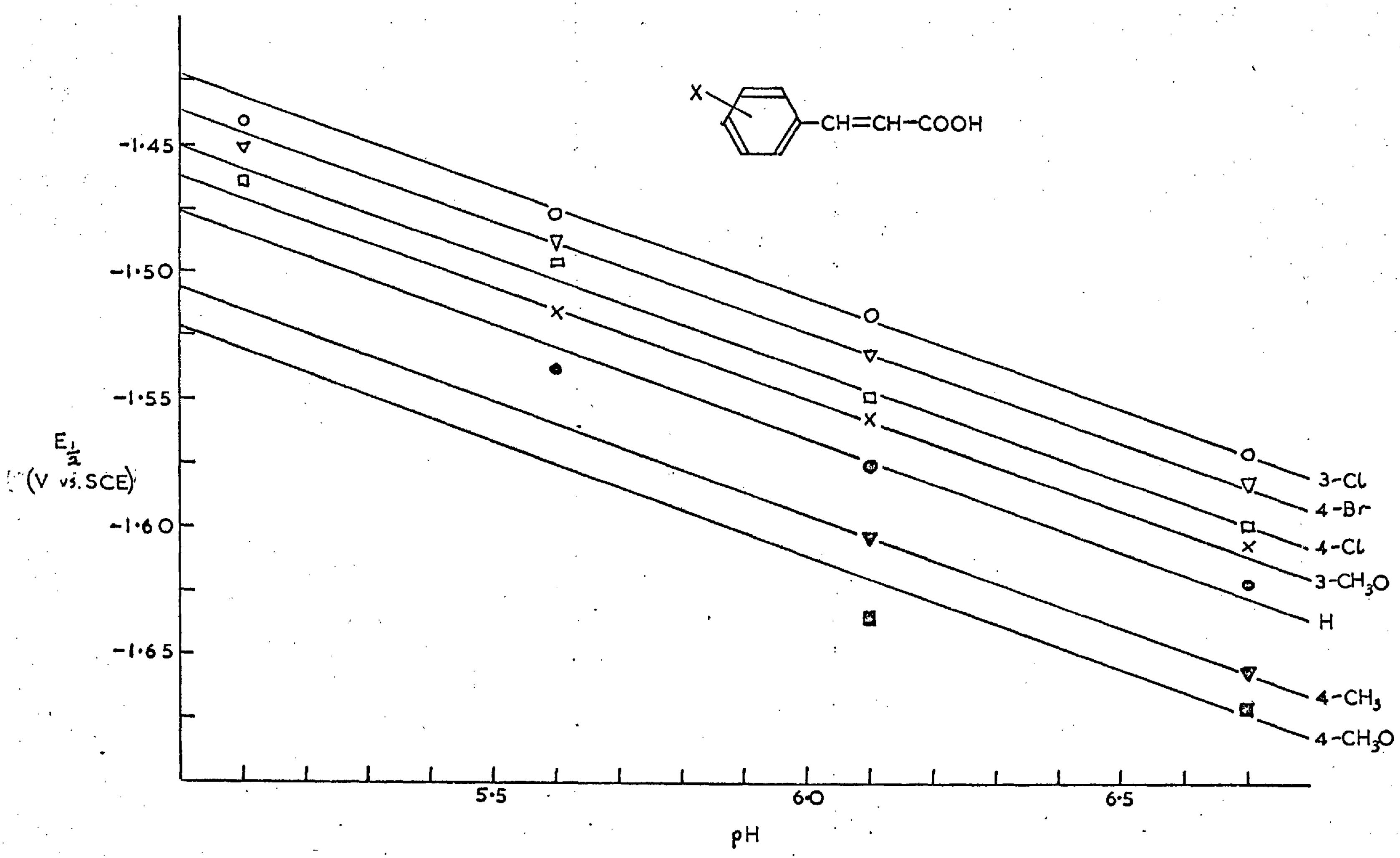


Figure 2.5 Dependence of half wave potentials of substituted cinnamic acids on pH in 50% ethanol.

measured. Accurate measurements of the half wave potential were made over the range pH 5 to 7, and showed no significant anomaly. The half wave potentials of the three acids (3-chloro, 4-bromo and 4-chloro) measured at pH 5.1 all deviated slightly from the straight line plot. However, it was not possible to say whether this represented a change in slope of the graph or an experimental error. On similar theoretical grounds it would be expected that at high pH values the anion would reduce without pre-protonation, the half-wave potential of the process being pH independent. Again, this region was not experimentally accessible.

2.5 Polarography of Cinnamic Acid Esters

The polarographic behaviour of cinnamic acid was compared with that of its methyl, ethyl, and benzyl esters, in which ionisation of the carboxyl group is impossible. In each case a single wave was observed, the height of which remained practically constant over the range pH 6 to 13 (Table 4)

Above pH 7.5 the half-wave potential of each ester was found to be independent of pH (Table 5), indicating reduction of the ester without pre-protonation.

Table 4

Polarographic Limiting Currents in μA for $5 \cdot 10^{-4}$ M 50% Ethanolic Solutions of Compounds of the Type $C_6H_5CH{=}CHCOOR$

Compound	pH								
R	5.6	6.1	6.7	7.3	7.8	8.2	8.7	10.7	13
CH_3-		1.87	1.81	1.57	1.49	1.46	1.36	1.36	1.23
C_2H_5-		1.94	2.05	1.84	1.73	1.57	1.57	1.57	1.47
C_6H_5-CH_2-	1.68	1.68	1.66	1.50	1.45	1.40	1.32	1.25	1.25

Table 5

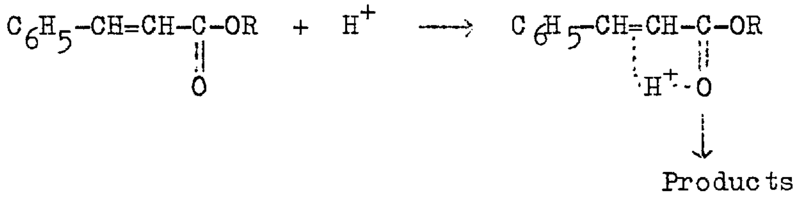
Polarographic Data for 50% Ethanolic Solutions of Compounds of the Type $C_6H_5CH{=}CHCOOR$

R	α [a]	$E_{1/2}$ [b] (V vs. SCE)
CH_3-	0.508	- 1.666
C_2H_5-	0.476	- 1.651
C_6H_5-CH_2-	0.495	- 1.638

[a] Measured at pH 6.7

[b] $E_{1/2}$ pH independent above pH 7.5

In the pH range 6 to 7.5 the half-wave potential was linearly dependent on pH and the electroactive species was thus a protonated form of the ester:



$$C_6H_5\text{-}CH{=}CH\text{-}\underset{\underset{O}{\|}}{C}\text{-}OR + H^+ \longrightarrow C_6H_5\text{-}CH{=}CH\text{-}\underset{\underset{H^+\cdots O}{\|}}{C}\text{-}OR \;\downarrow\; \text{Products}$$

The analogy between the structures of the acid and esters suggested that the acid was also reduced in the form of its mono-protonated anion.

2.6 Structural Effects

A linear relationship between half-wave potential and Hammett substituent constant was obtained for the substituted acids (Figure 2.6) and confirmed that cinnamic acids mono-substituted in the 3 or 4 position obeyed the modified Hammett equation[31]:

$$\Delta E_{1/2} = \sigma \rho'$$

The calculated value for the polarographic heterogeneous reaction constant ρ' was 0.16 V, from which the value of the Hammett reaction constant in dimensionless form is given by:

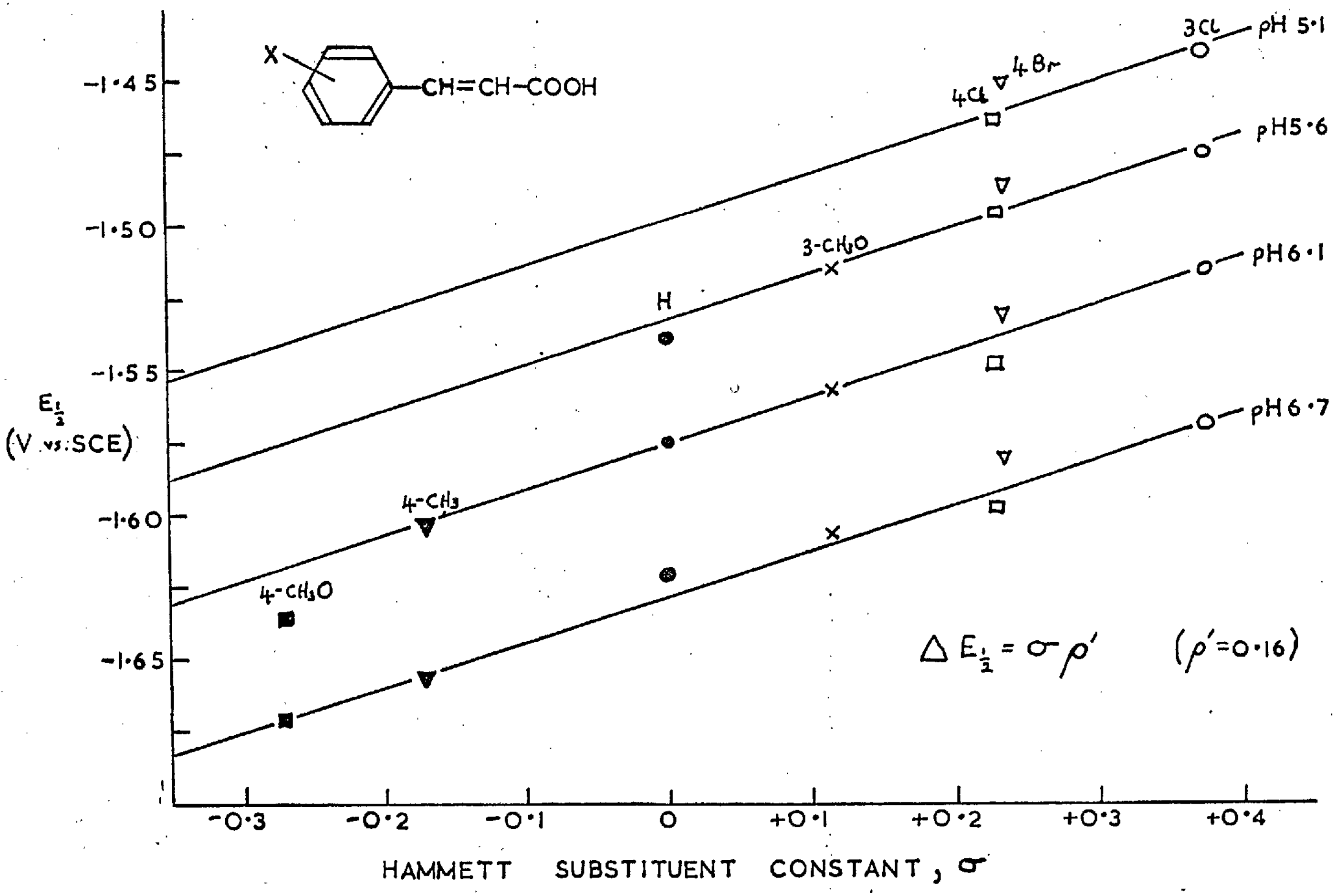


Figure 2.6 Dependence of half wave potentials on Hammett substituent constant for substituted cinnamic acids.

$$\rho = \frac{\alpha\ nF}{2.3\ RT} - \rho' = +2.8$$

This value of reaction constant is comparable to those measured for homogeneous reactions. The positive sign is in accordance with the fact that the electrode reaction was accelerated by electron withdrawing substituents having a negative (-I) inductive effect. Such substituents exert the greatest effect on the β carbon atom of the C-C double bond and it may be postulated that this was the electroactive centre in the molecule. A plot of the polarographic dissociation constant, pK', against the substituent constant, σ , showed little correlation and indicated that the substituent exerted little influence on the ionisation of the carboxyl group.

The differences in behaviour of the cis and trans isomers of cinnamic acid, as reported by Markman and Zinkova[81], appear unlikely in view of the structural similarity of the two isomers and their comparative ease of interconversion. One possible explanation of these results could be the non-quantitative chemical synthesis of the cis isomer. Chemical synthesis was not, therefore, attempted and instead trans-cis interconversion by irradiation from a UV source was used. The completeness of the conversion was established by spectrophotometry.

Polarograms of cis cinnamic acid were measured at pH 4.4 and 6.1 and compared with those of the trans isomer measured under identical conditions. A very slight shift towards more positive potentials was observed for the cis isomer, but owing to the poor definition of the waves, accurate measurement of $\Delta E_{1/2}$ was not possible. The wave heights for the two isomers, however, were the same. The cis isomer of 3- chlorocinnamic acid was next studied as this compound showed a well defined wave. Comparison of this wave with that of the corresponding trans acid showed that the diffusion coefficients of both isomers were identical. As expected the cis isomer was reduced at a slightly more positive potential and the difference in half-wave potential ($E_{1/2}$ cis - $E_{1/2}$ trans) was found to be 21 mV.

2.7 Experimental

Cinnamic acid, substituted cinnamic acids and the cinnamate esters were obtained commercially, with the exception of 4 - bromocinnamic acid which was synthesised from the corresponding aldehyde by a modified Doebner reaction[85]. $\alpha\beta$ Dihydrocinnamic acid was prepared by reduction of cinnamic acid with sodium amalgam. The purity of these compounds was checked by melting point determination, and by elemental analysis. A 10^{-2} M stock solution of each compound was prepared in absolute ethanol. Buffer solutions were prepared from AnalaR reagents using glass distilled water.

Apparatus

A Radelkis polarograph type OH-102 (Metrimpex, Hungary) was used to record polarograms by the conventional 2-electrode system. The studied solution was contained in a Kalousek cell with a separated reference SCE. Capillary constants measured in 0.1 M KCl at the potential of the SCE were $t = 4.0$ s, $m = 1.61$ mg s^{-1} at $h = 60$ cm.

Accurate measurements of the potential of the DME were made using a 3- electrode system. The potential of the DME was measured under zero current conditions against an auxiliary reference SCE using a Precision Potentiometer 7565 (Pye, Cambridge).

For the microcoulometric controlled potential electrolysis the Radelkis polarograph was used as a potentiostat. The cell was a modified H-cell[86] with a working volume of 0.5 ml.

The relative pH values of buffer solutions containing 50% ethanol were measured with a Vibron pH meter model 39A (E.I.L. Ltd., Surrey)

UV spectra were measured with an Ultrascan spectrophotometer (Hilger and Watts Ltd., London). The UV source used to convert <u>trans</u> cinnamic acid to its <u>cis</u> isomer was a 500 W xenon lamp.

Techniques

Solutions for polarography were prepared by mixing measured volumes of ethanol, stock solution of depolariser, water and aqueous buffer solution in a 10 ml graduated flask. The volume contraction on mixing ethanol and water was corrected by diluting to volume with aqueous ethanol. The solution was deoxygenated in the Kalousek cell by passage of a stream of nitrogen for 3 minutes. The possibility of hydrolysis of the esters occuring in the cell during the recording of a wave was eliminated by repeating the measurement after an interval of ten minutes. The observed change in wave height was negligible.

For the controlled potential electrolysis the solution was prepared as for polarography and a 0.5 ml aliquot was transferred to the microcoulometric cell. After the solution had been deoxygenated by passing a slow stream of nitrogen for 20 minutes it was electrolyzed for 3 hours at the potential at which the polarographic wave reached its limiting value. Polarograms were recorded at intervals of 1 hour to monitor the decrease in limiting current with time. The limiting current, measured at any time, showed no change after mixing the solution briefly with a stream of nitrogen. This confirmed that the homogeneity of the solution was maintained by the stirring effect of the falling mercury drops. The number of electrons transferred, n, was calculated from the equation[23]

$$n = \frac{K\ t}{2.30\ V\ F\ \log\ (i_o/i_t)}$$

where K is equal to the initial current divided by the initial concentration.

The conversion of <u>trans</u> cinnamic acid to its <u>cis</u> isomer was monitored continuously by spectrophotometry. A 5.10^{-5} M cinnamic acid solution in 50% ethanol was pumped from the quartz cell in which it was irradiated, through a flow through cell in the spectrophotometer, and then returned to the quartz cell for further irradiation. The overall change in the spectrum during irradiation showed a decrease in absorbance characteristic of a <u>trans-cis</u> isomerism; the wavelength of maximum absorption shifted from 273 nm to 264 nm, confirming the formation of <u>cis</u> cinnamic acid. A kinetic study showed the conversion was complete after 30 minutes. A 10^{-2} M solution was irradiated for a similar period and absorption spectra were measured on diluted aliquots before and after irradiation, to confirm that the conversion time was concentration independent. Solutions of <u>cis</u> cinnamic acid prepared in this way showed no change in absorption spectrum on being allowed to stand for 2 hours.

3 Polarographic Reduction of 4- Cyanocinnamic Acid and its Ethyl Ester

3.1 Introduction

The reduction of a series of cinnamic acids, monosubstituted in the 3- or 4- position, has been shown (Chapter 2) to obey the modified Hammett equation[31]

$$\Delta E_{1/2} = \sigma \rho'$$

One compound, 4- cyanocinnamic acid, was found to deviate from this equation. Half-wave potentials measured over the pH range 5 to 7 were found to be more than 100 mV more positive than those predicted by the Hammett equation for a substituent constant $\sigma = 0.628$ using the reaction constant, $\rho' = 0.16$ V, obtained for the other acids.

The anomalous behaviour of 4- cyano substituted derivatives in linear free energy relationships has been reported previously for aromatic carbonyl compounds[31]. The polarographic behaviour of substituted benzonitriles bearing a <u>para</u> carbonyl group, briefly reported[87], has now been studied in detail.[88] The nitrile group in 4- cyano-acetophenone and 4- cyanobenzaldehyde was reduced in acid solution via a protonated complex to a primary amino group. This four-electron wave was followed by a one-electron reduction of the carbonyl group. 4- cyanobenzophenone was reduced first to an alcohol which was then reduced further, the nitrile group remaining intact. An entirely different course of reduction was observed for 4- cyanobenzoic acid esters, 4- cyanobenzonitrile and 4- cyanobenzamide. It is apparent that the reduction of such compounds is estremely sensitive to small differences in reactivity and that generalizations are of little value.

3.2 General Polarographic Behaviour of 4- Cyanocinnamic Acid

In contrast to the other substituted cinnamic acids, 4- cyanocinnamic acid was reduced in acid solution to give a single polarographic wave. The height of this wave decreased with increasing pH value until at pH 5.5 it had reached approximately half its limiting value (Figure 3.1) A slight increase in wave height was observed between pH 6 and 7, while at higher pH values the single wave split into two. The wave at more positive potentials decreased in height with increasing pH value, although the total height of the two waves remained constant (Figure 3.2) The complete polarographic dissociation curve (Figure 3.3) showed the presence of three separate electrode processes; that in acid solution, I, and two processes above pH 7, II (the more positive wave) and III. The increase in wave height between pH 6 and 7 was attributed to a mixed electrode process in which reactions I and II occurred

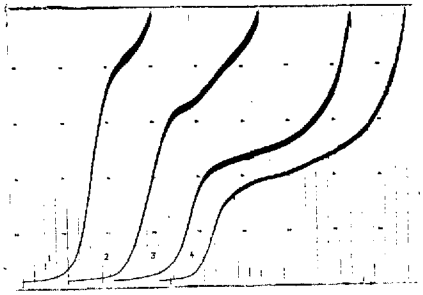


Figure 3.1

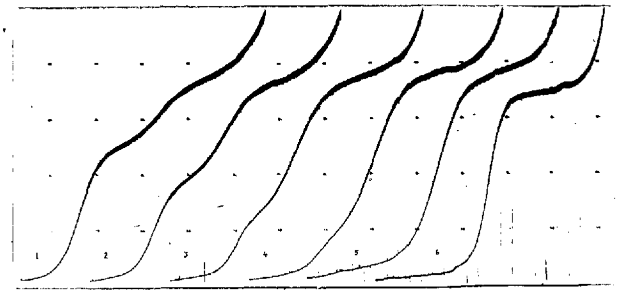


Figure 3.2

Figures 3.1-2. pH dependence of waves of 4-cyanocinnamic acid in 50% ethanol.

Figures 3.1 pH: (1) 1.68; (2) 3.52; (3) 4.77; (4) 5.81, Starting potentials: (1) -0.9; (2) -1.0; (3) -1.1; (4) -1.2 V vs. SCE. Sensitivity 6 μA f.s.d.; 100 mV/absc.

Figures 3.2 pH: (1) 7.9; (2) 8.3; (3) 8.7; (4) 9.2; (5) 11.0; (6) 13.0. Starting potential -1.4 V vs. SCE. Sensitivity 4 μA f.s.d.; 100 mV/absc.

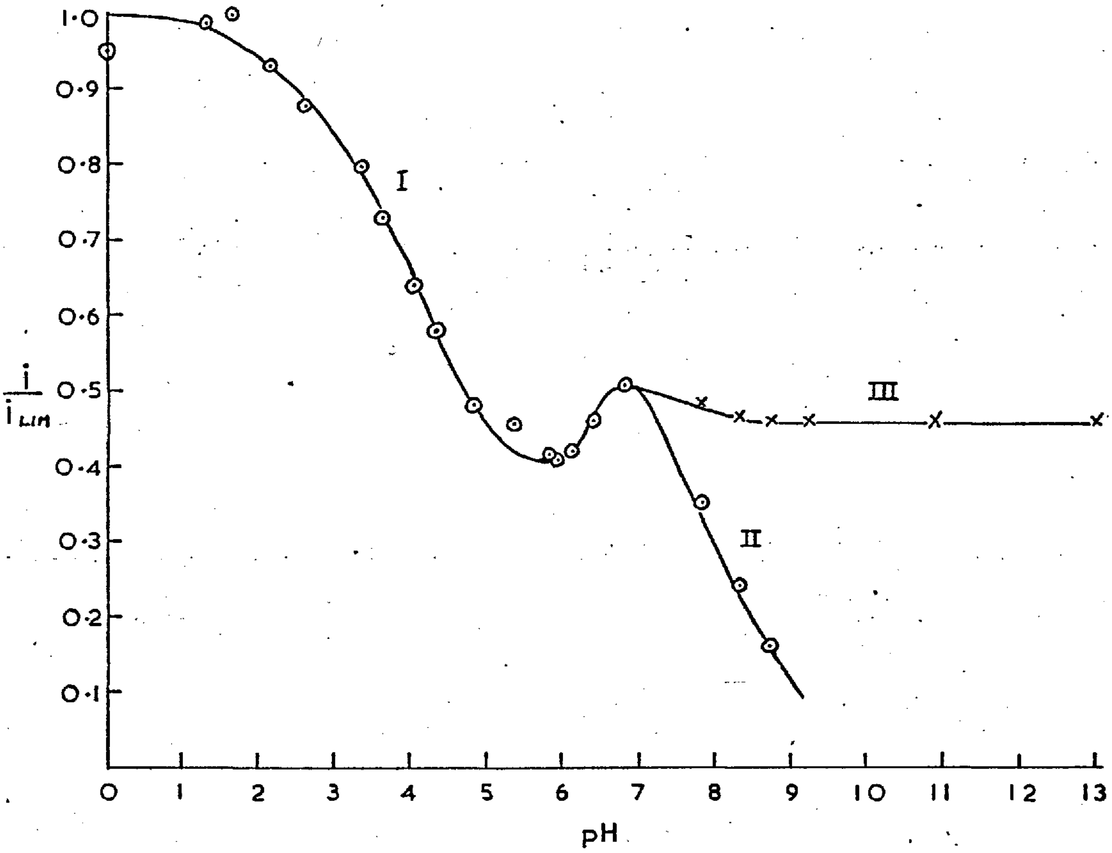


Figure 3.3 Polarographic dissociation curve of 4-cyanocinnamic acid in 50% ethanol. (⊙) first wave; (X) total wave height.

simultaneously. The commencement of this mixed process was further characterised by a slight increase followed by a sudden decrease in the n α value of the wave between pH 5.9 and 6.1. Logarithmic analysis of the wave shape gave values of n α in the region of the mixed process significantly different from those corresponding to processes I and II (Table 1). One further observation was made from the general shape of the waves; the slope of the wave at high pH values increased until at pH 13 the wave slope indicated apparent Nernstian reversibility ($\alpha = 1$).

3.3 Electrode Reactions

A comparison of wave heights for processes I, II, and III with the 2- electron wave for the unsubstituted acid indicated that processes II and III involved 2- electrons. As process I gave waves twice as high as II or III, I therefore corresponded to a 4- electron wave. Confirmation of these results was obtained by microcoulometric measurements at pH values corresponding to single waves for processes I, II and III (Table 2).

The residual solution from the controlled potential electrolysis was qualitatively analysed for the products of the electrode reaction. In acid solution (n = 4, electrode process I) the presence of a primary amine in the electrolysis products was proved by formation of a coloured Schiff's base with p- dimethylaminobenzaldehyde[89],

Table 1

Polarographic Limiting Currents and $n\alpha$ Values for 50% Ethanolic Solutions of 4- Cyanocinnamic Acid and its Ethyl Ester

pH	Acid				Ester	
	Currents $(\mu A)^a$		$n\alpha$		Currents $(\mu A)^a$	$n\alpha$
	1st wave	2nd wave	1st wave	2nd wave		
1.32	3.15		1.65		2.94	1.24
1.68	3.20		1.65		3.04	1.24
2.13	2.98		1.48		2.84	1.24
2.58	2.80		1.36		2.64	1.24
3.27	2.54		1.39		2.16	1.24
3.52	2.34		1.39		1.98	1.24
4.02	2.04		1.39		1.81	1.49
4.32	1.85		1.39		1.81	1.69
4.77	1.54		1.39		1.69	1.76
5.35	1.46		1.39		1.61	1.77
5.81	1.33		1.50		1.55	1.47
5.89	1.31		1.48		1.53	1.47
6.09	1.34		1.08		1.50	1.47
6.35	1.47		1.08		1.46	1.47
6.83	1.62		1.08		1.38	1.47
7.87	1.12	0.45	1.58		1.17	1.47
8.31	0.78	0.70	1.58		1.09	1.47
8.73	0.51	0.96			1.10	1.47
9.19	0.24	1.23			1.10	1.47
10.84		1.47		1.29	1.06	1.47
13.0		1.47		2.0		

a Depolariser concentration 5.10^{-4} M and by formation of a fluorescent Schiff's base with salicylaldehyde.

Table 2

Microcoulometrically Determined n values for 4- Cyanocinnamic Acid

pH	Medium	n
1.32	6 N Sulphuric acid in 50% ethanol	4.08
6.83	Acetate buffer in 50% ethanol	2.44; 1.95; 2.16
13	0.1 N Sodium hydroxide in 50% ethanol	1.80; 2.65

The following reactions were postulated as possible 2- electron reductions of 4- cyanocinnamic acid:

(i) fission of the C-CN bond to form free cyanide ion and cinnamic acid,

(ii) reduction of the $-C\equiv N$ group to form a substituted benzaldimine,

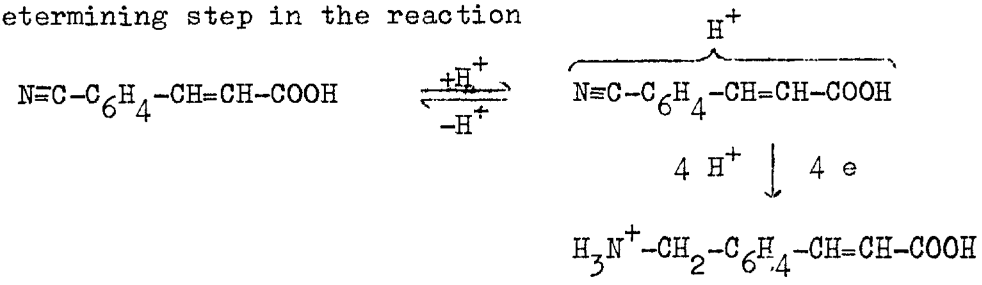
(iii) reduction of the C=C bond to give the saturated acid.

Unequivocal distinction between these possibilities was made by simultaneously testing for the presence of cyanide ion and monitoring the C=C bond concentration. The anodic polarographic wave of the cyanide ion provided a convenient analytical test for this species, while the C=C bond concentration was followed by UV spectrometry. The absence of cyanide ion in the solution after electrolysis was demonstrated at pH 6.8 and 13. The possibility of interference with the anodic wave was excluded by adding cyanide ion to the solution when a well defined anodic wave was observed.

The UV absorbance of the C=C bond at 283 nm was followed during the electrolysis at pH 6.8 and 13. After various periods of electrolysis the decrease in polarographic wave height was measured and a sample of the solution taken for analysis. The sample was diluted to a known volume and the absorbance measured; the C=C bond concentration was obtained from a prepared calibration curve. A direct 1:1 relationship was found to exist between the % decrease in wave height and the % decrease in C=C bond concentration at both pH 6.8 and 13. Thus the 2- electron processes II and III both resulted in reduction of the C=C bond to form the saturated acid.

3.4 Electrode Reaction Mechanisms

A graph of half-wave potential plotted as a function of pH (Figure 3.4) showed four linear regions corresponding to processes I, II, III, and the mixed process. Process I occured at low pH values where the acid was largely undissociated in solution, and the dependence of $E_{1/2}$ on pH suggested that protonation was the first, rate determining step in the reaction



$$N{\equiv}C{-}C_6H_4{-}CH{=}CH{-}COOH \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} \overbrace{N{\equiv}C{-}C_6H_4{-}CH{=}CH{-}COOH}^{H^+} \qquad I$$

$$4\ H^+ \Big\downarrow 4\ e$$

$$H_3N^+{-}CH_2{-}C_6H_4{-}CH{=}CH{-}COOH$$

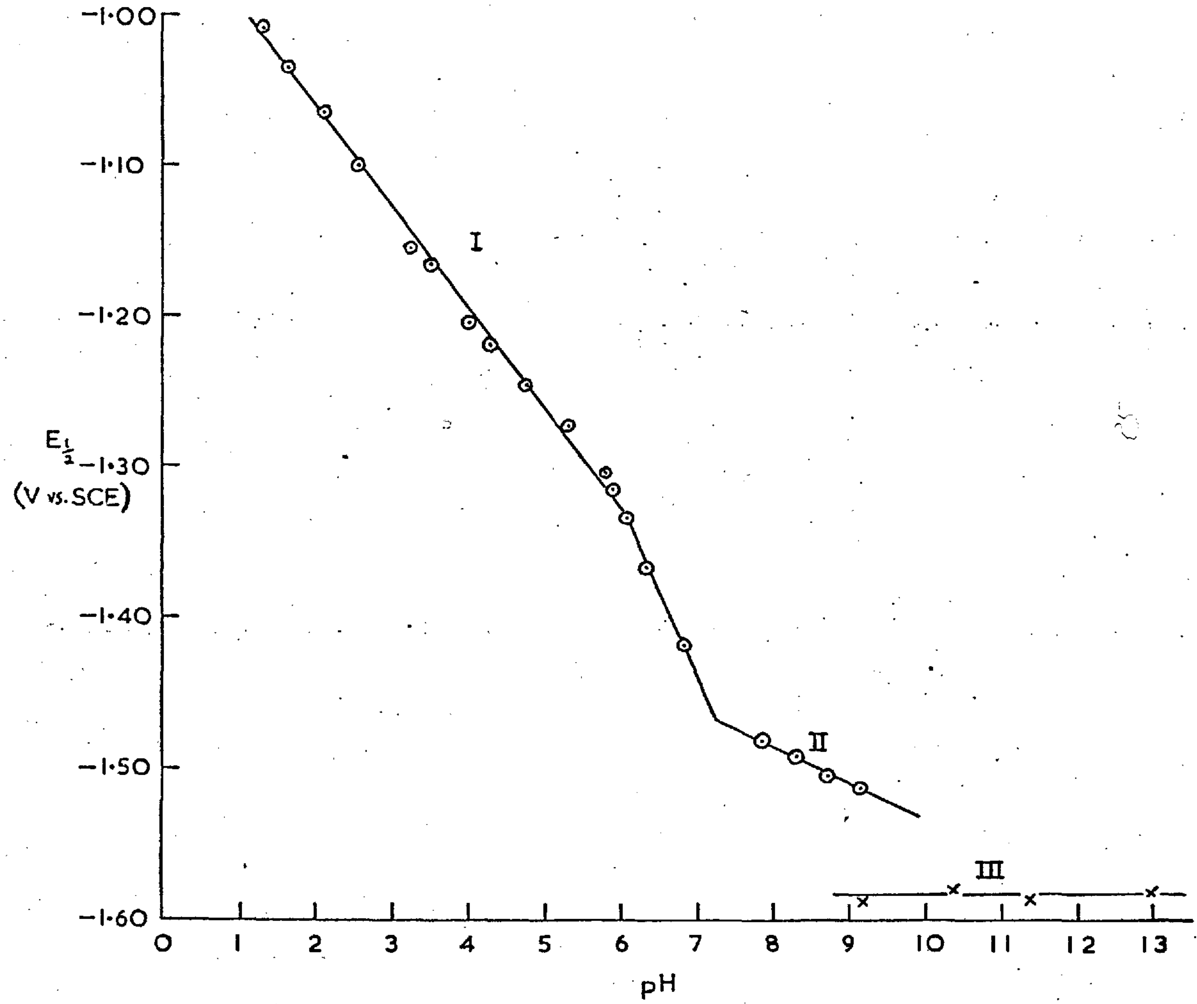
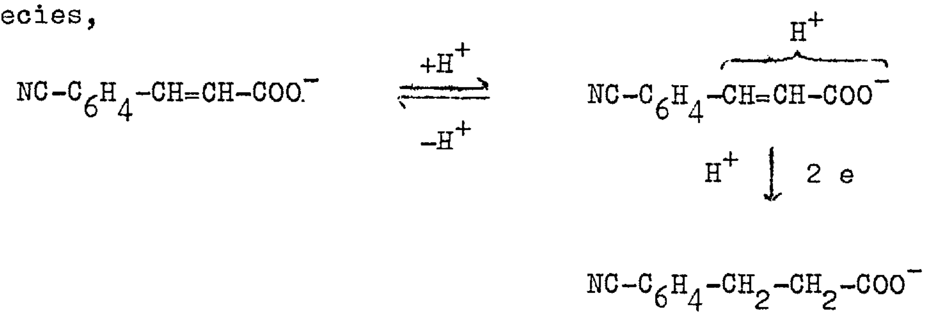


Figure 3.4 Dependence of half wave potentials of 4-cyanocinnamic acid on pH in 50% ethanol.

Reaction II occurred above pH 7 where the acid existed as an anion in solution; again a protonated complex was the electroactive species,



$$\mathrm{NC{-}C_6H_4{-}CH{=}CH{-}COO^-} \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} \mathrm{NC{-}C_6H_4{-}\overbrace{CH{=}CH{-}COO^-}^{H^+}} \;\; \Big\downarrow{\scriptstyle H^+\;2\,e} \;\; \mathrm{NC{-}C_6H_4{-}CH_2{-}CH_2{-}COO^-}$$

II

This reaction was identical to that previously found for cinnamic acids having electroinactive substituents. However, this latter group of compounds were reduced over a different pH range; accurate measurements of half-wave potentials were made over the range pH 5 to 7. Half-wave potentials of 4- cyanocinnamic acid measured in this range corresponded to a different electrode process (I and the mixed process). This accounted for the deviation observed for 4-cyanocinnamic acid in the Hammett equation. Extrapolation of the $E_{1/2}$ - pH plot for process II to the pH range 5 to 7 gave $E_{1/2}$ values approximately 100 mV more positive than those predicted by the Hammett equation. In so far as this procedure was justified it was suggested that the effect of the p-CN group on the C=C bond was not purely inductive; probably a conjugative effect was also involved.

Process III was also observed in alkaline solution where the anion predominated, but here the half-wave potential was pH independent and protonation was not the first step in the reaction. The overall reaction was formulated:

$$NC-C_6H_4-CH=CH-CO_2^- \xrightarrow[2\ e]{2\ H^+} NC-C_6H_4-CH_2-CH_2-CO_2^-$$

This reaction was clearly chemically irreversible, but logarithmic analysis of the wave shape at pH 13 indicated an apparently reversible two electron process.

An a.c. polarographic wave was observed at pH 13 (Figure 3.5), the height of which decreased with decreasing pH value until at pH 11 no wave was observed. This wave could indicate reversibility of the reaction at high pH values but, because the rather inadequate instrument used for this study had no effective means of eliminating the iR drop in the cell, might also be due to an adsorption effect at the electrode. Controlled alternating current oscillopolarography proved the irreversibility of the overall reaction (Figure 3.6) as did cyclic voltammetry (Figure 3.7). Using a wide range of potential sweep rates, from 0.025 to 1000 V s^{-1}, it was not possible to distinguish the electron addition from the subsequent chemical reactions.

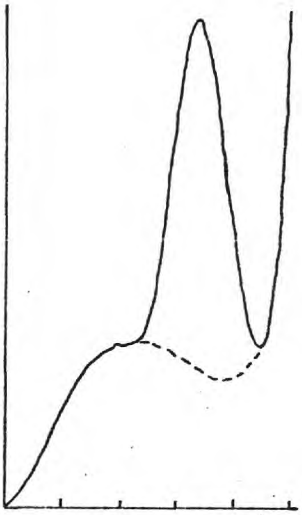


Figure 3.5 A.c. polarogram of 5.10^{-4} M 4-cyanocinnamic acid in 50% ethanol at pH 13. (---) base line obtained with supporting electrolyte. Starting potential -1.2 V vs. SCE. Sensitivity 1 μA f.s.d.; 100 mV/absc.

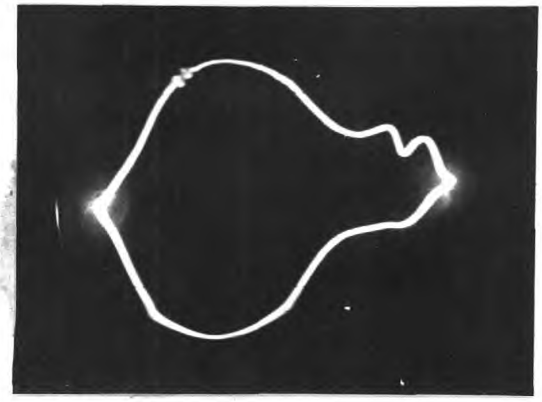


Figure 3.6 Oscillopolarographic dE/dt = f(E) curve for 5.10^{-4} M 4-cyanocinnamic acid in 50% ethanol at pH 13.

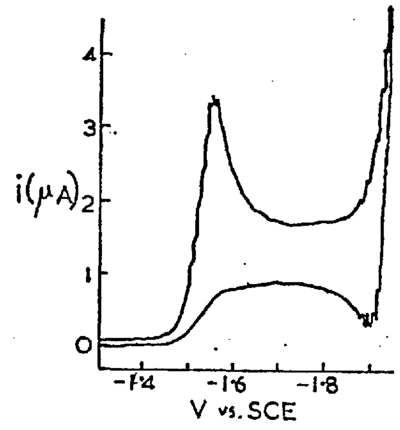


Figure 3.7 Cyclic voltammogram of 5.10^{-4} M 4- cyanocinnamic acid in 50% ethanol at pH 13. Voltage sweep rate, 25 mV/sec

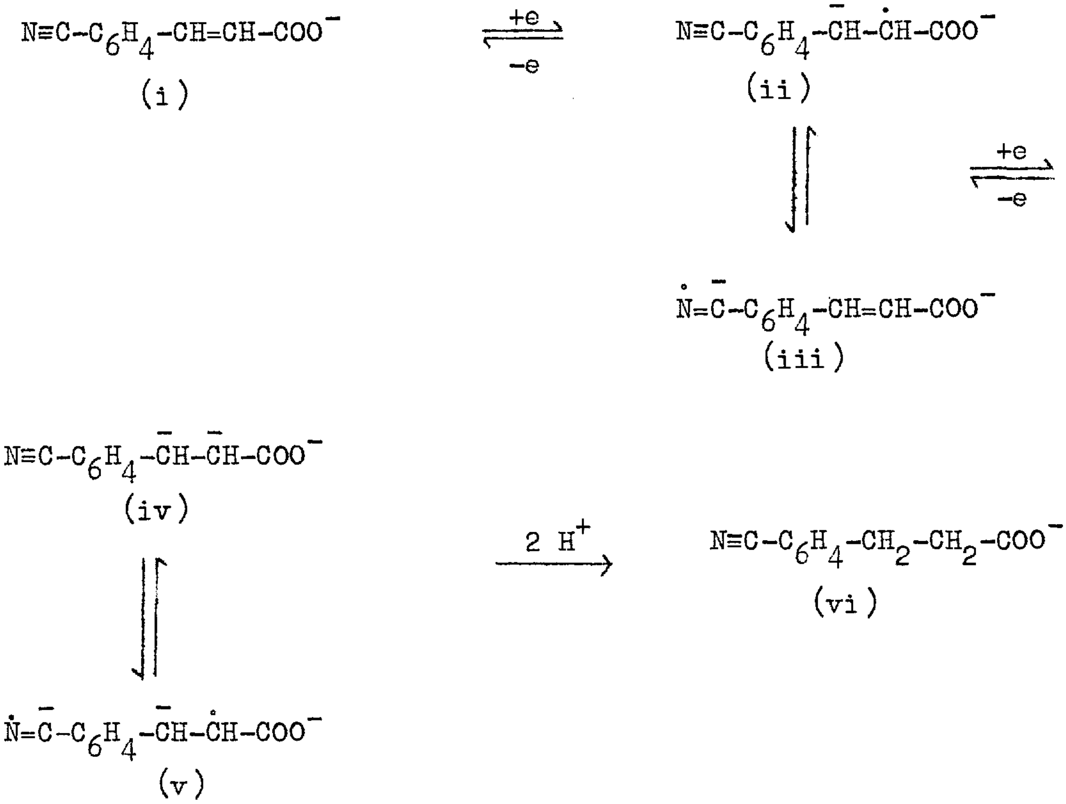
The type of electrode reaction involved in process III, in which electron transfer is followed by chemical reactions, has been discussed by Kivalo[90]. The process may be represented by the scheme:

$$A \quad + \quad n\,e \quad \underset{k_{b,h}}{\overset{k_{f,h}}{\rightleftharpoons}} \quad B \quad \underset{k_C}{\overset{k_B}{\rightleftharpoons}} \quad C$$

where $k_{f,h}$ and $k_{b,h}$ are the rates of the electron transfer reaction and k_B and k_C are the rates of the chemical reaction. The condition by which an apparently reversible polarographic wave is observed for an overall irreversible process is that the rate of electron transfer is very much faster than the rate of the subsequent chemical reaction. Alternatively, if the subsequent chemical reaction is reversible, then even if the electron transfer is slow, a reversible wave will be observed.

Two possible reaction sequences could account for process III for 4- cyanocinnamic acid:

(a) The reduction could occur by an EEC process



$$N{\equiv}C{-}C_6H_4{-}CH{=}CH{-}COO^- \underset{-e}{\overset{+e}{\rightleftharpoons}} N{\equiv}C{-}C_6H_4{-}\bar{C}H{-}\dot{C}H{-}COO^-$$

(i) (ii)

$$N{\equiv}C{-}C_6H_4{-}\bar{C}H{-}\dot{C}H{-}COO^- \rightleftharpoons \overset{\circ}{N}{=}\bar{C}{-}C_6H_4{-}CH{=}CH{-}COO^-$$

(ii) (iii)

$$\underset{-e}{\overset{+e}{\rightleftharpoons}}$$

$$N{\equiv}C{-}C_6H_4{-}\bar{C}H{-}\bar{C}H{-}COO^- \rightleftharpoons \dot{N}{=}\bar{C}{-}C_6H_4{-}\bar{C}H{-}\overset{\circ}{C}H{-}COO^-$$

(iv) (v)

$$\xrightarrow{2\ H^+} N{\equiv}C{-}C_6H_4{-}CH_2{-}CH_2{-}COO^-$$

(vi)

The addition of the first electron would result in the formation of the free radical (ii) which could rearrange to (iii) to achieve maximum separation between its charges centres. Similarly species (v) is a more probable product of the addition of the second electron than is (iv). The possibility that the addition of a proton might occur simultaneously with the second electron cannot be discounted.

(b) Alternatively an ECE mechanism could occur. This would involve a reversible protonation of (ii) or (iii) as the second step. This mechanism would result in the appearance of two 1- electron waves provided the rate of proton transfer was slow relative to the rate of electron transfer. As a single 2- electron wave was observed, this could only be accounted for if the rate of protonation was comparable to the rate of electron addition. In this case the half-wave potential would be dependent on pH, which was not, in fact, observed.

It is probable, therefore, that process III occurred through an EEC mechanism. The observed increase in wave slope on increasing the pH over the range 7-13 was attributed to the decrease in rate of protonation. At very high pH values the rate of protonation was so slow compared to the rate of electron addition that an apparently reversible wave was observed.

The rather anomalous behaviour of 4-cyanocinnamic acid at high pH values was compared with that of a related compound in which a similar total inductive effect operated on the C-C double bond. The compound 3,4 dichlorocinnamic acid ($\sigma = 0.600$, for 4- CN, $\sigma = 0.628$) showed no such unusual behaviour; its properties were completely analogous to those of the simple monosubstituted acids (Chapter 2).

In the case of 3,4 dichlorocinnamic acid there was no possibility of delocalising charge via a conjugated substituent and so an EEC type mechanism was impossible.

3.5 Polarographic Behaviour of Ethyl 4- Cyanocinnamate

Ethyl 4- cyanocinnamate was reduced in a single polarographic wave, the height of which varied with pH (Figure 3.8). At pH values above 7, hydrolysis of the ester occured and a second wave was observed at more negative potentials; at very high pH values the rate of hydrolysis became too rapid for accurate measurements of the ester wave. The second, hydrolysis wave, was due to reduction of the anion by processes II and III. Over the pH range 7 to 9, where two waves were observed for the anion, the hydrolysis wave was too poorly defined to be resolved into two waves. The polarographic dissociation curve for the ester showed three electrode processes: that in acid solution, IV, a mixed process between pH 4 and 8, V, and a process in alkaline solution, VI.

Comparison of wave heights of the ester with those of the acid suggested that process IV involved the transfer of 4 electrons, and process VI, 2 electrons. The pH dependence of half-wave potentials (Figure 3.9) showed that a protonated complex of the ester was the electroactive species up to pH 8, after which the ester was reduced in unprotonated form.

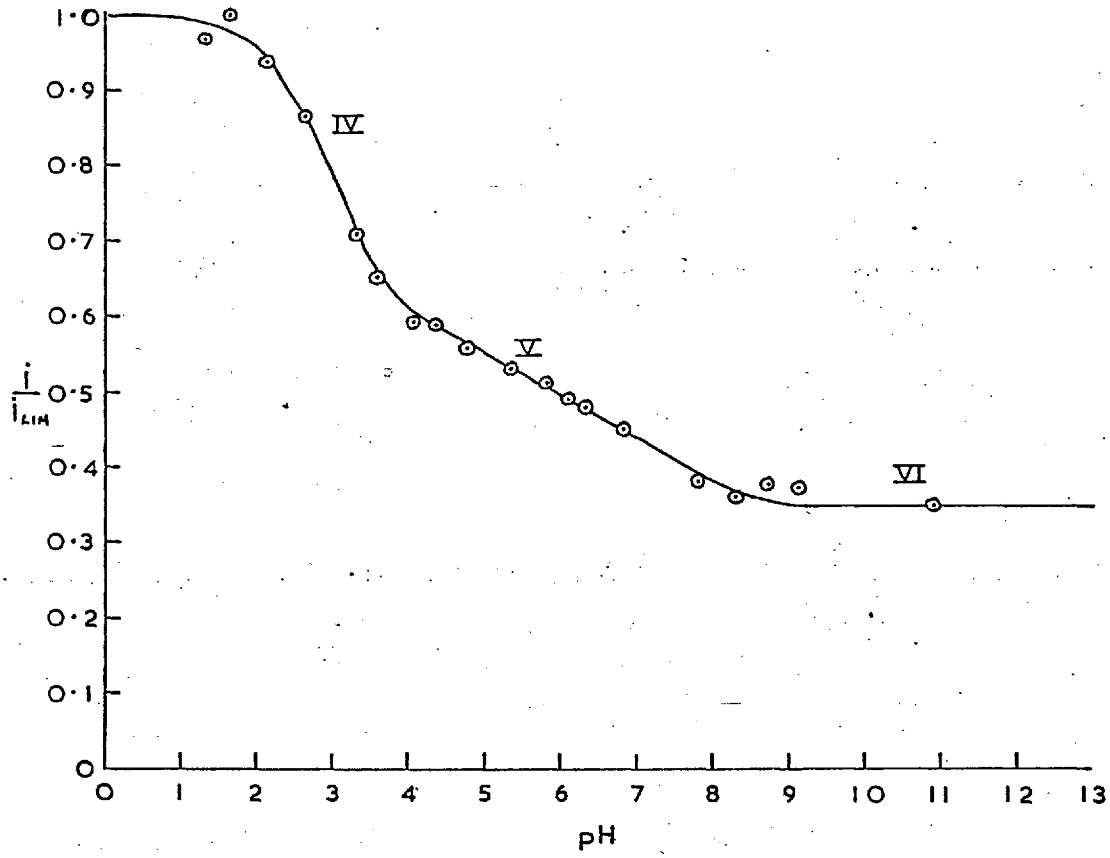


Figure 3.8 Polarographic dissociation curve of ethyl 4-cyanocinnamate in 50% ethanol.--

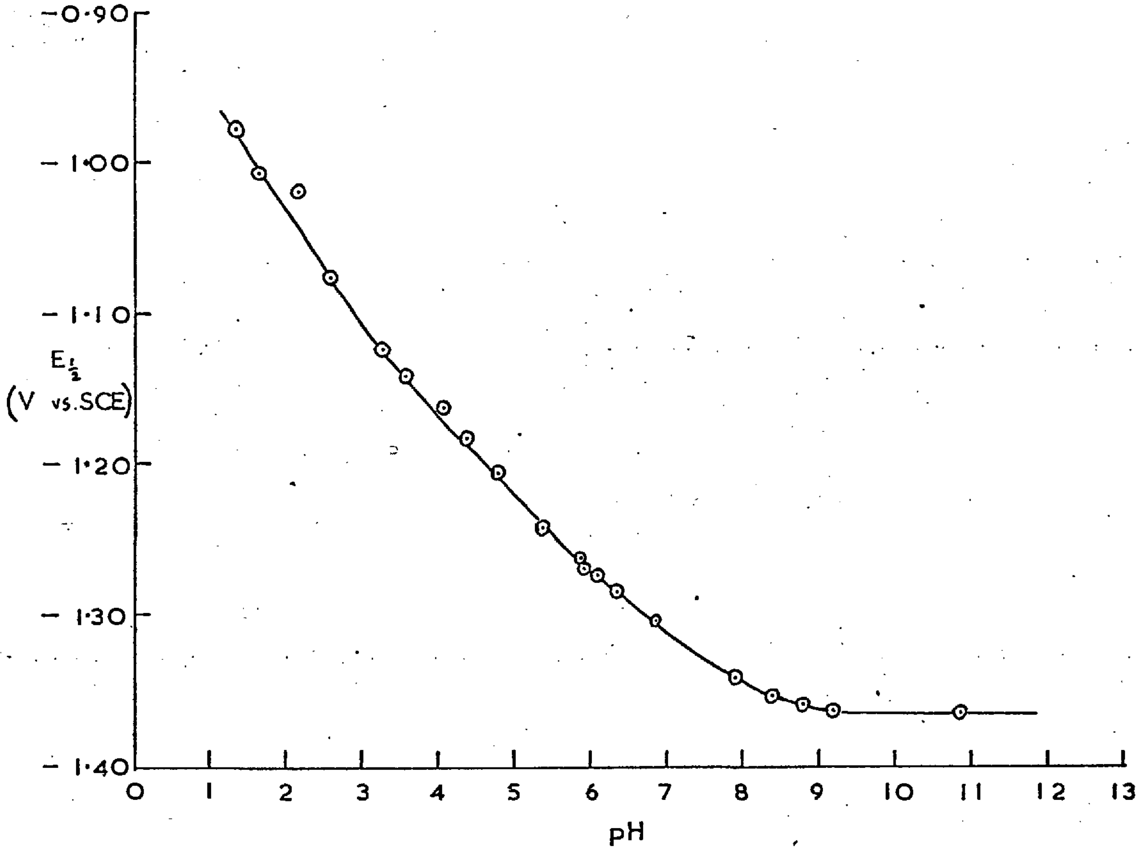
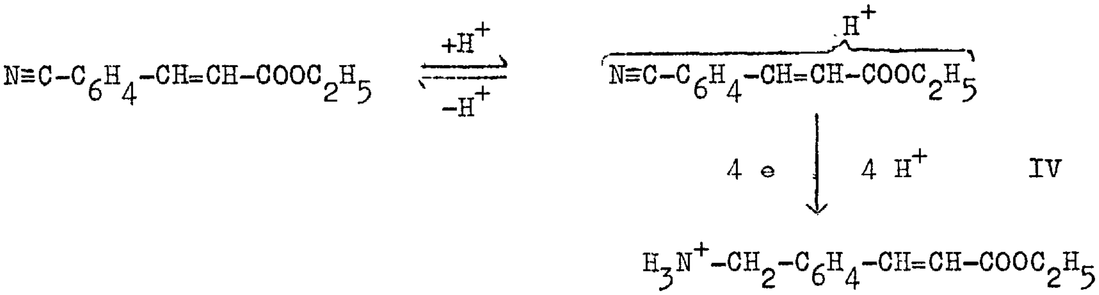


Figure 3.9 Dependence of half wave potentials of ethyl 4-cyanocinnamate on pH in 50% ethanol.

The structural analogy between the acid and ester suggested reaction IV for the ester was identical to reaction I for the acid,

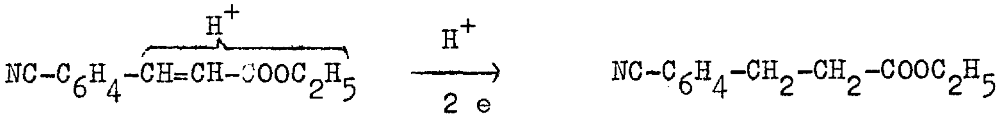


$$\begin{array}{lcc} N{\equiv}C-C_6H_4-CH{=}CH-COOC_2H_5 & \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} & \overbrace{N{\equiv}C-C_6H_4-CH{=}CH-COOC_2H_5}^{H^+} \\ & & 4\ e\ \Big\downarrow\ 4\ H^+ \qquad \mathrm{IV} \\ & & H_3N^+-CH_2-C_6H_4-CH{=}CH-COOC_2H_5 \end{array}$$

Similarly, reaction VI for the ester was analogous to reaction III for the acid, innwhich electron addition was followed by protonation,

$$NC-C_6H_4-CH{=}CH-COOC_2H_5 \xrightarrow[2\ e]{2\ H^+} NC-C_6H_4-CH_2-CH_2-COOC_2H_5 \quad \mathrm{VI}$$

The mixed process for the ester, V, involved reduction of the CN-group and the C=C bond. The $E_{1/2}$-pH plot did not show a significant change in slope in the region of the mixed process and it therefore seemed probable that in this region the C=C bond was reduced via a protonated complex,



$$NC-C_6H_4-\overbrace{CH{=}CH-COOC_2H_5}^{H^+} \xrightarrow[2\ e]{H^+} NC-C_6H_4-CH_2-CH_2-COOC_2H_5$$

Simultaneous occurrence of this reaction and reaction IV were observed as the mixed process V. As with the acid, the beginning of the mixed process was characterised by an increase in nα value followed by a sudden decrease between pH 5.4 and 5.6 (Table 1)

3.6 Experimental

Reagents

4- cyanocinnamic acid and 3,4 dichlorocinnamic acid were synthesised from the corresponding aldehydes by a modified Doebner reaction[85].

Ethyl 4- cyanocinnamate was synthesised from the parent acid. Treatment of the acid with thionyl chloride yielded the acid chloride which was then reacted with ethanol. The ester was distilled under reduced pressure and then recrystallised from small volumes of ethanol. The compound does not appear to have been reported before; it was obtained as a white crystalline solid, m.p. 67.5° to 68.5° C, and its composition was established by elemental analysis (Calc: C 71.62; H 5.51; N 6.96 %. Found: C 71.47; H 5.76; N 6.67 %). The structure of the compound was confirmed by IR and NMR spectrometry.

A 5.10^{-3} M stock solution of each compound was prepared in absolute ethanol.

Apparatus

Apparatus for d.c. polarography, half-wave potential measurements and microcoulometry has been described previously (Chapter 2). The DME capillary constants measured at the potential of the SCE in

0.1 M potassium chloride solution were $t = 4.7$ s., $m = 1.45$ mg s^{-1}, at $h = 60$ cm.

A.c polarograms were obtained with a General Purpose polarograph and Univector (Cambridge Ltd.). A 3- electrode cell was used in which a platinum wire counter electrode was placed near to the DME. The counter electrode was connected to the reference SCE through a 5000 μF capacitor.

Oscillopolarograms at controlled alternating current were measured with a Polaroscope P 576 (Krizik, Prague) at a hanging mercury drop electrode (HMDE).

Cyclic voltammograms were also measured at a HMDE using the d.c. polarograph for slow sweep rates and an instrument specially designed for fast sweep rates[91].

Absorbance measurements in the UV were made with a DB spectrophotometer (Beckmann Instruments Ltd., Fife) using 1 cm quartz cells.

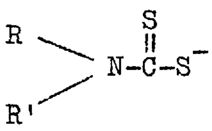
4. Polarographic Determination of Derivatives of Dithiocarbamic Acid

4.1 Introduction

In Chapters 2 and 3 it has been shown how d.c. polarography can be used to establish the course of organic electrode processes and how some related techniques can be used to supplement this information. This approach provides a convenient starting point for the development of any polarographic method of analysis and has been applied to the determination of derivatives of dithiocarbamic acid. These compounds are widely used as fungicides and there is a need for analytical methods applicable at the residue level. At the present time polarographic methods have only been applied in a limited way in pesticide residue analysis.[92] Although d.c. polarography can be made an extremely sensitive analytical method by use of suitable refined apparatus[3], such instruments are not widely available. Therefore, to obtain greater sensitivity than is offered by most commerical d.c. polarographs, the application of a.c. polarography and linear potential sweep chronoamperometry to the determination of dithiocarbamic acid derivatives has been considered.

The derivatives of dithiocarbamic acids which have been used as pesticides can be divided into three main types:[93]

(i) Simple substituted dithiocarbamic acid salts,

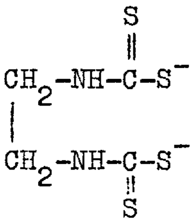


M^{n+}/n where $R = CH_3$, etc.

$R' = H, CH_3$, etc.

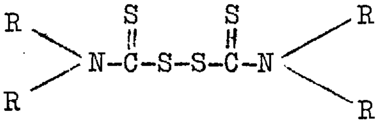
$M = Na^+, Fe^{3+}, Zn^{2+}$, etc.

(ii) Salts of ethylene bis dithiocarbamic acid,



$2\ M^{n+}$ where $M = Na^+, Zn^{2+}, Mn^{2+}, Cu^{2+}, Fe^{3+}$, etc.

(iii) Substituted thiuram disulphides,



where $R = CH_3$, etc.

The recognised analytical methods for these compounds are based on conversion of the sulphur to carbon disulphide which is then determined colorimetrically, e.g. after reaction with Viles reagent[94]. The sensitivity of this somewhat lengthy procedure is limited. Moreover, the method is only semi-specific in that it cannot distinguish between dithiocarbamates and thiuram disulphides.

There is no agreement as to the mechanism of the fungitoxity of these compounds but it is thought to depend on the labile dithiocarbamate species, rather than on the heavy metal ion, when this is present. For this reason analytical methods are more meaningful if based on a determination of the dithiocarbamate species rather than the metal ion. Thus in the present investigation, analysis of the dithiocarbamate *via* polarographic determination of the metal ion has not been attempted.

4.2 Simple Substituted Dithiocarbamates

The d.c. polarographic behaviour of simple substituted dithiocarbamates has been described by several authors. Gregg and Tyler[95] reported that the diethyldithiocarbamate anion showed anodic polarographic waves and postulated that these corresponded to oxidation of the ions to tetra-ethyl thiuram disulphide. Zuman *et al*[96] showed subsequently that this was not a thermodynamically reversible system and that the anodic waves corresponded to formation of insoluble mercury salts at the DME. Nangniot has described the polarographic behaviour of the zinc[97] and iron[98] salts of dimethyldithiocarbamic acid.

The sodium salts of alkyl dithiocarbamic acids were soluble in water and were most stable in alkaline solutions. The iron and zinc salts of dimethyldithiocarbamic acid (sold as Ferbam and Ziram, respectively) were insoluble in water but were soluble in alkaline solutions of EDTA. Ziram was soluble in 0.1 M sodium hydroxide solution. Sodium diethyldithiocarbamate (NaDDC) was chosen as a model substance representative of this type of compound, because it is commercially available in a high degree of purity.

A d.c. polarogram of NaDDC showed two anodic waves in alkaline solution. That at more negative potentials ($E_{1/2}$ = - 0.6 V vs. SCE), I, was concentration independent over the range 1.10^{-4} to 1.10^{-3} M. The more positive wave ($E_{1/2}$ = - 0.4 V vs. SCE), II, showed a concentration dependence (Table 1). At high concentrations the DME drop rate became erratic and it was impossible to obtain reproducible polarograms (Figure 4.1).

The height of wave I was linearly dependent on the height of the mercury reservoir, and this, together with its concentration independence, indicated that the wave was adsorption controlled. This conclusion was confirmed by oscilloscopic examination of the i-t curves corresponding to the limiting currents of waves I and II. The i-t curve for wave I (Figure 4.2a) had a shape characteristic of a process in which the reaction is unable to proceed at a surface covered by adsorption. Wave II, however, also showed an i-t curve influenced by adsorption (Figure 4.2b) but in this case the reaction was able to proceed at the covered surface.

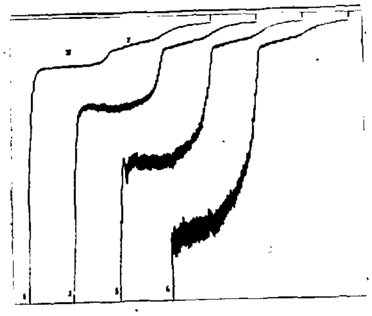
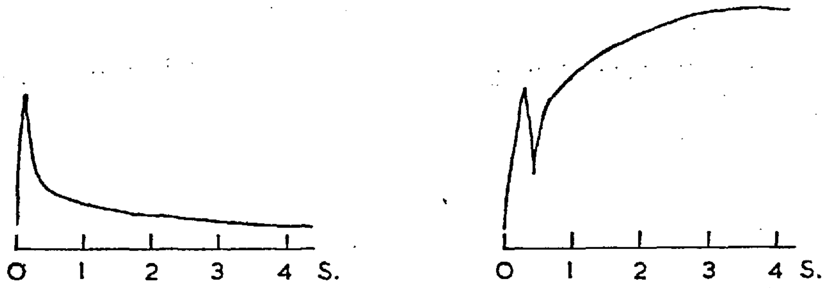


Figure 4.1 Concentration dependence of d.c. polarographic waves of NaDDC. Concentrations: (1) 2.10^{-4}; (2) 4.10^{-4}; (3) 6.10^{-4}; (4) 8.10^{-4} M. Starting potential -0.7 V vs. SCE. Sensitivity 6 μA f.s.d.; 100 mV/absc.



(a) (b)

Figure 4.2 Current-time curves for NaDDC at pH 11. Electrode potentials (a) -0.6 (b) -0.4 V vs. SCE.

Table 1

Comparison of Limiting Currents (μA) Obtained by Polarographic Techniques for Sodium Diethyldithiocarbamate in Ammonia Buffer pH 11

Concentration	D.c Polarography		A.c Polarography		Potential Sweep Chronoamperometry[a]	
M	I	II	I	II	I	II
2.10^{-6}			0.03		0.05	
4.10^{-6}			0.07		0.11	
6.10^{-6}			0.10		0.16	
8.10^{-6}			0.14		0.22	
1.10^{-5}			0.17		0.27	
2.10^{-5}			0.54		0.61	
4.10^{-5}			1.08		1.15	
6.10^{-5}			1.60		1.74	
8.10^{-5}			2.13		2.30	
1.10^{-4}	0.29	0	2.64	0	2.67	0
2.10^{-4}	0.29	0.34	4.54	0.64	3.05	4.8
4.10^{-4}	0.29	1.42	6.30	2.05	3.05	17.6
6.10^{-4}	0.29	2.50	6.43	3.46	3.05	28.8
8.10^{-4}	0.29	4.08	6.40	4.84		
1.10^{-3}	0.29		6.40	6.24		

I Adsorption Wave
II Diffusion Wave
a Cathodic Potential Sweep

The polarographic behaviour exhibited by NaDDC was characteristic of that shown by anions which form insoluble mercury salts and has been observed for halide ions[99,100] and other inorganic anions[101,102]. The pre-wave I, following the Brdička[12] treatment of adsorption waves, corresponded to the formation of an insoluble monolayer of reaction product adsorbed on the DME drop surface. Further oxidation was then hindered until a more positive potential was reached when the barrier to the charge transfer reaction was overcome, resulting in the discontinuous commencement of wave II. Identification of the reaction products for this system was not possible using the techniques previously applied (microcoulometry followed by product analysis). It is known that the products of reactions of this type are labile and so cannot be isolated. Furthermore, the determination of n was precluded because NaDDC reacted directly with mercury and so the mercury pool which collected in the cell during electrolysis constituted an interference. Attempts to cover the mercury pool with an inert, water immiscible, solvent were unsuccessful. It must be concluded that this system was too complex to be characterized completely by polarographic methods. However, the qualitative description of the electrode process which has been given was adequate for the development of analytical methods.

To increase the sensitivity of the direct polarographic determination of NaDDC the technique of linear potential sweep chronoamperometry at a DME was applied. Using this method a linear potential sweep of 0.5 V is applied to each drop late in its lifetime while its surface area is only changing slowly. The cell current is displayed on a long persistence oscilloscope as a function of potential. Instruments were used in which (i) the drop time was adjusted to be approximately equal to the sweep repetition rate, which was then synchronised with the drop, and (ii) the drop was detached mechanically at the end of each potential sweep.

Anodic potential sweeps (from negative to positive potentials) showed two peaks in the concentration range 10^{-3} to 10^{-4} M (Figure 4.3). The height of the more negative peak, I, was concentration independent while peak II showed a rectilinear concentration dependence. Peak I clearly corresponded to the d.c. polarographic pre-wave and peak II to the diffusion controlled wave.

Cathodic potential sweeps (from positive to negative potentials) also showed the same two peaks, but the peak currents obtained were several times greater (Figure 4.4). At concentrations above 6.10^{-4} M peak I (the concentration independent pre-wave) was obscured by the larger peak II, which required a reduction in instrument sensitivity to accomodate it. This increase in sensitivity was attributed to pre-concentration of the insoluble mercury salt on the drop surface during the delay period (5 s) during which the drop grew to maximum

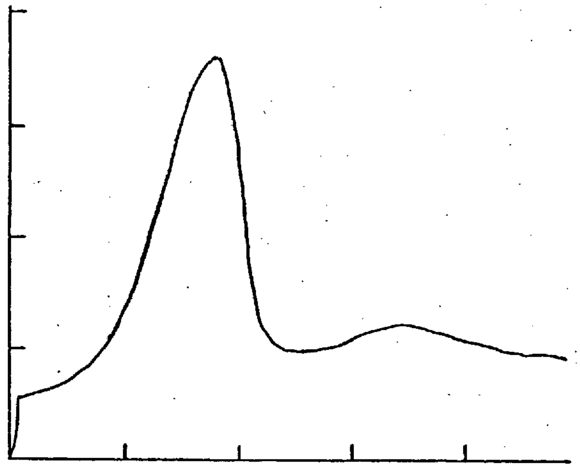


Figure 4.3 Linear potential sweep oscillogram for 5.10^{-4} M NaDDC. Anodic potential sweep, starting potential -0.7 V vs. SCE. Sensitivity, vertical 2.5 μA/division; horizontal, 100 mV/division.

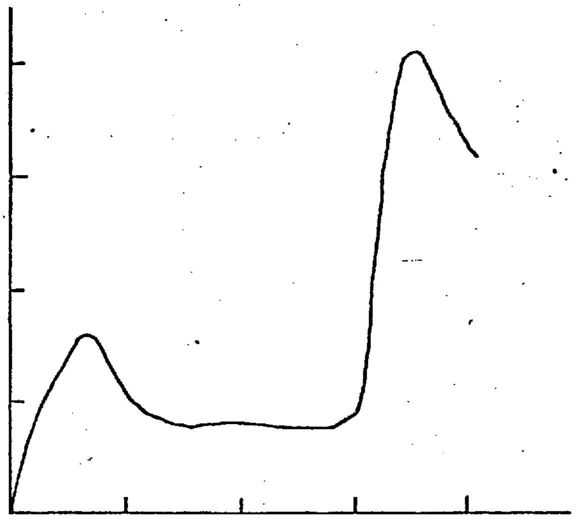


Figure 4.4 Linear potential sweep oscillogram for 5.10^{-4} M NaDDC. Cathodic potential sweep, starting potential -0.3 V vs. SCE. Sensitivity, vertical 6 μA/division; horizontal, 100 mV/division.

size before application of the potential sweep. At concentrations below 10^{-4} M, peak II disappeared and peak I became concentration dependent (Table 1) over the range 10^{-4} to 10^{-6} M. The consecutive use of the two peaks obtained by cathodic potential sweeps enabled a linear peak height-concentration relationship to be established over the range 1.10^{-6} to 6.10^{-4} M.

Successful use of the instrument in which the delay-sweep cycle was triggered by the current pulse obtained from a freely falling DME, required a capillary with a natural drop time between 6.5 and 7 s. In the presence of NaDDC, particularly at high concentrations, the capillary was found to drop erratically presumably due to deposition of solid material in and around the capillary orifice. This effect resulted in random triggering of the sweep generator and it was hoped to overcome the problem by use of an instrument employing mechanical drop detachment. A considerable improvement was, in fact, observed and the detection limit was lowered to 10^{-7} to 10^{-8} M. However, below 10^{-6} M peak heights were not reproducible.

A completely different approach to the problem was provided by the use of a.c. polarography. A.c polarographic waves have been observed for halide ions[100] and it seemed likely that an organic species undergoing a similar electrode reaction would also show an a.c. polarographic response.

In alkaline solution NaDDC showed two waves in the concentration range 10^{-3} to 10^{-4} M (Figure 4.5) at potentials corresponding to the d.c. waves. The concentration dependence of these two peaks followed the pattern previously observed with d.c. polarography. Peak I was concentration independent over the range 10^{-3} to 10^{-4} M but linearly dependent in the range 10^{-6} to 10^{-4} M. Peak II showed a rectilinear peak height-concentration relationship over the range 10^{-3} to 10^{-4} M but disappeared below 10^{-4} M. The use of these two peaks gave a rectilinear peak height-concentration relationship over the range 10^{-6} to 10^{-3} M (Table 1).

The concentration at which the diffusion wave II was no longer observed corresponded to that which just formed a monolayer at the drop surface. This was obviously a function of the surface area of the drop and therefore varied with different DME capillaries. However, the observed concentration of 10^{-4} M reported here was a typical value and was in agreement with that reported for a series of inorganic anions[101].

A concentration of 10^{-6} M must be taken as the lower limit attainable with the apparatus used, as at this level the instrument noise became comparable to the signal. A.c. ripple was observed on the d.c. output of the a.c. polarograph at twice the applied frequency of 35 Hz; this frequency doubling was due to the rectifier bridge

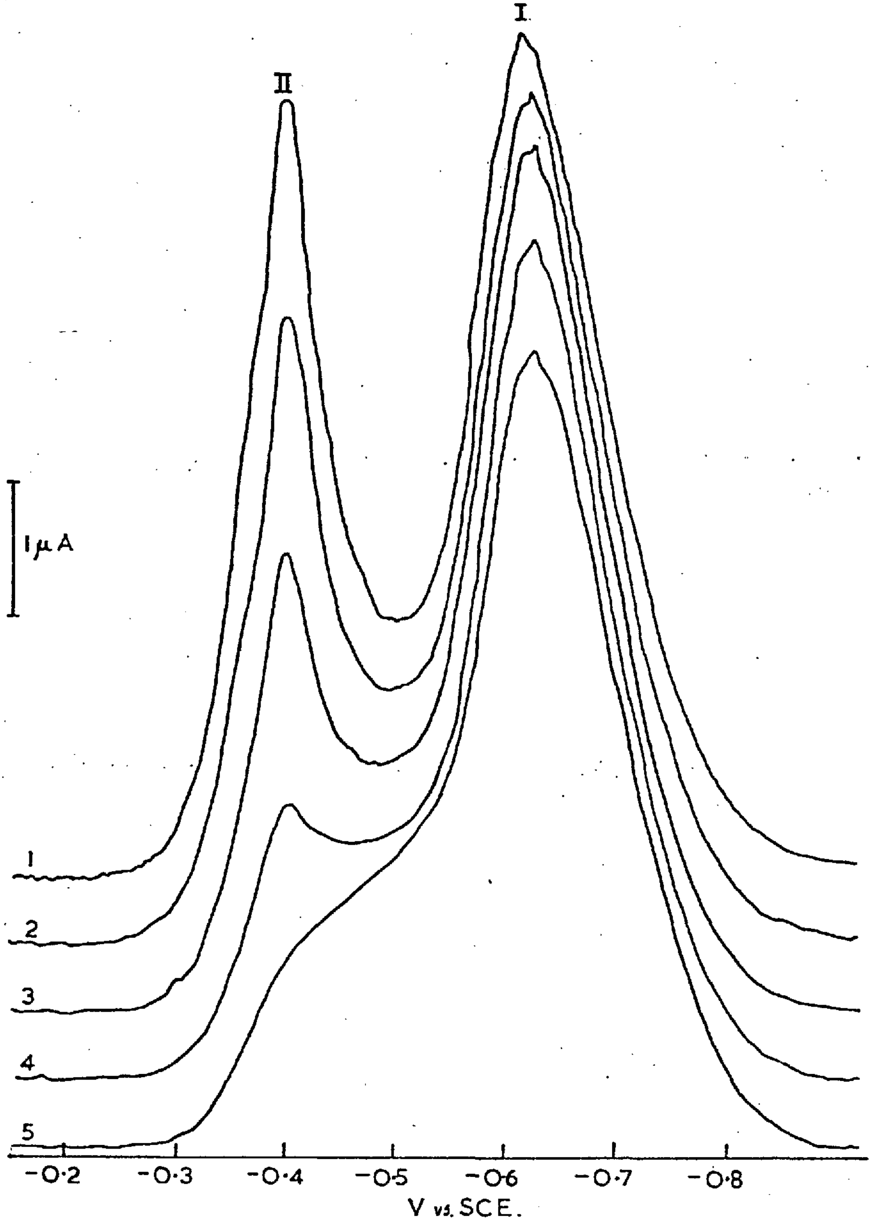


Figure 4.5 Concentration dependence of a.c. polarographic waves of NaDDC at pH 11. Concentrations: (1) 10.10^{-4}; (2) 8.10^{-4}; (3) 6.10^{-4}; (4) 4.10^{-4}; (5) 2.10^{-4} M.

circuit in the polarograph. The recording system used incorporated parallel T filters tuned to frequencies of 1.6, 0.8, 0.8, and 0.4 Hz, which were effective in filtering low frequency oscillations due to drop growth, but did not significantly reduce the 70 Hz noise. The limit of detection of this system could undoubtedly be extended by the use of a solid state a.c. polarograph[48].

At high concentrations, e.g. 10^{-3} M, when both waves were well developed, it was apparent that the width of wave I at half height, 144 mV, was considerably greater than the corresponding value for wave II, 88 mV (Figure 4.5). Theory predicts that the width of an a.c. wave at half height is 90.5/n mV for low frequencies[47]. However, because the instrument used in this work employed phase sensitive detection, the increase in sensitivity is obtained at the expense of distorting the wave shape. It was not, therefore, possible to derive n values from this information.

4.3 Salts of Ethylene bis Dithiocarbamic Acid

The chemical behaviour of salts of ethylene *bis* dithiocarbamic acid (EDC) is considerably more complex than that of simple alkyl dithiocarbamates. The EDC anion is unstable and decomposes with loss of hydrogen sulphide and/or carbon disulphide to give a variety of products among which have been identified ethylene diamine, ethylene thiuram disulphide, ethylene thiourea, and ethylene *bis* isothiocyanate.

It has been postulated that these breakdown products are responsible for the fungitoxic activity of the compounds[103].

Nangniot[104] has briefly described the polarographic determination of the zinc salt of EDC (commercially, zineb). Other polarographic determinations of zineb have been based on the zincate ion or on the acid decomposition of the sample to ethylene diamine, which was converted into a copper complex, the metal ion content of which was determined[105].

The sodium salt of EDC was soluble in water and, as with the alkyl dithiocarbamates, was most stable in alkaline solution. The heavy metal salts of EDC (Zn-EDC, zineb; Mn-EDC, maneb; Cu-Fe-Zn-EDC, cufram-Z) were soluble in strongly alkaline solutions of EDTA. The solutions decomposed slowly on standing but observed variations were insignificant for a few hours after the solutions had been freshly prepared.

The d.c. polarographic behaviour of EDC was far more complex than that of NaDDC. Four waves were observed (Figure 4.6). Wave I was cathodic, wave II a mixed cathodic-anodic wave and waves III and IV anodic. From the dependence of wave height upon concentration, waves I and III were shown to be concentration independent and thus probably adsorption waves, while wave II showed a rectilinear concentration dependence over the range $1 \cdot 10^{-4}$ to $1 \cdot 10^{-3}$ M

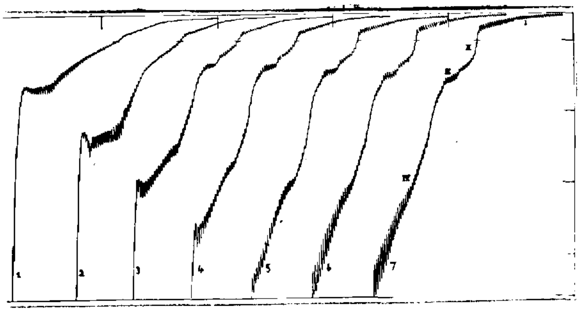


Figure 4.6 Concentration dependence of d.c. polarographic waves of EDC at pH 11. Concentrations: (1) 1.10^{-4}; (2) 2.10^{-4}; (3) 3.10^{-4}; (4) 4.10^{-4}; (5) 6.10^{-4}; (6) 8.10^{-4}; (7) 10.10^{-4} M. Sensitivity 3 μA f.s.d.; 500 mV/absc.
Starting potential -0.9 V vs. SCE.

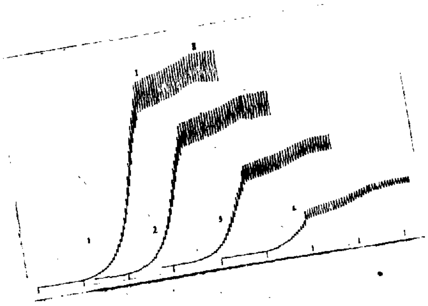
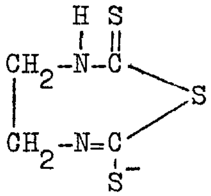


Figure 4.7 Concentration dependence of d.c. polarographic waves of thiram in 50% ethanol at pH 11. Concentrations: (1) 8.10^{-4}; (2) 6.10^{-4}; (3) 4.10^{-4}; (4) 2.10^{-4} M. Sensitivity 2.5 μA f.s.d.; 100 mV/absc.
Starting potential -0.25 V vs. SCE.

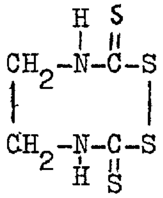
Wave IV was concentration dependent but reached a limiting wave height above 3.10^{-4} M. Characterisation of the waves from their dependence on mercury reservoir height was inconclusive as the waves were too poorly defined for unambiguous measurement.

The general form of the polarographic waves suggested the presence of two electroactive species. Because it was the major constituent, wave IV was attributed to the EDC anion. By analogy to the behaviour of NaDDC wave III therefore corresponded to the formation of a monolayer of an insoluble mercury-EDC compound at the drop surface. The mixed oxidation reduction wave II was due to the presence of some breakdown product of EDC, and wave I was therefore due to reduction of this breakdown product in the adsorbed state.

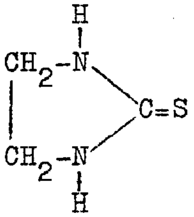
The polarographic behaviour of some of the postulated breakdown products was studied in an attempt to identify the electroactive species responsible for wave II. Ethylene thiuram monosulphide,



ethylene thiuram disulphide



and ethylene thiourea



were examined. In alkaline solution ethylene thiuram monosulphide was found to give a composite anodic-cathodic wave with a cathodic adsorption wave identical in form to waves I and II. Ethylene thiuram disulphide gave a single cathodic wave while ethylene thiourea was electroinactive. Further confirmation that ethylene thiuram monosulphide was the electroactive breakdown product was obtained by making standard additions of the compound to an EDC solution at pH 10 and 13. In each case wave II increased in height. A detailed study of the polarographic behaviour of ethylene thiuram monosulphide was not attempted. The anodic part of the wave presumably corresponded to the mercury salt formation expected of a compound with a thiol group, while several possible reduction schemes could account for the cathodic waves.

The amount of ethylene thiuram monosulphide present in the EDC solution varied with the history of the sample. Commercial samples of maneb, zineb and cufram Z contained varying amounts while samples of freshly synthesised NaEDC always showed the presence of some of the breakdown product.

A.c. polarography proved to be of little analytical application for this system. Three peaks were observed in the concentration range 10^{-4} to 10^{-3} M, and from their potentials the first corresponded to the d.c. wave IV and the third to wave I. The middle a.c. peak could have corresponded to d.c. waves II or III or to both of them. The a.c. peaks showed no reproducible or well defined concentration dependence which was of analytical utility.

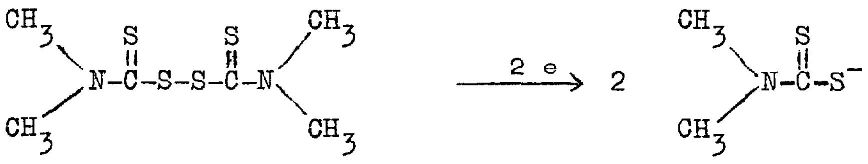
In view of the limited range of concentrations for which d.c. polarography was applicable (up to 6.10^{-4} M) and the inapplicability of a.c. polarography it was concluded that the direct polarographic determination of ethylene bis dithiocarbamate was of limited analytical utility. D.c. polarography, however, provided a convenient means of estimating the extent of decomposition of the compounds.

4.4 Substituted Thiuram Disulphides

Only one thiuram disulphide, the tetramethyl derivative, (Thiram or Arasan) has found acceptance as a fungicide. The tetra-ethyl compound is used as a rubber additive and as a drug (Antabuse) for the treatment of alcoholism. It has been suggested that the fungitoxicity of thiram is due to its breakdown to form the dimethyldithiocarbamate anion[106]. The d.c. polarographic behaviour of thiram has been described previously. Gullstrom and Burchfield[107] observed a wave in 50% dioxane solution, while Nangniot[108] has given a more comprehensive account of the determination of residues of thiram in plants. Gregg and Tyler[95] have described the polarographic behaviour of tetra-ethyl thiuram disulphide, while Taylor[109] has determined the compound by linear potential sweep chronoamperometry.

Thiram was found to be insoluble in water but moderately soluble in ethanol. The d.c. polarographic behaviour of the compound was in accordance with that reported by Nangniot[108]. Two cathodic waves were observed, the more positive of which, II, was concentration dependent and the more negative, I, was independent of concentration (Figure 4.7). The height of wave II was directly proportional to the square root of the mercury reservoir height, while wave I was proportional directly to h. Thus, it was concluded that wave II was diffusion controlled and wave I was a Brdička adsorption wave corresponding to reduction of thiram adsorbed on the electrode surface.

Comparison of wave heights of thiram with other compounds confirmed that the reduction involved two electrons corresponding to the postulated reaction,



Confirmation that this, in fact, was the course of the electrode reaction was obtained by cyclic voltammetric investigation of the analogous reaction of tetra-ethyl thiuram disulphide. The steady state cyclic voltammogram of sodium di-ethyl dithiocarbamate at slow potential sweep rates showed two anodic peaks corresponding to formation of insoluble mono- and bulk layers (Figure 4.8). The subsequent cathodic half-cycle showed a large peak corresponding to dissolution of the bulk layer followed by a peak due to monolayer reduction. The steady state cyclic voltammogram of tetra-ethyl thiuram disulphide showed an identical pattern except that the cathodic peak corresponding to monolayer dissolution was obscured by a larger cathodic peak at a slightly more negative potential corresponding to reduction of the S-S bond (Figure 4.9).

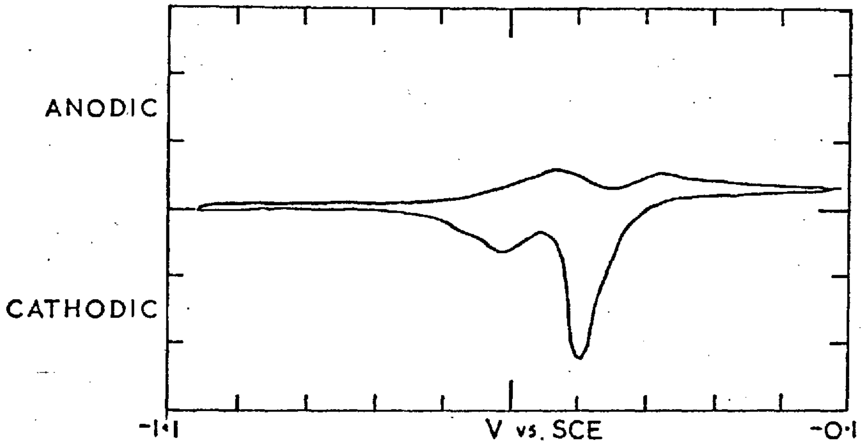


Figure 4.8 Cyclic voltammogram of 5.10^{-4} M NaDDC in 50% ethanol at pH 11. Potential sweep rate 1 V s^{-1}. Vertical sensitivity 10 μA/division.

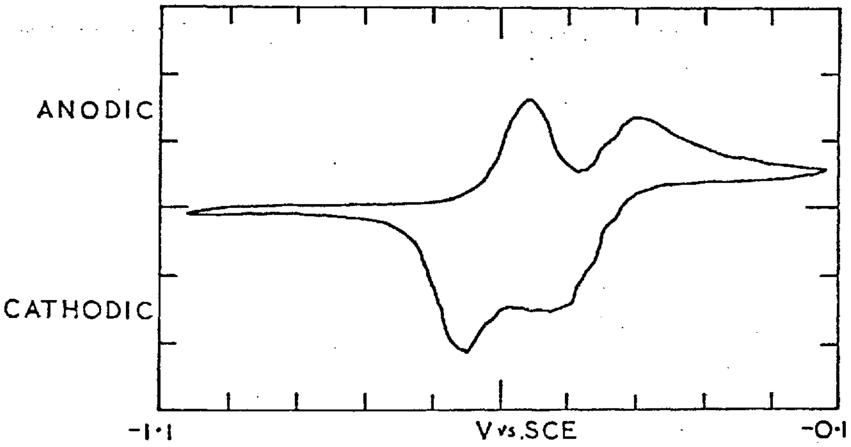


Figure 4.9 Cyclic voltammogram of 5.10^{-4} M tetra-ethyl thiuram disulphide in 50% ethanol at pH 11. Potential sweep rate 1 V s^{-1}. Vertical sensitivity 10 μA/division.

Thiram was observed to give a single a.c. polarographic wave, I, at a concentration of 1.10^{-4} M. At higher concentrations a second poorly defined wave, II, was observed at more positive potentials and the height of peak I reached a limiting value (Figure 4.10). The height of peak II increased with increasing concentration but because it was so poorly developed it was difficult to obtain an analytically useful relationship between peak current and concentration. At concentrations below 1.10^{-4} M the height of the single peak, I, was concentration dependent and a rectilinear calibration curve was obtained for the concentration range 10^{-6} to 10^{-4} M.

The course of the reduction of thiram was not typical of processes which give rise to a.c. waves. In general, well developed a.c. waves are only observed for thermodynamically reversible systems. Although the reduction of thiram was not reversible in this sense the possibility of an anodic reaction due to mercury salt formation existed, following the cathodic reduction of the S-S bond. It was, presumably, this reaction sequence which allowed the passage of an a.c. current.

4.5 Experimental

Sodium dimethyldithiocarbamate, sodium diethyldithiocarbamate, tetraethyl thiuram disulphide, and tetramethyl thiuram disulphide were laboratory reagents. All other dithiocarbamate derivatives were

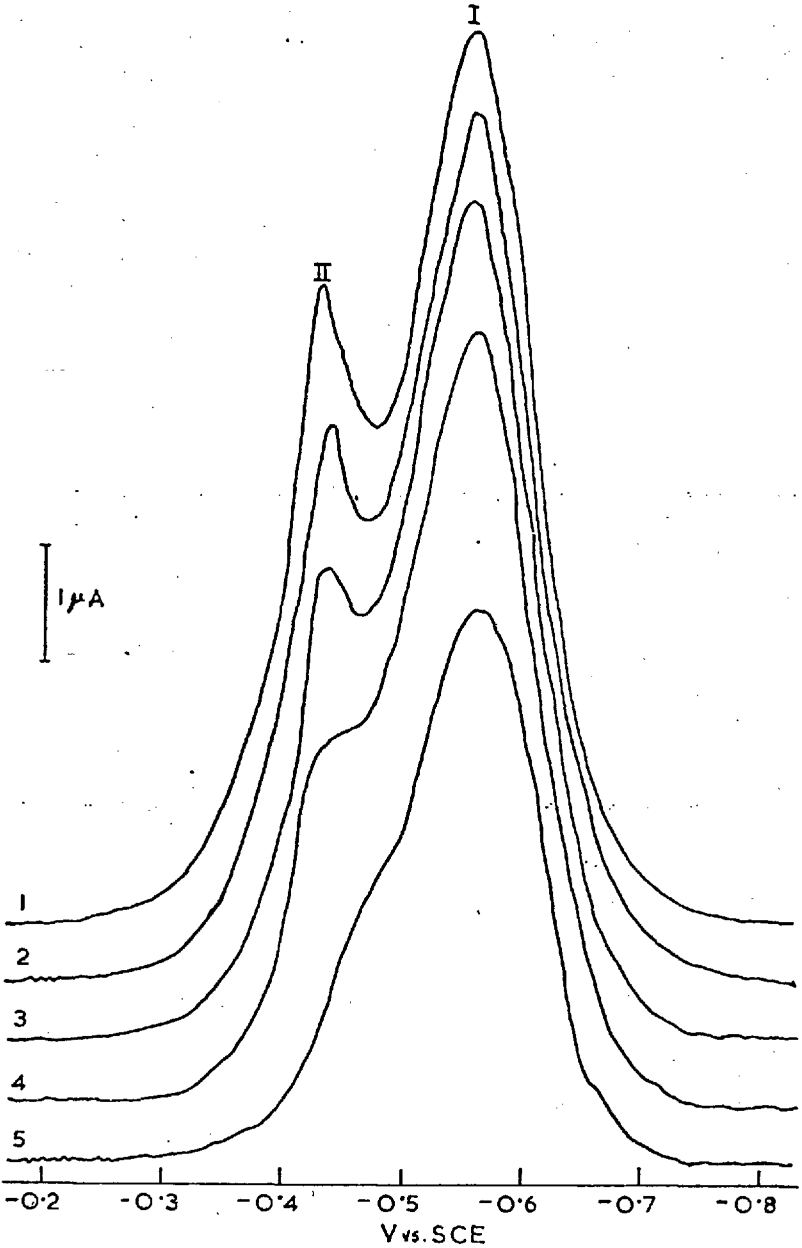


Figure 4.10 Concentration dependence of a.c. polarographic waves of thiram in 50% ethanol at pH 11. Concentrations: (1) 10.10^{-4}; (2) 8.10^{-4}; (3) 6.10^{-4}; (4) 4.10^{-4}; (5) 2.10^{-4} M.

commercial samples. Sodium ethylene bis dithiocarbamate was synthesised from ethylene diamine and carbon disulphide using two different methods.[110,111]

Apparatus

Apparatus for d.c. polarography has been described previously (Chapter 2). The characteristics of the DME measured in 0.1 M potassium chloride at the potential of the SCE were $t = 3.82$ s, $m = 2.32$ mg s^{-1} at $h = 65$ cm.

A.c. polarograms were measured with a Univector and General Purpose Polarograph (Cambridge Ltd.) with the Radelkis polarograph used as current recorder. The 5 KΩ sensitivity shunt was removed from the G.P. polarograph by removing the connections to cell +ve and Meter -ve terminals and shorting them together. This eliminated the zero and damping controls from the G.P. polarograph; subsequently the sensitivity, zero and damping controls on the current recorder were used. The cell arrangement has been described previously (Chapter 3).

Linear potential sweep chronoamperometric measurements at a DME were made with the K-1000 Cathode Ray Polarograph and the Davis Differential Cathode Ray Polarograph (Southern Analytical Ltd., Surrey) used in its single cell mode. The cells supplied with these instruments were not used as they incorporated a mercury pool anode which was inappropriate for studying compounds which react with mercury.

Cyclic voltammograms at a HMDE were obtained using a specially designed apparatus based on an operational amplifier summing potentiostat constructed from PF85AU amplifiers (Philbrick-Nexus Research Incorporated, Chichester). The triangular wave form was obtained from a Model 3300 A Function Generator (Hewlett-Packard, Bucks.) which was externally d.c. biased so that the wave was unidirectional, i.e. from 0 to -1 V. The two function generator outputs were matched; one was connected to the potentiostat, the other was used to drive the oscilloscope horizontal amplifier. The oscilloscope was a Model 175 A(Hewlett-Packard, Bucks.) with a High Gain Vertical Amplifier 1752 A and Auxiliary Plug-in 1780 A. At low sweep rates, where it was necessary to use a high gain current amplifier, a.c. pick-up in the cell obscured the oscilloscope trace. To eliminate this a parallel T filter tuned to 50 Hz was inserted between the potentiostat current amplifier and the oscilloscope. The filter was most satisfactory if isolated from the oscilloscope with a unity gain voltage follower. The filter showed an attenuation of 0.68 from d.c. up to 0.1 Hz.

5 Determination of Derivatives of Dithiocarbamic Acid by Cathodic Stripping Voltammetry

5.1 Introduction

It has been shown (Chapter 4) that, at a mercury electrode, alkyl dithiocarbamates form insoluble salts which can be redissolved at negative potentials to give a cathodic current. This reaction has been made the basis of a sensitive analytical method using the technique of cathodic stripping voltammetry.

There has been considerable recent interest in stripping voltammetry because it represents, potentially at least, the most sensitive electroanalytical technique available[112, 113, 114]. Most work, however, has been concerned with anodic stripping which invariably is based on the electrode reaction whereby a metal ion is reversibly reduced to form a mercury amalgam. Cathodic stripping analysis is limited by the few reactions in which the products of reversible oxidation are concentrated at an electrode. Thus the technique has been applied principally to the determination of halide ions at mercury[115, 116] and silver[117] electrodes. Some important groups of organic compounds are known which form insoluble mercury species; these include barbiturates, thiols and dithiocarbamates. Only the latter group will be considered here.

Cathodic stripping analysis involves three separate steps. The first stage is a pre-electrolysis for a measured time with the electrode maintained at a relatively positive potential. During this period the solution is stirred (or the electrode rotated) and an anodic current flows corresponding to the formation of the insoluble compound at the electrode. In the second stage, lasting from 5 to 30 s, the electrode potential remains unaltered but the solution is no longer stirred. During this rest period the anodic current decays rapidly to zero. In the final stage the electroactive material present on the electrode is determined by any one of a number of electroanalytical methods. Usually, a linear potential sweep from positive to negative potentials is applied while the cathodic cell current is recorded[115]. Others have applied a potential step, and electronically integrated the current with time[116]. The few methods which have been applied reflects not a lack of choice but the infrequency with which cathodic stripping voltammetry has been used. A much wider range of electrochemical techniques have been utilised in anodic stripping analysis.

It is not generally recognized that many of the factors which complicate anodic stripping voltammetry occur to a lesser extent or not at all in the analogous cathodic technique. The ultimate sensitivity in anodic stripping is limited by the purity of the supporting electrolyte because the pre-electrolysis potential is negative and interferences can also be reduced. This effect is much less apparent in cathodic stripping because the electrolysis potential is relatively positive where fewer substances are electroactive. Difficulties associated with amalgam formation such as 'tailing' of stripping peaks due to slow diffusion of the metal ion from the bulk of the electrode do not occur with cathodic stripping because the deposited material remains on the electrode surface.

In the present investigation cathodic stripping voltammetry has been applied to the determination of alkyl dithiocarbamates and subsequently to other dithiocarbamic acid derivatives. Two different electrode configurations have been compared by means of a d.c. polarograph. An operational amplifier instrument has also been constructed and evaluated for stripping analysis.

5.2 Electrode Systems

The first electrode to be studied was a hanging mercury drop, the behaviour of which was investigated in quiet and stirred solutions. After pre-electrolysis in a quiet solution of NaDDC, application of a slow linear potential sweep to a HMDE gave two stripping peaks corresponding to dissolution of the bulk, and mono-layers (Figure 5.1a). A graph of peak current against electrolysis time showed that the height of peak I, the monolayer, remained constant while peak II, the bulk layer, varied randomly.

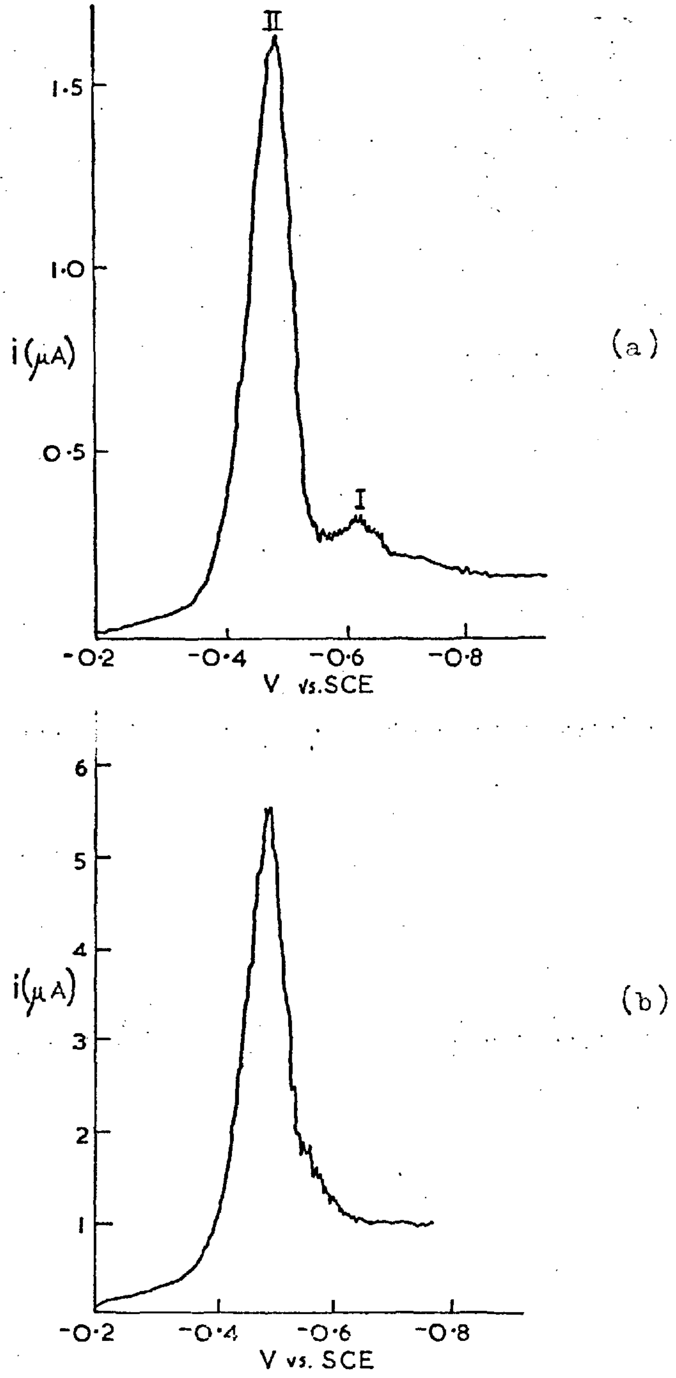


Figure 5.1 Stripping peaks for 2.10^{-5} M NaDDC. 4 minutes electrolysis at a HMDE at 0.0 V vs. SCE in (a) unstirred and (b) stirred solution. Potential scan 25 mV/s.

When the solution was stirred during the electrolysis, a considerable increase in peak current was observed. Under these conditions a separate peak corresponding to monolayer formation was barely detectable. (Figure 5.1b) At constant potential scan rate and mercury drop surface area, the height of the mono-layer peak would be expected to be a constant. Thus, on decreasing the instrument sensitivity to accommodate the larger bulk layer obtained on stirring the solution, the separate mono layer peak was no longer observed. Alternatively, it is possible that under stirred conditions a discrete monolayer was not formed at the electrode surface.

For a given pre-electrolysis period it was observed that greater sensitivity was obtained on increasing the rate of stirring of the solution. However, at fast stirring rates the mercury drop became unstable and was easily detached from the glass capillary from which it was extruded. Other disadvantages were encountered in the use of this electrode. It was very difficult to obtain a reproducible drop size even by use of a micrometer syringe. The drop was sensitive to vibration and to changes in temperature, although the 0.5 ml mercury reservoir was insulated with expanded polystyrene.

In an effort to overcome these difficulties it was decided to investigate the use of a mercury film electrode consisting of a thin, coherent film of mercury supported on a substrate such as platinum[118,119] or nickel[119, 120]. For cathodic stripping it was not necessary that the film of mercury was of uniform or reproducible thickness. It was, however, important that the substrate was completely covered with mercury and that the surface area was constant. Platinum was used as a substrate exclusively; a convenient electrode was formed by sealing a wire (0.5 x 10 mm) into a glass tube. The platinum was coated with mercury using the dipping technique described by Enke[118]. Despite recent criticisms of this method[121] it proved quite satisfactory in practice.

Using the mercury film electrode it was found that maximum sensitivity was obtained by stirring the solution at a rate just less than that which caused the solution to break up into bubbles. Under these conditions it was possible to determine concentrations down to 1.10^{-6} M with a 2 minute electrolysis period. In order to determine lower concentrations, it was necessary to extent the pre-electrolysis period and this resulted in a considerable decrease in precision. This effect was attributed to the difficulty of stirring a solution reproducibly for long periods and has also been noted by Joyce and Westcott[119].

The problem was overcome by rotating the electrode at constant speed (600 r.p.m.) during the pre-electrolysis instead of stirring the solution. Well defined stripping peaks were obtained down to a concentration of 1.10^{-7} M NaDDC (0.015 ppm) with a precision of $\pm 0.2 \times 10^{-7}$ M, following a 2 minute electrolysis period. It was possible to extend the lower concentration limit to 1.10^{-8} M (0.0015 ppm) by use of longer pre-electrolysis periods. A 5 minute electrolysis gave a mean precision of $\pm 2 \times 10^{-8}$ M (Figure 5.2).

The effect of pre-electrolysis time and potential sweep rate on the determination was investigated. Using the small range of sweep rates available it was established that peak current was directly proportional to the potential sweep rate up to 100 mV s^{-1}. This result was in agreement with the equation of Roe and Toni[120] for stripping from a thin film. The effect of pre-electrolysis time was more complex (Figure 5.3). After long periods the solution became depleted in dithiocarbamate and the peak height reached a limiting value. Slight non-linearity at short electrolysis times was probably a result of timing errors which would be more pronounced for short periods. Maximum sensitivity was obtained when the dithiocarbamate was quantitatively deposited on the electrode. However, because this required inconveniently long electrolysis times it was preferable to use a fixed electrolysis time (e.g. 2 minutes) during which a reproducible fraction of the depolariser was deposited.

5.3 Operational Amplifier Instrument

Although the use of a conventional d.c. polarograph has been shown to be feasible for cathodic stripping analysis, it was thought that

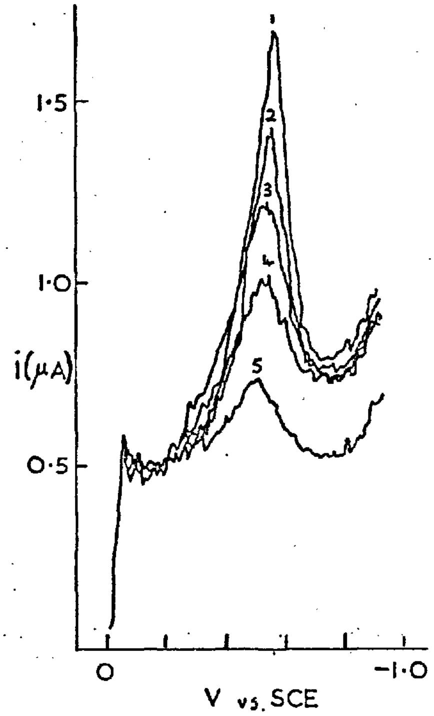


Figure 5.2 Concentration dependence of stripping peaks for NaDDC. 5 minute electrolysis at 0.0 V vs. SCE at a rotated mercury film electrode. Concentrations: (1) 10.10^{-8}; (2) 8.10^{-8}; (3) 6.10^{-8}; (4) 4.10^{-8}; (5) 2.10^{-8} M. Potential scan 100 mV/s.

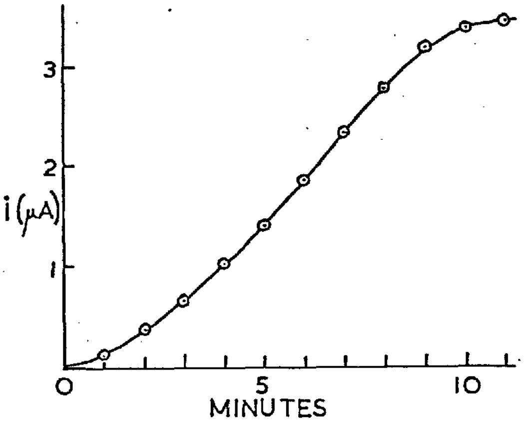


Figure 5.3 Dependence of stripping peak for 1.10^{-7} M NaDDC on electrolysis time. Electrolysis at 0.0 V vs. SCE at a rotated mercury film electrode. Potential scan 100 mV/s.

some improvement would be obtained by the use of a more sophisticated apparatus. An operational amplifier instrument was therefore designed which incorporated the more recent developments in electroanalytical instrumentation. The instrument was designed to be as versatile as possible and provision was made for the application of positive and negative potential sweeps to the electrode. This allowed for the possible future application of the instrument in anodic stripping; in the present investigation only cathodic stripping was considered.

Greatest sensitivity in stripping analysis is obtained by use of a fast potential sweep; the use of a potential step [116] is equivalent to an almost infinitely fast rate of potential scan. In the latter case the possibility of distinguishing between two components in a mixture is precluded and this approach was not therefore used. It is essential in stripping analysis for the read-out system to provide a permanent or semi-permanent record, because the current-potential curve cannot be retraced without repeating the pre-electrolysis. Possibilities for read out systems include a pen recorder, a UV recorder or a storage oscilloscope. The last two instruments are most versatile, permitting the use of fast and also slow potential sweeps, but were not available. The instrument was therefore designed for use with a pen recorder; a maximum potential sweep rate of 100 mV s^{-1} was provided.

The complete instrument circuit diagram is shown (Figure 5.4). Amplifiers 1, 2, and 3 formed a conventional summing potentiostat. The input signals to the potentiostat were a d.c. level (through R_3) and a d.c. ramp (through R_2). The d.c. level was obtained from the amplifier stabilised power supply, potential divided through R_4 and P_1. Switch S_1 provided for changing the polarity of the d.c. level, which was displayed on voltmeter V_1. The d.c. ramp was obtained from amplifier 4 which was connected as an integrator, having input resistors R_5 and P_2 and feedback capacitor C_1. The constant voltage input to the integrator was obtained by potential dividing the power supply through R_6 and R_7. The amplifier input current offset was adjusted to zero by potentiometer P_3 connected to the input through R_8. Sweep polarity was selected by switch S_2 while switch S_3 provided a Run-Hold-Reset sequence for the integrator, the output of which was displayed on V_2. The setting up procedure for the integrator was as follows. With S_3 in the Hold position P_3 was adjusted until the integrator output (measured on V_2 or, preferably, with a more sensitive voltmeter) remained at a constant value. Switching S_3 to Run then produced a ramp function and P_2 was adjusted until the sweep rate was exactly 100 mV s^{-1}. In the Reset position, capacitor C_1 was shorted through R_9 and the integrator output was reset to zero.

A bounding circuit, consisting of diodes D_1 and D_2, resistors R_{10} to R_{13} and potentiometers P_5 and P_6, was used to limit the upper and lower integrator output levels to not more than ± 3 volts. Adjustment of P_5 or P_6 allowed the lower or upper limit to be varied.

The cell current was converted to an output voltage by amplifier 3, which, through its feedback resistor R_{14}, maintained the working electrode at earth potential. Capacitor C_2 served to prevent oscillation of amplifier 3. Provision was made to integrate the output signal via amplifier 5 having input resistor R_{15} and feedback capacitor C_3. The current offset zero was provided by potentiometer P_4 and resistor R_{16}, and the Integrate-Hold-Reset sequence was controlled by switch S_3.

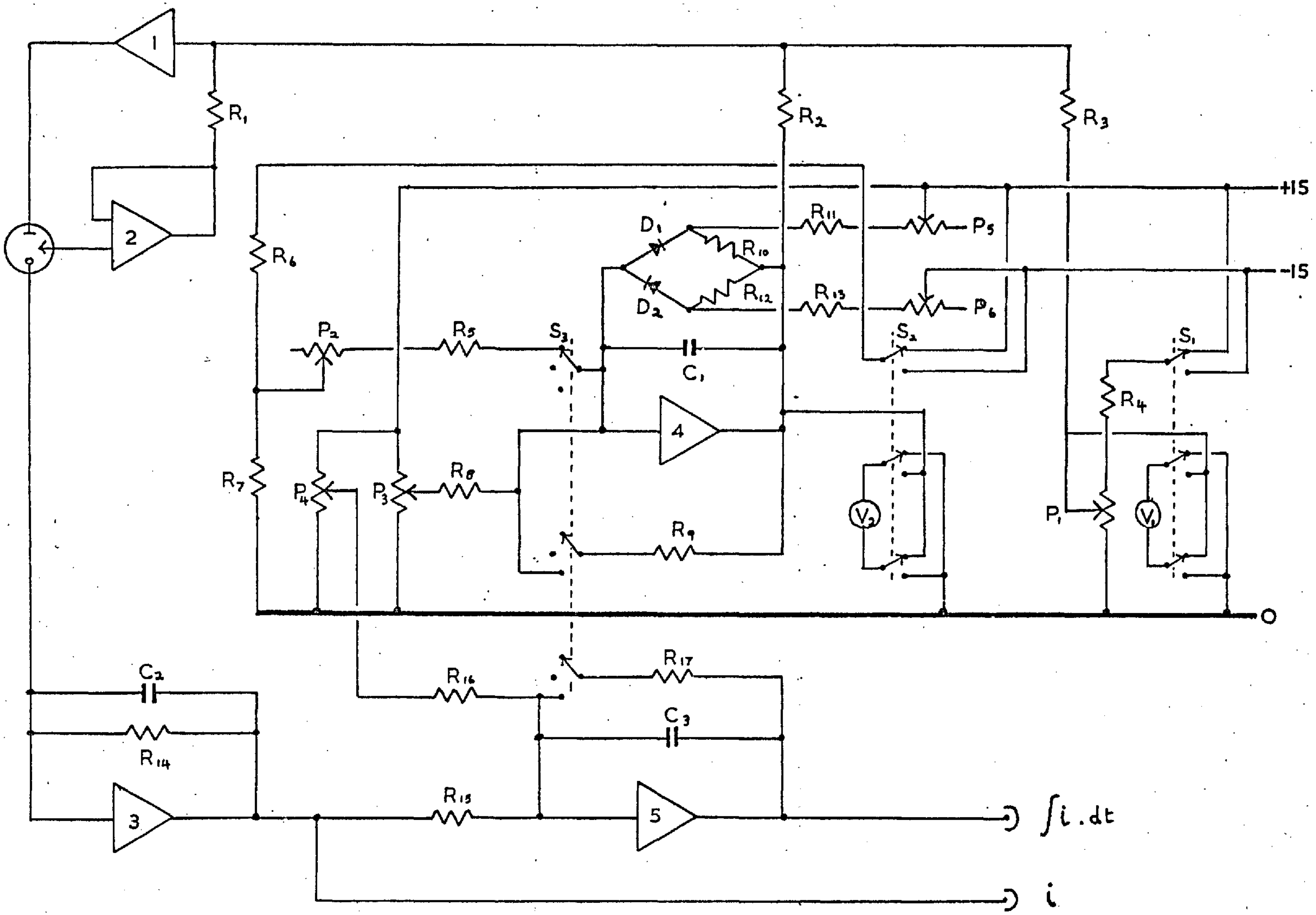


Figure 5.4 Operational amplifier instrument for stripping analysis.

Table 1

List of Components

Amplifiers		
1 to 5	PF85AU	(Philbrick-Nexus Research, Inc., Chichester)
Power Supply	ED50	(Coutant Electronics Ltd., Reading)
Potentiometers		
P_1	1K Helipot	(Beckmann Instruments Ltd., Fife)
P_2	500K	P_2 to P_6 single turn linear carbon track.
P_3, P_4	50K	
P_5, P_6	100K	
Capacitors		
C_1	2 μF ± 5%	Polystyrene
C_2	47 pF	Polystyrene
C_3	1 μF ± 5%	Polystyrene
Diodes		
D_1, D_2	FD300	(S.G.S. Fairchild, Ltd., Bucks)

Resistors

All resistors were ± 2% Metal Oxide 1 W, except R_8 and R_{16} which were ± 5% Hystab 1/2 W.

R_1	100K	R_{10}	1K
R_2	100K	R_{11}	5K
R_3	100K	R_{12}	1K
R_4	6.5K	R_{13}	5K
R_5	1K	R_{14}	10K
R_6	200K	R_{15}	100K
R_7	1K	R_{16}	20M
R_8	20M	R_{17}	100
R_9	100		

Switches

S_1	3- Pole 2- Way rotary
S_2	3- Pole 2- Way rotary
S_3	3- Pole 2- Way rotary

Meters

V_1, V_2	0 to 3 V.

To evaluate the performance of this instrument it was applied to the determination of NaDDC by cathodic stripping analysis. Subsequently the determination of thiram and ethylene bis dithiocarbamates was investigated. Stripping peaks obtained for NaDDC were considerably more noise free than those obtained with a polarograph based on a motor driven potentiometer (Figure 5.5), but the precision of the method was not better than that obtained previously. Integration of the output signal with respect to time gave a wave shaped response (Figure 5.6). In this case the total output signal obtained from the instrument was increased and it was therefore expected that the lower sensitivity limit would be decreased. In practice it was found that while the detection limit was decreased, quantitative measurements were not obtainable below 10^{-8} M (0.0015 ppm). This level, however, was thought to be quite adequate for pesticide residue analysis. Difficulties experienced at low concentrations were largely chemical in origin and were due to such effects as adsorption on the cell walls and hydrolysis of the dithiocarbamate. The sensitivity limit set by the instrument was determined by the drift of amplifiers 3 and 5. The voltage offset drift of amplifier 3 was less than 0.1% of the signal at the 10^{-8} M level. The output drift of the integrator amplifier 5 was larger, but it was possible to keep this to 1% of the signal during the 10 s required for a 1 V potential sweep. The use of a chopper stabilised amplifier would

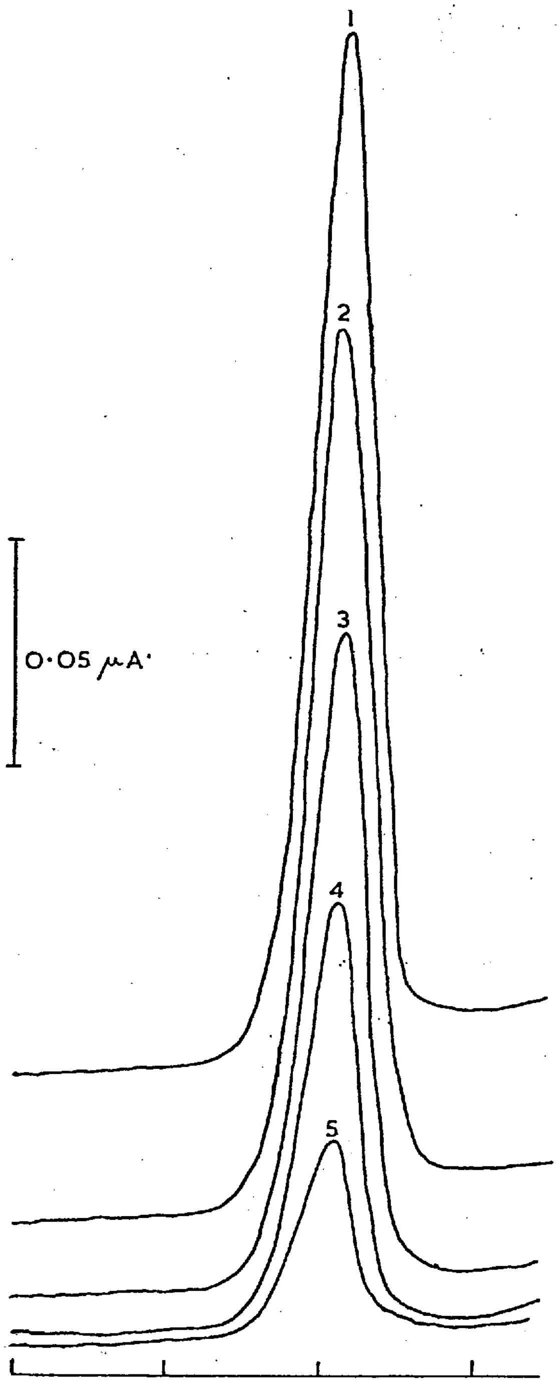


Figure 5.5 Concentration dependence of stripping peaks for NaDDC. 2 minutes electrolysis at -0.1 V vs. SCE at a rotated mercury film electrode. Concentrations: (1) 10.10^{-8}; (2) 8.10^{-8}; (3) 6.10^{-8}; (4) 4.10^{-8}; (5) 2.10^{-8} M. Potential scan 100 mV/s; horizontal sensitivity 2 s/division.

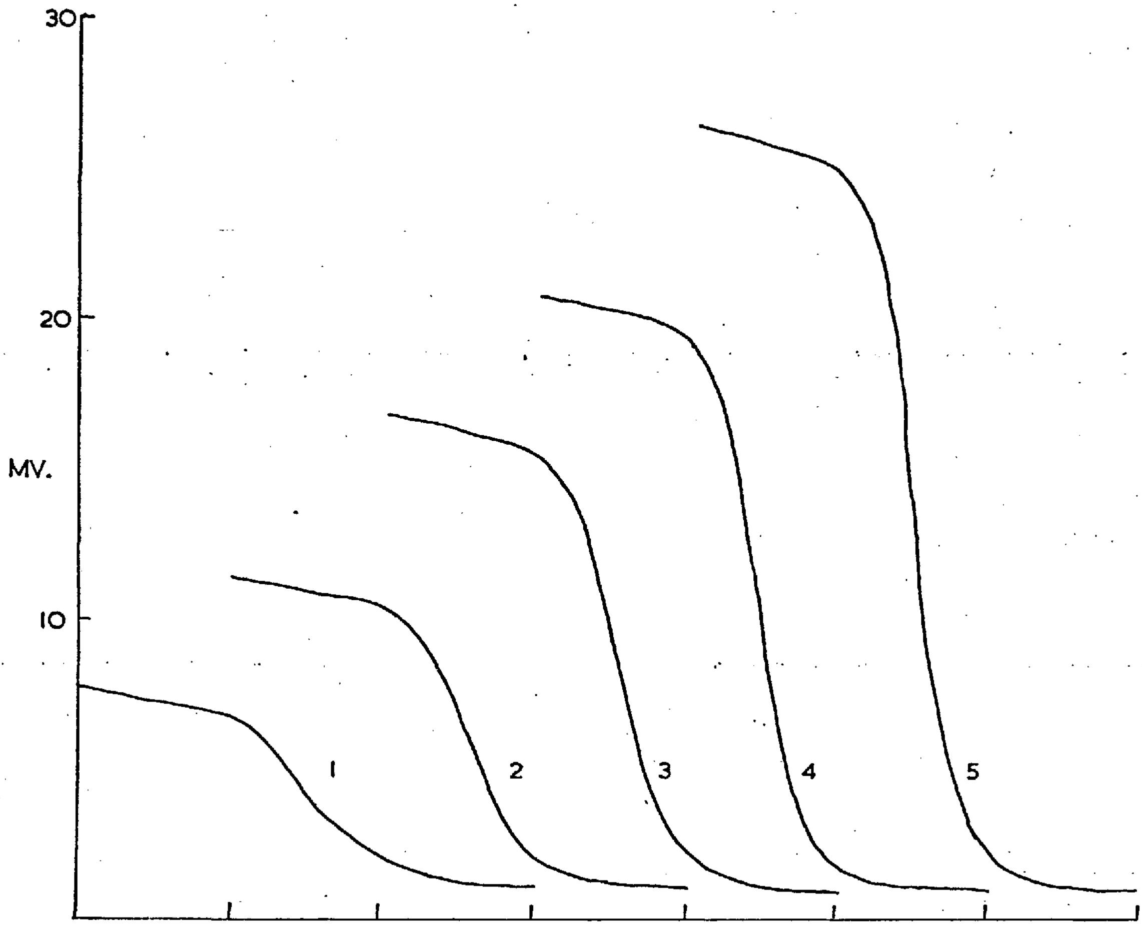


Figure 5.6 Concentration dependence of integrated stripping peaks for NaDDC at pH 11. 2 minutes electrolysis at -0.1 V vs. SCE at a rotated mercury film electrode. Concentrations: (1) 2.10^{-8}; (2) 4.10^{-8}; (3) 6.10^{-8}; (4) 8.10^{-8}; (5) 10.10^{-8} M. Horizontal sensitivity 2 s/division.

undoubtedly be a significant improvement for the study of a well defined chemical system such as the stripping of chloride ion.

The direct analysis of thiram by cathodic stripping was found to be possible after reduction of the S-S bond with ascorbic acid. Ascorbic acid itself was oxidised at about 0.0 V vs. SCE but did not interfere if the pre-electrolysis was at a more negative potential. It was found that electrolysis at -0.1 V vs. SCE also prevented interference from the chloride ion which was invariably present. The behaviour of ethylene bis dithiocarbamates was more complex. Three stripping peaks were observed, the first of which was proportional to the analytical concentration of the anion. The second two peaks were attributed to ethylene thiuram monosulphide. The determination was found to limited to a concentration range of 10^{-6} to 10^{-8} M using a 2 minute electrolysis period; at higher concentrations the peak reached a limiting height independent of concentration.

5.4 Experimental

The reagents used have been described previously (Chapter 4).

Preliminary experiments were made with the Radelkis polarograph OH-102.

For the controlled potential stripping analysis using the operational amplifier instrument a platinum wire counter electrode and high impedance calomel reference electrode were used. The working electrode, mounted in a gas tight stirring glad, was rotated at 600 r.p.m. by means of a squirrel-cage motor. The cell was thermostatted at 25° C. A Servoscribe recorder (Goerz Electro, Wien) was used.

Procedure

To a 10 ml graduated flask 1 ml buffer (1 M ammonia - 1 M ammonium nitrate) and an aliquot of stock dithiocarbamate solution were added. For thiram solutions 1 ml of 1 M ascorbic acid was also added. The solution was transferred to the cell and degassed with oxygen free nitrogen for three minutes. The squirrel-cage motor was started.

On the operational amplifier instrument, the d.c. level was set to 0.1 V. The integrator was switched to Run and its lower bound adjusted (P_5) to -1.0 V. This ensured that any insoluble salt formed at the electrode during the setting-up procedure was reduced. The integrator was switched to Reset and a stop clock started simultaneously. After 2 minutes the motor was switched off and a 10 s delay period allowed for the solution to become quiet. The integrator was again switched to Run and the output recorded either directly or as its integral.

6 A Three Electrode Controlled Alternating Current Oscilloscopic Polarograph

6.1 Introduction

Although the technique of controlled alternating current oscilloscopic polarography was introduced[55,56] as an auxiliary method for studying polarographic electrode processes, it has not found wide acceptance for this purpose. Most reported applications (as in Chapter 3) have used the method to establish the chemical reversibility of a system. Kalvoda[58] has given a comprehensive account of analytical applications of the method, but it is virtually unused for this purpose outside Czechoslovakia.

The technique involves the application of a controlled a.c. current to a polarographic cell, while the working electrode potential is measured as a function of time and displayed oscilloscopically. Most information is obtained if the electrode potential-time curve is differentiated and displayed as a function of time, or preferably, as a function of the electrode potential. This latter $dE/dt = f(E)$ curve has the well known elliptical shape with incisions corresponding to depolarisers. Commercially available apparatus, the Polaroscope (Laboratorní přístroje, Czechoslovakia) has been used in most applications of this technique. This instrument employs an a.c. sine wave current derived from the a.c. mains at a frequency of

50 Hz. Also, the working electrode potential is measured with respect to a large unpolarised electrode such as a mercury pool, rather than an auxiliary reference electrode, as in chronopotentiometry.

It was thought that the technique would be of greater application, for example in the study of kinetically controlled electrode reactions, if the a.c. current frequency were variable. A further improvement would be obtained if the electrode potential were measured as a function of a true reference electrode potential under potentiostatic conditions. Some circuits have been described as alternatives to the 'Polaroscope'. Thus Roughton[122] has suggested a transistorised circuit for the application of a controlled a.c. current to a two-electrode cell and for obtaining the function dE/dt. Some interest has been shown in the use of currents with waveforms other than sine waves, chiefly square[123, 124] and triangular waves[123]. Sturrock[125] has described an operaticnal amplifier instrument for the application of a square wave current to a three electrode cell. The direction of the constant current was reversed at preset values of the working electrode potential, and the results were displayed as $dE/dt = f(E)$. An operational amplifier circuit has been designed for the application of a controlled a.c. current to a cell, and for obtaining the $dE/dt = f(E)$ curve under potentiostatic conditions. The instrument has been evaluated for sine, triangular and square wave currents at different frequencies.

6.2 The Instrument

The essential features were (i) a circuit to control the current through the cell and (ii) a high input impedance circuit to measure the potential difference between the working electrode and a reference electrode. The complete circuit diagram is shown (Figure 6.1). The galvanostat configuration (amplifiers 1 and 2) has been described previously[70].

No attempt was made to obtain the current waveforms from operational amplifier circuits, although techniques are readily available for the generation of sine, triangular and square waves of variable frequency. Instead a commercially available signal generator (Model 3300 A Function Generator, Hewlett-Packard, Bucks.) was used. The signal generator output was potential divided through P_1 and isolated from the gelvanostat by the voltage follower amplifier 1. The follower output was connected through R_1 to the summing point of the current control amplifier 2. The d.c. current through the cell was derived from the amplifier power supply, potential divided through R_9 and P_2, and connected to the summing point of amplifier 2 through R_2. The current output of amplifiers 1 and 2 was limited to 2 mA, and when currents greater than this were required it was necessary to use the current booster amplifiers 1 B and 2 B. Amplifier 2 maintained the current between the working and counter

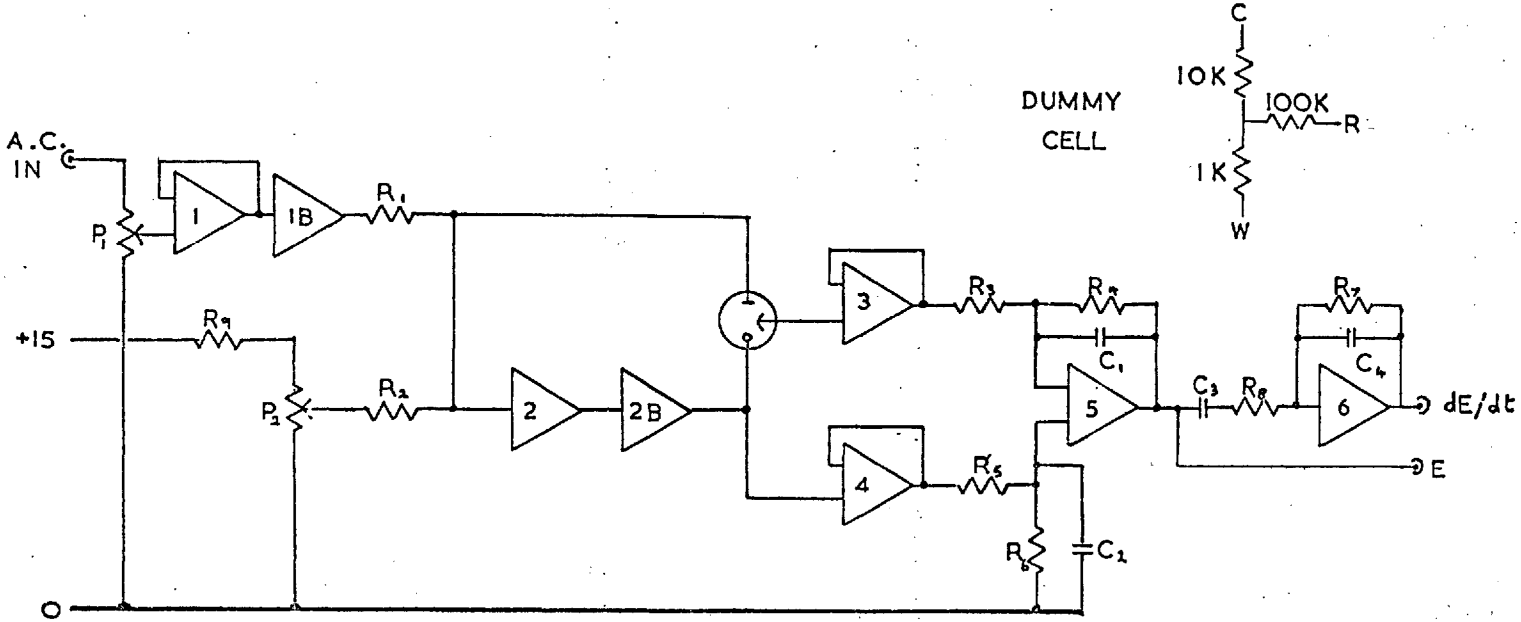


Figure 6.1 Controlled a.c. current polarograph.

electrodes equal to the sum of the currents through R_1 and R_2; the counter electrode was maintained at earth potential.

The reference and working electrodes were connected to the high impedance (500 MΩ) inputs of the unity gain follower amplifiers 3 and 4. The difference between the potentials of the low impedance outputs of amplifiers 3 and 4 was measured by the unity gain difference amplifier 5. Capacitors C_1 and C_2 were the smallest possible necessary to prevent oscillation of amplifier 5, and were selected to provide a matched capacitative load at the two amplifier inputs. The output of amplifier 5 was the potential of the working electrode with respect to the reference electrode, i.e. E. Differentiation of E was achieved by amplifier 6. Components C_3 and R_7 were chosen to give a differentiator time constant of 0.001 s. Capacitor C_4 was selected to eliminate amplifier oscillation while R_8 served to limit the amplifier gain to 100 for very high frequency random noise pulse transients. The necessary presence of C_4 and R_8 detracted from the ideal response of the differentiator at high frequencies. The frequency for 1% deviation from ideality was calculated to be 1.6 K Hz and for 50% deviation 16 K Hz. The $dE/dt = f(E)$ curve was displayed by connecting the output of amplifier 5 to the oscilloscope horizontal amplifier (Model 175 A, Hewlett-Packard, Bucks with Auxiliary Plug-in 1780 A and High Gain Vertical Amplifier 1752 A) and the output of amplifier 6 to the vertical amplifier. It was possible to observe the $E = f(t)$ and $dE/dt = f(E)$ curve by connecting the outputs of amplifiers 5 and 6 respectively to the oscilloscope vertical amplifier and using the built in oscilloscope time base.

Setting-up procedure was virtually unnecessary with this circuit. To avoid overloading the amplifiers when the current booster amplifiers were not used the potential across P_1 was adjusted to 2 V. This ensured that the current through R_1 was never greater than 2 mA, and the limiting current outputs of amplifiers 1 and 2 were not exceeded. When the current booster amplifiers were used the potential across P_1 was adjusted to 10 V, the limiting output voltage of the amplifiers. With $R_1 = 1\ K\Omega$ the maximum current obtainable was 10 mA.

Table 1

List of Components

Amplifiers 1 to 6	PF85AU		(Philbrick-Nexus Research Inc., Chichester)
Amplifiers 1B and 2B	P66A		(Philbrick-Nexus Research Inc., Chichester)
Amplifier Power Supply	ED50		(Coutant Electronics Ltd., Reading)
P_1	100K	Helipot	(Beckmann Instruments Ltd., Fife)
P_2	1K	Helipot	(Beckmann Instruments Ltd., Fife)
R_1	1K		
R_2	100K		
R_3-R_6	1K	All resistors Metal Oxide ± 2%, 1 W	
R_7	10K		
R_8	100K		
R_9	6.5K		
C_1	100pF	Polystyrene	
C_2	50pF	Polystyrene	
C_3	0.1μF	Paper	
C_4	0.001μF	Paper	

6.3 Evaluation of the Instrument

The overall performance of the instrument was evaluated using a dummy cell consisting of fixed resistors. The frequency response of the circuit was established using a pure sine wave signal, while a triangular wave was used to allow any distortion to be readily observed. The output of amplifier 5 was monitored on the oscilloscope as a function of time. The circuit showed an overall unity gain up to a frequency of 100 K Hz, which was the highest attainable with the signal generator. The output of amplifier 6 was next monitored on the oscilloscope as a function of time. The gain of this circuit increased with frequency up to 5 K Hz, and the gain decreased above 10 K Hz. The Bode diagram (log frequency-log gain plot) was characteristic of a differentiator. The differentiator output was observed for a triangular wave input signal; ideally differentiation of a triangular wave gives a square wave. At a frequency of 1 K Hz a reasonably undistorted square wave was obtained with a rise time of 0.1 ms. At a low frequency of 10 Hz the noise gain of the differentiator became appreciable. Differentiator output signals at frequencies of 50 Hz and 500 Hz are shown (Figure 6.2 and 6.3).

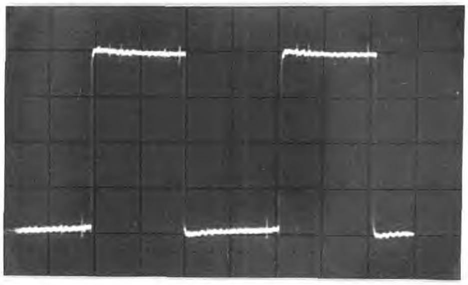


Figure 6.2 Differentiator output with dummy cell. Input signal 50 Hz triangular wave. Vertical sensitivity 0.05 V/division. Time base 5 ms/division.

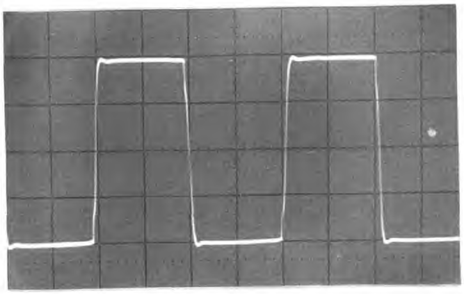


Figure 6.3 Differentiator output with dummy cell. Input signal 500 Hz triangular wave. Vertical sensitivity 0.5 V/division. Time base 0.5 ms/division.

To evaluate the performance of the instrument with an electrochemical cell the reversible reduction of thallium(I) in hydrochloric acid was studied. The working electrode was a hanging mercury drop, the counter electrode a platinum wire and the reference electrode a high impedance saturated calomel electrode. Due to the inverting property of the operational amplifiers, negative electrode potentials were displayed on the right hand side of the oscilloscope and the cathodic branch of the curve was observed below the graticule zero line. With a low frequency sine wave input signal a well developed oscillogram (Figure 6.4a) was obtained. The use of a triangular wave signal resulted in an almost identical oscillogram (Figure 6.4b) while a square wave signal gave some distortion (Figure 6.4c). This distortion was due to the poor response of the circuit to the very high frequencies which are important harmonics of square wave signals.

On increasing the frequency of the input signal it was necessary to increase the a.c. current through the cell to allow the working electrode potential to reach its positive and negative limits. This effect was attributed to the decrease in resistance of the double layer capacity at high frequencies. At high current densities a displacement between the anodic and cathodic indentation potentials was observed (Figure 6.5).

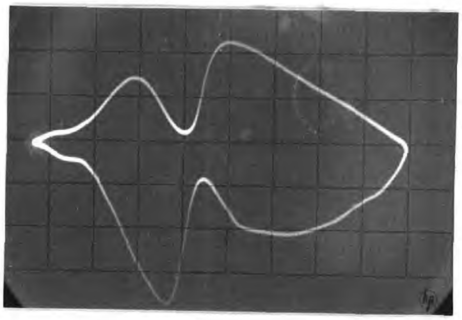


Figure 6.4a. Sine wave

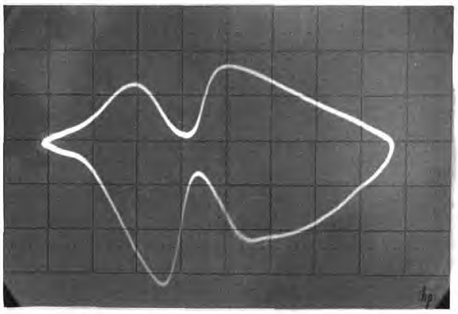


Figure 6.4b. Triangular wave

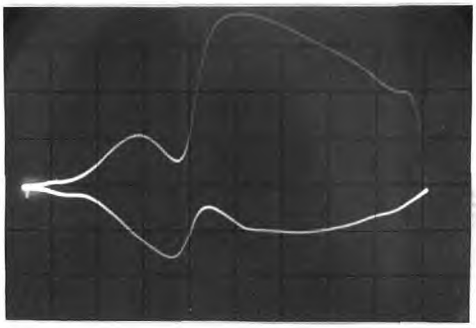


Figure 6.4c. Square wave

Figure 6.4 $dE/dt = f(E)$ curve for 5.10^{-4} M Tl^+ in 0.5 M hydrochloric acid. Vertical and horizontal sensitivity uncalibrated. Input signal 50 Hz (a) sine wave (b) triangular wave (c) square wave.

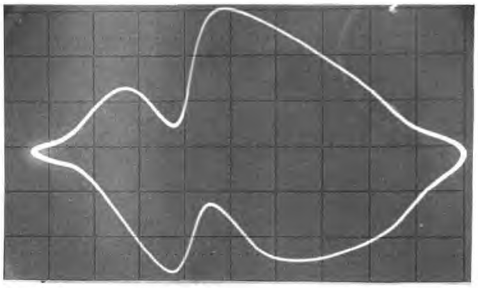


Figure 6.5 $dE/dt = f(E)$ curve for 5.10^{-4} M Tl^+ in 0.5 M hydrochloric acid. Vertical and horizontal sensitivity uncalibrated. Input signal 200 Hz sine wave.

Sturrock[125] also noted this effect with a square wave current. The displacement was due to uncompensated iR drop in the cell. It has been pointed out[71, 72] that iR compensation with a three-electrode system can never be complete. In the majority of cells the uncompensated iR drop can be made negligibly small, e.g. by placing the Luggin reference probe near the working electrode. In the present case, where the currents involved were of the order of milliamps, the effect was significant. The displacement between cathodic and anodic branches of the curve became particularly apparent with supporting electrolytes of low conductivity where the uncompensated iR drop was greatest.

It was concluded that the instrument was of little application for the study of systems with low electrolyte conductivites at high frequencies. No attempt was therefore made to investigate the behaviour of an electrode reaction involving chemical kinetics. However, at low frequencies and for normal low resistance solutions the performance of the instrument was superior to the Polaroscope.

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