POLAROGRAPHY IN ANHYDROUS ORGANIC SOLVENTS

By

HAROLD LYONS

Master of Science

Oklahoma Agricultural and Mechanical College

Stillwater, Oklahoma

1949

Submitted to the Faculty of the Graduate School of

the Oklahoma Agricultural and Mechanical College

in Partial Fulfillment of the Requirements

for the Degree of

DOCTOR OF PHILOSOPHY

1952

POLAROGRAPHY IN ANHYDROUS ORGANIC SOLVENTS

HAROLD LYONS

DOCTOR OF PHILOSOPHY

1952

THESIS AND ABSTRACT APPROVED:

Paul Arthur
Thesis Adviser

O.C. Dermer
Faculty Representative

D.C. McIntosh
Dean of the Graduate School

ACKNOWLEDGEMENT

The author wishes to express his thanks to Dr. Paul Arthur under whose direction this work was done, and whose advice and encouragement made it possible. He also wishes to express his thanks to the Chemistry Department for assistance in the form of a graduate fellowship while this work was being done.

TABLE OF CONTENTS

Historical

In 1903 Kucera[15] constructed a dropping mercury electrode for the purpose of studying the electrocapillary curve of mercury in solutions of various electrolytes. During the course of his investigations, Professor Kucera noted some peculiar inflections in the electrocapillary curve when reducible substances were present, and it was at his suggestion that Jaroslav Heyrovsky commenced the investigation of these phenomena which eventually led to the development of the polarographic method of analysis.[7,9]

Although this method of analysis was applied to organic as well as inorganic compounds almost from the beginning,[29] the major developments came in the inorganic field, since the reduction of many simple metal ions is reversible and these gave waves capable of interpretation in the light of electrochemical laws known at that time.

There were many suggestions among the early workers for fixing some reference point on the wave so that identifications could be made. One of the earliest suggestions[7] was that the potential at which an increase in the applied voltage produced an increase in the current of 10^{-8} amperes be taken and called the "deposition potential" of the ion. In 1932 Semerano[28] suggested that the applied potential at which the wave had a slope of 35° 16' was more characteristic. Shikata[30] used that value of the applied voltage at which an increase of 10 millivolts produced a rise in current of 1.9×10^{-8} amperes, calling this value the "reduction potential".

All of the above methods were strictly empirical, and were unreliable, since the observed potential changed with the concentration, with galvanometer sensitivity and with too many other factors. Consequently, polarography was placed on a sound scientific basis only when Heyrovsky and Ilkovic[10] showed the theoretical significance of the polarographic wave, and suggested the use of the half wave potential for each substance. This value is, for many substances, independent of concentration, and is in general independent of drop time and galvanometer sensitivity.

The development of the theory of the half wave potential and diffusion current stimulated a large volume of work in both organic and inorganic polarographic analysis. Several rather complete bibliographies of polarographic literature have been published, the most recent being that of the Leeds and Northrup Co.[17] which covers the literature up to 1950.

Early workers in the field[1,25] reported that dissolved oxygen interferes with the wave of the substance under study. Oxygen is easily reduced at the dropping mercury electrode to give a polarogram of two waves. The first wave is believed to be due to the reduction of molecular oxygen to hydrogen peroxide.[8]

$$O_2 + 2H^+ + 2e \longrightarrow H_2O_2 \quad \text{(acid solution)}$$

$$O_2 + 2H_2O + 2e \longrightarrow H_2O_2 + 2OH^- \quad \text{(neutral or alkaline solution)}$$

The second wave is believed to be due to the reduction of hydrogen peroxide, either to water, or to the hydroxyl ion.

$$H_2O_2 + 2H^+ + 2e \longrightarrow 2H_2O \quad \text{(acid solution)}$$

$$H_2O_2 + 2e \longrightarrow 2OH^- \quad \text{(alkaline solution)}$$

All of these reactions are irreversible at the dropping mercury electrode, and the overvoltage of each is high.

Strnad[33] reported that small concentrations of heavy metal ions exert a pronounced effect on the waves of oxygen. Vitek[35] noted that the diffusion current of oxygen is several times larger in anhydrous methanol than in water, and attributed this to the greater solubility of oxygen in methanol.

Although a large volume of work has been published using mixtures of organic solvents and water (e.g., that of Page et al[23], Smith et al[31], and Wawzonek et al[36]) there has been comparatively little published work on polarography using anhydrous organic solvents.

In 1942, Bachman and Astle published two papers dealing with polarography of inorganic compounds in glacial acetic acid.[3,4] These authors obtained normal waves for Pb^{++}, Cd^{++}, Zn^{++}, Co^{++}, Cr^{++}, Sb^{++} and Ni^{++}, using a chloranil-glacial acetic acid electrode as a reference. They were unable to obtain good curves for Cu^{++}, Fe^{+++}, Hg^{++} or Pb^{++++}. Bachman and Astle also studied the electrocapillary curve of mercury in ammonium acetate solutions in glacial acetic acid, and found that a double maximum was present in the curve. Upon the addition of water this double maximum coalesced into the usual single maximum.

In 1949 Lewis, Quackenbush, and De Vries[18] studied organic peroxides polarographically, using a solution of equal volumes of absolute methanol and thiophene-free benzene. These authors claimed that a resistance of 4,000 ohms through the cell was the maximum which would permit good results to be obtained with automatic recording. They used a mercury pool anode as reference in neutral solution, and an external saturated calomel electrode when acid or alkaline solutions were to be used.

In 1950, Porks and Hansen[24] suggested the use of glycol ethers as nonaqueous solvents in polarographic analysis and described the use of Cellosolve (ethylene glycol monomethyl ether) as a solvent for the direct polarographic determination of tetraethyl lead in gasoline using either tetra-n-butylammonium iodide or anhydrous HCl as the carrier electrolyte.

These authors had earlier tried purified dioxane as a solvent and reported that it gives satisfactory results when fresh, but deteriorates rapidly in storage due to peroxide formation, etc. In their work with Cellosolve, Porks and Hansen used the mercury pool anode as a reference electrode.

Gentry[6] briefly described some experiments using ethylene glycol as a solvent in polarography.

At Oklahoma A. and M. College, Black[5] and Allison[2] investigated polarographic behavior in anhydrous methanol solutions. Black reported that no limiting current for nickel was discernible in methanol-water solutions where the methanol concentration exceeded 91% by volume. He also failed to obtain a wave from a solution of benzaldehyde in n-butyl alcohol. Allison noted the extreme importance of thorough removal of oxygen prior to the making of the polarogram. By bubbling tank nitrogen through a solution of sodium pyrogallate, he was able to eliminate the masking effect of the oxygen, and obtained good waves of lead in anhydrous methanol.

Introduction

Polarographic analysis is based on a study of the current-voltage curves obtained when solutions of electro-oxidizable or electro-reducible substances are electrolyzed in a cell in which one electrode is very small and easily polarizable while the other electrode is large and practically non-polarizable. These current-voltage curves may be plotted manually, or they may be recorded automatically on an instrument called the polarograph, which was invented by Heyrovsky and Shikata.[11] The curves themselves are called polarograms.

In order for the discussions which follow to be more easily comprehensible, a typical polarogram, with its characteristic parts labelled, is shown in Figure 1.

The "half wave" potential is, under the proper conditions, characteristic of the substance producing the wave. This potential is determined graphically, by measuring the potential at which the midpoint of the wave between the projected residual current line and the flat upper portion of the curve, (the limiting current line) occurs. The half wave potential will shift slightly with temperature, and with changes in the nature and concentration of the indifferent carrier electrolyte. Literature values usually specify the half wave potential versus the saturated calomel electrode for a specific carrier salt solution.

The diffusion current is a function of the concentration of the ion whose deposition potential has been reached. If conditions are held constant, and suitable standards are available, the wave height gives quantitative information. Accuracy is limited by the reproducibility of the wave, and the accuracy with which measurement of the wave height can be made.

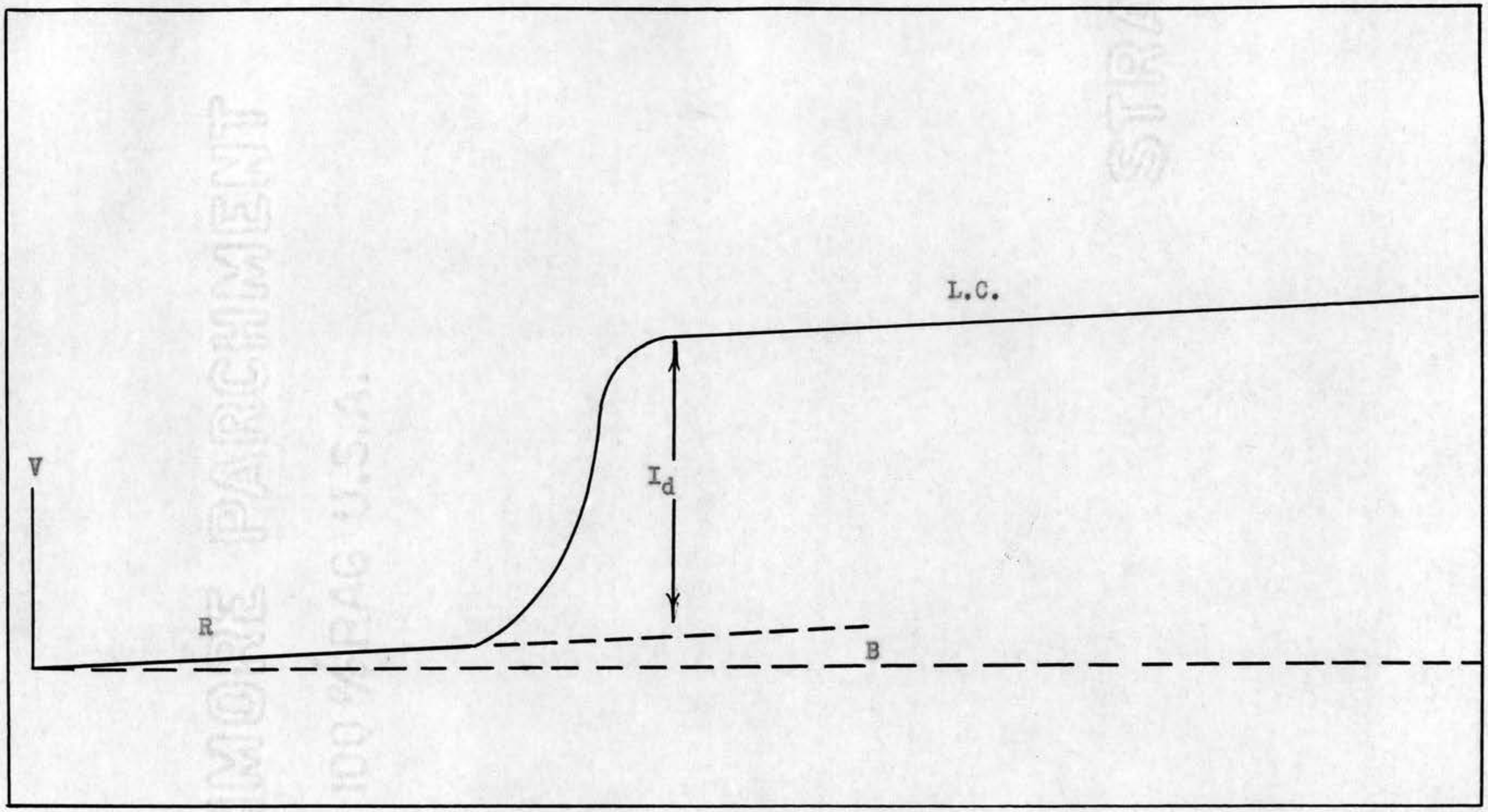

Fig. 1 A Typical Polarogram

L.C.- Limiting current line

I_d - Diffusion current

R - Residual current line

B - Zero current line (base)

V - Zero voltage line (base)

Taylor[34] has recently discussed the merits of various methods used for obtaining quantitative results.

The apparatus used in making polarograms consists of a battery which operates through a potentiometric circuit to supply a variable, known voltage, a current measuring device such as a galvanometer or microammeter, and the polarographic electrolysis cell. The cell itself is made up of a dropping mercury electrode or other microelectrode, and a non-polarizable reference electrode.

The dropping mercury electrode consists of a mercury reservoir connected to a fine capillary tube of about 0.05 mm. internal diameter from which drops of mercury fall at regular intervals, usually 3 to 6 seconds. Capillary tubing of this size may be obtained as "marine barometer tubing" from the Corning Glass Works, Corning, New York. A pool of mercury at the bottom of the electrolysis vessel is frequently used as a reference anode and, providing the carrier electrolyte contains an anion which forms a reversible system with the mercurous ion, this will function satisfactorily as the non-polarizable electrode. This is true because the reaction at the anode will involve the oxidation of mercury to mercurous ion, which will then react with the anion to form an insoluble salt, and thus provide a reversible system.

The galvanometer is usually one with approximately a 15 second period, and is further damped to a 20 to 40 second period. The galvanometer is extremely sensitive, the one in the Sargent Model XII instrument having a sensitivity of 0.003 microamperes per millimeter scale deflection.

The range of the galvanometer is greatly extended by the use of an Ayrton shunt which provides means for measuring currents in various steps up to 1000 times the normal range of the galvanometer.

A potentiometer and battery are used to apply various known voltages across the electrodes.

General Diffusion Current Theory

The phenomenon of the limiting current obtained with the dropping mercury electrode, and under certain conditions with solid microelectrodes, is caused by the extreme state of concentration polarization which results from the depletion of the electro-reducible or electro-oxidizable substance at the electrode surface by the electrode reaction. Under the conditions of a limiting current, the reducible or oxidizable substance is reduced or oxidized as rapidly as it reaches the electrode surface and its concentration at the electrode surface remains negligible as compared to its concentration in the body of the solution. Under these conditions, the limiting current is substantially independent of the applied E.M.F. within certain limits, and is governed solely by the rate at which the reducible or oxidizable substance reaches the electrode surface from the body of the solution.

The reducible or oxidizable ions may arrive at the electrode surface as a result of two forces, an electrical force proportional to the electrical potential difference between the electrode and the solution, and a diffusional force, proportional to the concentration gradient between the electrode surface and the bulk of the solution. Therefore, for reducible or oxidizable ions, the limiting current may be regarded as the sum of the diffusion current and the electrical migration current.

By the addition of a large excess of an indifferent salt (one whose ions do not take part in the electrode reaction, and whose concentration is 50 to 100 times that of the ion to be analyzed) the forces of attraction or repulsion by the electrode can be made so small as to be negligible, and in this case, the ions will arrive at the electrode only as a result of a diffusive force, and the limiting current will be a function of the rate of diffusion to the electrode. This "blanketing out" of the electrical forces on the reacting ions is made possible by the fact that all of the ions in solution take part in current transport, and the fraction of the total current carried by any species of ion depends primarily on its concentration, and to a lesser degree on its charge and intrinsic mobility.

In the case of reducible or oxidizable uncharged substances, diffusion plays the major role in determining the limiting current, even where the ionic concentration of the solution is quite small. In the case of dipolar uncharged molecules, however, there may be an appreciable amount of electrical migration when the ionic concentration of the solution is low.

The theoretical equation for the current "i_t", at any time, "t", during the life of a mercury drop, was originally derived by Ilkovic and is

$$i_t = 0.732\ n\ F\ D^{\frac{1}{2}}\ C\ m^{2/3}\ t^{1/6}$$

where "i_t" is expressed in amperes, 0.732 is a combination of numerical constants arising from the geometry of the dropping mercury electrode, "n" is the number of electrons involved in the electrode reaction, "F" is Faraday's constant and is expressed in coulombs, "D" is the diffusion coefficient of the substance involved in the electrode reaction and is in $cm^2\ sec^{-1}$, "C", the concentration is in moles per cm^3, "m" is the weight of mercury flowing from the capillary per second and is in grams per second, and "t" is in seconds.

Since the magnitude of the currents involved is quite small, it is more convenient to express "i_t" in microamperes, "C" in millimoles per liter and "m" in mg. sec.$^{-1}$; evaluating "F" (96,500 coulombs), the equation thus becomes

$$i_t = 706\ n\ D^{1/2}\ C\ m^{2/3}\ t^{1/6}$$

The average current is defined as the hypothetical constant current, which, flowing for a length of time equal to the drop time, would produce the same quantity of electricity as the quantity associated with each drop. Mathematically, the average current i_d is defined by

$$i_d = \frac{1}{t} \int_{o}^{t_{max}} i_t\ dt$$

By substituting the second form of the Ilkovic equation, we obtain

$$i_d = \frac{706\ n\ D^{1/2}\ C\ m^{2/3}}{t_{max}} \int_{o}^{t_{max}} t^{1/6}\ dt$$

and after integrating,

$$i_d = 605n\ D^{1/2}\ C\ m^{2/3}\ t_{max}^{1/6}$$

where "t_{max}" equals the drop time in seconds.

The fact that the preceding form of the Ilkovic equation is not wholly adequate has been recognized for some time. In particular, it does not account for the observed variation of the diffusion current "constant" $i_d/C\ m^{2/3}\ t^{1/6}$ with the characteristics (rate of mercury flow and drop time) of the dropping electrode.[20] Recently Strehlow and Von Stackelberg,[32] and Lingane and Loveridge[21] independently demonstrated that the fault of the Ilkovic equation lies in its neglect of the curvature of the electrode surface, and they developed a modified equation which takes this curvature into account. This new equation is, at 25°C

$$i_d = 607n\ D^{1/2}\ C\ m^{2/3}\ t^{1/6} \left\{ 1 + \frac{A\ D^{1/2}\ t^{1/6}}{m^{1/3}} \right\}$$

where the various quantities are expressed in the customary units, and the value of constant A has been evaluated at 17 by Strehlow and Von Stackelberg and at 39 by Lingane and Loveridge.

It is evident from the foregoing relations that the maximum current and the true average current are both directly proportional to the concentration of the electro-reducible or electro-oxidizable substance in the body of the solution. It is not possible to measure the maximum current accurately because the galvanometer usually used is too sluggish to follow the total change in current during the life of a drop, and hence the maximum of the observed oscillations is smaller than the true maximum current. For this reason, the average of the galvanometer oscillations is usually measured in practical work and it is assumed that this average is equal to the true average current. A visible recording polarograph employing an undamped, high speed recording system has recently been placed on the market by the Rutherford Instrument Co. With this instrument Schulman, Battey and Jelatis[27] recommend use of the maximum recorder oscillations, claiming that increased sensitivity is gained by this method of measurement.

Theory of Half Wave Potential

This theory will be discussed first for the simplest case, the reduction of simple metal ions. It is recognized that the term "simple metal ion" may be a misnomer, since in polar solvents the ions of metals are more or less strongly combined with molecules of the solvent. Although the "aquo complex ions" are true complexes, they are unique, and may be classified as separate from other complex ions, and for the sake of simplicity they will be referred to as "simple metal ions".

There are four possibilities in the reduction or oxidation of simple metal ions at the dropping electrode:

1. Reduction to the metallic state of ions of metals that are soluble in mercury, resulting in the formation of an amalgam on the surface of the dropping electrode.

2. Reduction to the metallic state, where the metal is insoluble in mercury, and is deposited in the solid state at the dropping electrode.

3. Reduction or oxidation from one ionic state to another, as Cr^{+++} to Cr^{++}.

4. Combination of 3 with either 1 or 2 so that two or more waves are obtained, e.g. $Cr^{+++} \longrightarrow Cr^{++} \longrightarrow Cr^{0}$.

Reduction of Simple Ions That Are Soluble in Mercury

In this case, the electrode reaction is

$$M^{n+} + ne + Hg = M\,(Hg) \qquad \text{Eq. 1}$$

If this reaction is reversible and rapid compared to the rate of diffusion of the metal to the electrode surface, the dropping mercury electrode will be subject only to concentration polarization, and its potential at any point on the wave will be[19]

$$E_{d.e.} = E^{o} - \frac{RT}{nF} \ln \frac{C_a^o\, f_a}{aHg\; C_s^o\, f_s} \qquad \text{Eq. 2}$$

where C_a^o is the concentration of the amalgam formed on the surface of the mercury drops, C_s^o is the concentration of the reducible metal ions in the layer of solution at the surface of the drops, f_a and f_s are the corresponding activity coefficients, and aHg is the activity of mercury in the amalgam. E_o is the standard potential of the amalgam, that is, the E.M.F. of the cell Reference Electrode/M^{n+}/M (Hg).

Since the amalgams formed at the dropping mercury electrode are very dilute, aHg will approach the activity of pure mercury and may be regarded as a constant. Therefore,

$$E_{d.e.} = E' - \frac{RT}{nF} \ln \frac{C_a^o\ f_a}{C_s^o\ f_s} \qquad \text{Eq. 3}$$

where $E' = E_a^o + \frac{RT}{nF} \ln aHg$

When an excess of supporting electrolyte is present to eliminate the migration current, the reducible ions will reach the surface of the dropping mercury electrode only by diffusion, and the values of C_s^o and the current are governed by the rate of diffusion. In order to express C_s^o as a function of the current, Heyrovsky and Ilkovic[10] assumed that the rate of diffusion was directly proportional to the difference in concentration between the depleted surface layer and the body of the solution. On this basis, the current at any point on the wave should be given by the equation

$$i = k_s\ (C_s - C_s^o) \qquad \text{Eq. 4}$$

where C_s is the constant concentration of the metal ions in the body of the solution, and the proportionality constant k_s is defined by the Ilkovic equation, and at 25°C is equal to $605n\ D^{1/2}\ m^{2/3}\ t^{1/6}$.

When a constant diffusion current, i_d, has been attained, C_s^o has decreased to a value which is negligibly small compared to the concentration of the metal ions in the body of the solution. At this point C_s^o in the preceding equation can be neglected, and we have

$$i_d = k_s\ C_s \qquad \text{Eq. 5}$$

By combining the previous two equations, the following expression for C_s^o at any point on the wave is obtained

$$C_o^s = C_s - \frac{i}{k_s} = \frac{i_d - i}{k_s} \qquad \text{Eq. 6}$$

or

$$C_s^o = C_s \; \frac{i_d - i}{i_d} \qquad \text{Eq. 7}$$

The value of C_s^o decreases in direct proportion to the increase in current. At the midpoint of the wave, where $i = \frac{i_d}{2}$, C_s^o is equal to one half of C_s, and so forth for other points on the wave.

The concentration of the amalgam formed at any point on the wave is directly proportional to the current;

$$C_a^o = k' \, i = \frac{i}{k_a} \qquad \text{Eq. 8}$$

where k_a is similar to k_s except that it is a function of the diffusion coefficient of the metal atoms in the amalgam rather than that of the meal ions in the solution.

When the relations expressed in equations 6 and 8 are substituted into equation 3 which is

$$E_{d.e.} = E' - \frac{RT}{nF} \ln \frac{C_a^o \, f_a}{C_s^o \, f_s} \qquad \text{Eq. 3}$$

where $E' = E_a^o + \frac{RT}{nF} \ln aHg$

we obtain

$$E_{d.e.} = E' - \frac{RT}{nF} \ln \frac{f_a \, k_s}{f_s \, k_a} - \frac{RT}{nF} \ln \frac{i}{i_d - i} \qquad \text{Eq. 9}$$

where $E_{d.e.}$ and i are the corresponding values at any point on the curve. The half wave potential, $E\frac{1}{2}$, is defined as the value of $E_{d.e.}$ at the midpoint of the wave, where $i = \frac{i_d}{2}$. At this point, the last log term in equation 9 becomes zero, and we have

$$E_{\frac{1}{2}} = E' - \frac{RT}{nF} \ln \frac{f_a\, k_s}{f_s\, k_a} \qquad \text{Eq. 10}$$

and at 25°C equation 9 simplifies to

$$E_{d.e.} = E_{\frac{1}{2}} - \frac{0.0591}{n} \log \frac{i}{i_d - i} \qquad \text{Eq. 11}$$

This is a fundamental equation of the polarographic wave and was first developed by Heyrovsky and Ilkovic.[10]

It is common practice to employ a stationary layer of mercury on the bottom of the cell as the non-polarizable electrode. When this is done, the half wave potential is obtained by measuring the E.M.F. of this quiet electrode against an external reference electrode, and algebraically subtracting the value obtained, from the half wave value of the total applied E.M.F.[14]

If there is any appreciable i R drop in the cell circuit, it must be subtracted from the total applied E.M.F. before computing the half wave potential. The cell resistance is usually less than 1000 ohms in aqueous solutions, and, in the presence of sufficient supporting electrolyte, this correction is usually negligibly small. In the case of non-aqueous solutions, the cell resistances are usually considerably higher, and the correction for i R drop may be significant.

From equation 11, it may be seen that a plot of $E_{d.e.}$ versus log $\frac{i}{i_d - i}$ should produce a straight line with the slope equal to $\frac{0.0591}{n}$ at 25°C, and the potential where the log term becomes zero should be the half wave potential. These predictions have been verified experimentally.[12] It should be noted that although the slope of the wave itself depends on both the concentration of the reducible ion and the value of "n", the slope of the log plot depends on "n" only, and is independent of concentration, because the ratio $\frac{i}{i_d - i}$ is independent of concentration at any given value of $E_{d.e.}$.

The most important characteristic of the half wave potential is that it is constant and independent of the concentration of the reducible metal ions, provided that the supporting electrolyte concentration and the temperature are kept constant.

The temperature coefficient for the shift in half wave potential has been experimentally determined for thallous ion in 0.1N KCl solution at 25°C and found to be -0.9 mv./deg.

Reduction of Ions of Metals That Are Insoluble in Mercury

The reduction to the metallic state of the simple ion of a metal that is insoluble in mercury may be represented by

$$M^{n+} + ne = M_{(s)} \qquad \text{Eq. 12}$$

If the activity of the deposited metal is assumed to be constant and independent of current density, then $E_{d.e.}$ at any point on the wave should depend only on the activity of the metal ions in solution, and should be given by

$$E_{d.e.} = E^o_m + \frac{RT}{nF} \ln C^o_s f_s \qquad \text{Eq. 13}$$

where E^o_m is the ordinary standard potential of the solid metal, C^o_s is the concentration of the metal ions at the surface of the dropping electrode, and f_s is the corresponding activity coefficient. As in the previous case, C^o_s will be given by equation 6 or 7, and hence the equation of the polarographic wave will be

$$E_{d.e.} = E^o_m - \frac{RT}{nF} \ln \frac{k_s}{f_s} + \frac{RT}{nF} \ln (i_d - i) \qquad \text{Eq. 14}$$

and the half wave potential should be given by

$$E_{\frac{1}{2}} = E^{o}_{m} - \frac{RT}{nF} \ln \frac{k_s}{f_s} + \frac{RT}{nF} \ln \frac{i_d}{2} \qquad \text{Eq. 15}$$

or, since $i_d = k_s\, C_s$ Eq. 5

$$E_{\frac{1}{2}} = E^{o}_{m} + \frac{RT}{nF} \ln f_s + \frac{RT}{nF} \ln \frac{C_s}{2} \qquad \text{Eq. 16}$$

where C_s is the concentration of the metal ions in the body of the solution. From this equation, it appears that the half wave potential will not be constant, but will be shifted by $\frac{0.0591}{n}$ volts to a more positive value for a tenfold increase in concentration of the metal ions. An exact test of this conclusion is rendered difficult by the fact that there are very few metals which are sufficiently insoluble in mercury for equations 12 and 13 to be valid. The ions of the metals that are sufficiently insoluble in mercury, (Fe, Cr, Mo, W, V, etc.) are usually present as complexes in aqueous solution, and are reduced irreversibly.

Reduction and Oxidation of Metal Ions From One Oxidation State to Another

The reduction of a simple metal ion to a lower oxidation state may be represented by

$$M^{n+} + ae = M^{(n-a)^{+}} \qquad \text{Eq. 17}$$

In this case the dropping mercury electrode functions as an indifferent, or "noble" electrode, and if the foregoing reaction is rapid and reversible, its potential should obey the equation

$$E_{d.e.} = E^{o} - \frac{RT}{nF} \ln \frac{C^{o}_{red}\, f_{red}}{C^{o}_{ox}\, f_{ox}} \qquad \text{Eq. 18}$$

where C^{o}_{red} and C^{o}_{ox} are the concentrations of the metal ions in the lower and higher oxidation states at the electrode surface, the "f" terms are the corresponding activity coefficients, and E^o is the standard potential of the reaction.

The equation of the polarographic wave will depend on whether or not any of the reduced form is present originally in the solution. If none of the reduced form is present originally, then the concentration of the reduced form produced at the electrode surface at any point on the wave will be directly proportional to the current:

$$C^o_{red} = k' i = \frac{i}{k_{red}} \qquad \text{Eq. 19}$$

where k_{red} is proportional to the square root of the diffusion coefficient of the reduced form.

The following equation may be derived,

$$E_{d.e.} = E^o - \frac{0.0591}{a} \log \frac{f_{red}\, k_{ox}}{f_{ox}\, k_{red}} - \frac{0.0591}{a} \log \frac{i}{i_d - i} \qquad \text{Eq. 20}$$

and

$$E_{\frac{1}{2}} = E^o - \frac{0.0591}{a} \log \frac{f_{red}\, k_{ox}}{f_{ox}\, k_{red}} \qquad \text{Eq. 21}$$

and hence we have

$$E_{d.e.} = E_{\frac{1}{2}} - \frac{0.0591}{a} \log \frac{i}{i_d - i} \qquad \text{Eq. 22}$$

This equation is similar in form to equation 11 which was derived for the reduction to the metallic state of simple ions of metals that are soluble in mercury, and hence, the wave characteristics of the two cases may be expected to be similar.

Under the foregoing conditions, the wave is entirely cathodic. If the original solution also contains the reduced form, the wave will lie partly above and partly below the zero current line on the polarogram, provided that the reaction is rapid and reversible. If the original solution does not contain any of the oxidized form, the wave will be entirely anodic. The convention usually followed is that of giving a negative sign to an anodic current.

The anodic limiting diffusion current is directly proportional to the concentration of the reduced form in the body of the solution.

$$-(i_d)_a = k_{red}\, C_{red} \qquad \text{Eq. 23}$$

The constant "k_{red}" is the same as that in equation 19, and is proportional to the square root of the diffusion coefficient of the reduced form.

When the reduced form is present in the original solution, its concentration at the electrode surface at any point on either a cathodic or anodic wave will be given by

$$C^o_{red} = C_{red} + \frac{i}{k_{red}} = \frac{(i_d)_a + i}{k} \qquad \text{Eq. 24}$$

For the concentration of the oxidized form at the electrode surface, the following equation applies:

$$C^o_{ox} = \frac{(i_d)_a - i}{k_{ox}} \qquad \text{Eq. 25}$$

When these relations are substituted into equation 18, the following general equation is obtained

$$E_{d.e.} = E^o - \frac{0.0591}{a} \log \frac{f_{red} \cdot k_{ox}}{f_{ox} \cdot k_{red}} - \frac{0.0591}{a} \log \frac{i - (i_d)_a}{(i_d)_c - i} \qquad \text{Eq. 26}$$

When $C_{red} = 0$ and hence $(i_d)_a = 0$, this equation becomes identical with equation 20, and the wave is entirely cathodic. When $C_{ox} = 0$, so that $(i_d)_c = 0$, and the wave is entirely anodic, equation 26 becomes

$$E_{d.e.} = E^o - \frac{0.0591}{a} \log \frac{f_{red} \cdot k_{ox}}{f_{ox} \cdot k_{red}} - \frac{0.0591}{a} \log \frac{i - (i_d)_a}{-i} \qquad \text{Eq. 27}$$

or, $$E_{d.e.} = E_{\frac{1}{2}} + \frac{0.0591}{a} \log \frac{i}{(i_d)_a - i} \qquad \text{Eq. 28}$$

It may also be shown that the half wave potential of a composite cathodic-anodic wave is the same as either a separate cathodic or anodic wave. Therefore, the general equation for all three types of waves is

$$E_{d.e.} = E_{\frac{1}{2}} - \frac{0.0591}{a} \log \frac{i - (i_d)_a}{(i_d)_c - i} \qquad \text{Eq. 29}$$

When the concentration of the oxidized and reduced forms in the original solution are equal, the ratio of the cathodic and anodic diffusion currents is given by the equation

$$\frac{(i_d)_c}{(i_d)_a} = \frac{k_{ox}}{k_{red}} = \left(\frac{D_{ox}}{D_{red}}\right)^{\frac{1}{2}} \qquad \text{Eq. 30}$$

This relation can be used to determine experimentally the quantity $\frac{k_{ox}}{k_{red}}$ which is required for the calculation of the half wave potential by equation 21.

Stepwise Reduction of Simple Metal Ions

When the free energies of the various oxidation states of a metal ion are sufficiently different from each other, reduction from higher to lower oxidation states can take place in steps at the dropping mercury electrode to give a polarogram consisting of two or more separate waves.

Organic Polarographic Waves

Organic polarographic waves are most similar to inorganic waves involving the change from one ionic oxidation state to another, since in both cases, the dropping mercury or other indicator electrode acts as an indifferent or "noble" electrode. An excellent discussion of this subject is presented by O. H. Müller.[22]

For reversible organic oxidation systems the same types of waves are obtained as in inorganic waves involving changes between two ionic oxidation states, depending on whether the oxidized or reduced form, or both, are present in the original solution.

In organic polarography, an organic solvent is frequently added to the aqueous solution to dissolve enough material for analysis. This organic solvent may have an effect upon the diffusion coefficient of the reacting substance, and also upon the surface tension of the mercury. This latter effect will be noted by changes in drop time. These changes will ordinarily have little effect upon the diffusion current since "t" is raised to the 1/6 power in the Ilkovic equation. Müller states that as a rule, the diffusion current should be inversely proportional to the square root of the viscosity of the solution.

Since most organic oxidations and reductions involve hydrogen, it is apparent that the half wave potential will be significant only if the pH at the interface is known and constant, which means that adequate buffering is very important. At the Fourth Annual Symposium on Analytical Chemistry in 1951, P. J. Elving also stressed the important influence of ionic strength upon the reproducibility of organic polarographic waves.

Most organic oxidations and reductions are irreversible, and since polarographic theory is based on reversibility of reactions, it is surprising how closely the polarographic behavior of a large number of organic systems follows that of systems which are reversible.

Purpose

The purpose of this work was to investigate the various factors upon which the obtaining of reproducible polarograms in anhydrous organic solvents depends, and to attempt to develop a technique that would be generally applicable to such solvents. In addition to the above, a further aim was to attempt to demonstrate the utility of non-aqueous polarography by applying it to the detection or estimation of substances which are not susceptible to aqueous polarographic analysis.

Experimental

Most of the polarograms prepared during this investigation were made on the Sargent-Heyrovsky Model XII Automatic Polarograph. The principal electrolysis cell was a Sargent No. S-29306 cell. This is a glass cell fitted with gas inlet and outlet tubes for degassing the solution in the cell and means for admitting the dropping mercury electrode through a fairly close fitting opening so as to restrict the access of air to the solution in the cell. A platinum wire (used for making electrical contact with the mercury pool) is sealed into the base of the cell. A dropping mercury electrode of conventional design was used for all polarograms. Special pains were taken to keep the capillary dry, and it was not used for aqueous solutions. Since it was found necessary to develop a special reference electrode and a special apparatus to determine the pool potential versus this electrode, these will be described in a later section.

Each solution was freed of oxygen by bubbling a stream of nitrogen through it for forty minutes. The nitrogen was previously washed by bubbling through two towers of alkaline pyrogallate solution to remove oxygen, dried by passing through a concentrated sulfuric acid tower, and then bubbled through a tower containing the solvent under study.

The early part of the experimental work was directed toward repeating some of the work reported by Allison[2] and Black[5] to determine whether any variables which must be controlled to obtain reproducible polarograms had been unaccounted for. This work was largely done in anhydrous methanol solution. The techniques learned in this phase of the work were then extended to other solvents and other reducible substances.

Unless otherwise specified in the following pages, all solutions of organic solvents are understood to be anhydrous.

Reagents

Acetic Acid - C. P. Reagent Grade acetic acid from the Du Pont Co. was used without further purification except where otherwise noted.

Acetone - C. P. acetone from the Mallinckrodt Chemical Works was dried for at least 24 hours over anhydrous potassium carbonate, and then distilled over fresh anhydrous potassium carbonate in a thoroughly dried distillation apparatus equipped with a three ball Snyder fractionating column, with the receiver closed and protected with a $CaCl_2$ drying tube.37

Acetyl Bromide - Freshly opened white label acetyl bromide from the Eastman Kodak Co. was used without further purification.

Acetyl Chloride - Freshly opened Reagent Grade acetyl chloride from the Merck Co. was used without further purification.

β-Phenylpropionyl Chloride - White label Eastman Kodak β-phenylpropionyl chloride was used without further purification.

Benzoyl Bromide - White label Eastman Kodak benzoyl bromide was used without further purification.

Benzoyl Chloride - White label Eastman Kodak benzoyl chloride was used without purification.

Cadmium Chloride - Anhydrous-Reagent Grade-Baker and Adamson cadmium chloride from the General Chemical Co. was dried at 110°C before use.

Ethanol - Absolute ethanol from the U. S. Industrial Alcohol Co. was used without further purification.

Lead Acetate - C. P. lead acetate from the J. T. Baker Co. was used without further purification.

Lead Chloride - C. P. lead chloride from the J. T. Baker Co. was used without further purification.

Lithium Chloride - C. P. lithium chloride from the J. T. Baker Co. was dried at 110°C before use.

Mercury - Redistilled Reagent Grade mercury (Baker and Adamson Chemical) from the General Chemical Co. was dried in a desiccator over concentrated sulfuric acid before use.

Methanol - Reagent Grade, Baker and Adamson methanol from the General Chemical Co. was used without further purification.

Nitrogen - Water-pumped tank nitrogen was washed by bubbling through two towers of alkaline pyrogallate solution to remove oxygen, dried by passing through a concentrated sulfuric acid tower, and then bubbled through a tower containing the solvent under study.

Potassium Carbonate - Reagent Grade anhydrous potassium carbonate from the Merck Co. was used without further purification.

Propionyl Bromide - White label propionyl bromide from the Eastman Kodak Co. was used without further purification.

Propionyl Chloride - White label propionyl chloride from the Eastman Kodak Co. was used without further purification.

Pyridine - Analytical Reagent Grade pyridine from the Mallinckrodt Chemical Co. was redistilled over NaOH and stored over NaOH.

Tetra-n-butylammonium Iodide -(m.p. 141°C) was prepared, according to the method described by Laitonen and Wawzonek,[16] from tri-n-butylamine and n-butyl iodide and recrystallized three times from anhydrous ethyl acetate.

Methanol

Early attempts to get reproducible and characteristic polarograms in methanol, using LiCl (0.1M) as carrier, resulted in failure, for even when no reducible substance was added, irregular and unreproducible waves were obtained. The technique followed during these early unsuccessful runs was to place the solution in the polarographic cell over a mercury pool anode, and then pass in treated nitrogen for forty minutes, prior to the making of the polarogram.

Further experiments showed that the irregularity could be eliminated, and meaningful curves obtained in methanol, if the solutions were degassed in the cell <u>before the addition of the mercury pool</u>. A similar phenomenon for aqueous solutions is explained by Kolthoff and Lingane[13] on the basis that if mercury is added to the solution before the oxygen is removed, the metal reacts with the oxygen and water to form H_2O_2, which is reduced at about -1.0 volts. If some such reaction should occur in organic solvents, both the peroxides and the mercury ions formed might explain the irregularities obtained. Relatively large amounts of mercury may dissolve when such a solution contains ions such as sulfide, iodide, thiosulfate, or large amounts of chloride or bromide, which have a great affinity for mercury. Allison had used the technique of degassing before adding the mercury pool, but apparently had not recognized its importance.

All other runs made during this work were made by degassing the solution prior to the addition of the mercury pool.

Polarograms were made of methanol solutions which were 0.002 M with lead acetate and 1 M with lithium chloride. These polarograms had characteristic flat residual current and diffusion current lines, and a fairly steep and regular wave. The observed half wave potential was -0.36 volts versus the mercury pool anode. This value agrees quite well with the -0.35 volt half wave potential reported by Allison for the same system.

A series of four polarograms was run in quick succession on a single solution of 0.005 M cadmium chloride in methanol containing 0.1 M lithium chloride. A normal Cd^{++} wave was obtained in the first run with a half wave potential of -0.66 volts versus the mercury pool anode. Beginning with the second polarogram, and increasing in height with each successive polarogram, a second wave appeared. The cadmium wave height decreased in each case by an amount approximately equal to the height of the second wave, which appeared at a less negative potential than the cadmium wave. (Fig. 2) The half wave potential of the second wave was not constant, as readings of -0.33 volts, -0.26 volts and -0.20 volts were obtained versus the mercury pool.

It is believed that this second wave was due to gradual absorption of oxygen from the air despite attempts to maintain a nitrogen atmosphere over the solution during the runs. The first reduction wave of oxygen in water corresponds to the production of $H_2O_2 + OH^-$ in neutral or alkaline solution, and if a similar reaction should occur in methanol, the OH^- thus liberated could react with Cd^{++} to form insoluble $Cd(OH)_2$.

In order to determine whether the second wave was due to electrolysis products or to oxygen from the atmosphere, a polarogram was run on 0.005 M $CdCl_2$ in methanol containing 0.1 M lithium chloride, out to -1.0 volt getting a normal curve with one wave. The solution was then let stand for 45 minutes while nitrogen was passed over its surface as during the making of a polarogram and then another polarogram was run. This

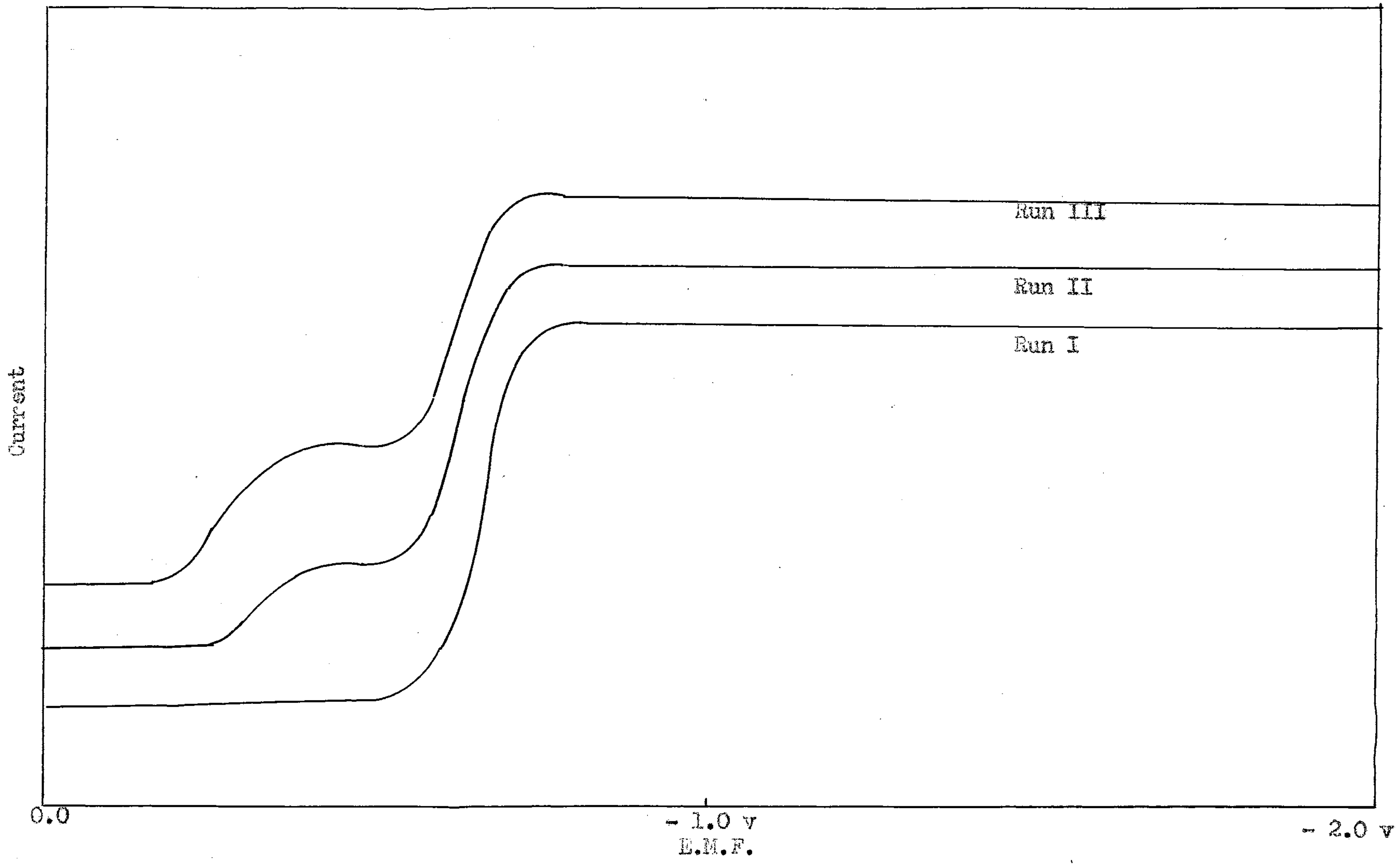

Fig. 2 Cadmium Chloride in Methanol Containing 0.1M LiCl

polarogram gave a definite second wave, as described before. The same solution in the cell was then degassed for an additional 30 minutes, and a polarogram prepared which showed only a single wave, the normal Cd^{++} wave. The results of these experiments indicated that the second wave was due to atmospheric oxygen absorption, and pointed to a great need for adequate protection from the atmosphere if a series of polarograms are to be run on the same solution without intermittent degassing.

Ethanol

A polarogram of 0.005 M cadmium chloride in ethanol containing 0.1 M lithium chloride was made. A smooth and characteristic wave for Cd^{++} was obtained, its half wave potential being -0.63 volts versus the mercury pool anode. When three polarograms were made in rapid succession on the same solution, a second wave, with a half wave potential of -0.40 volts versus the mercury pool, appeared on the third run, and it was noted that there was a decrease in the wave height of the Cd^{++} wave, the decrease being approximately equal to the height of this new second wave. It was suspected that this second wave was due to oxygen absorption from the atmosphere, as in the case of the methanol solution, and the following experiment was performed to investigate this possibility.

A 0.005 M solution of cadmium chloride in ethanol that was 0.1 M in lithium chloride was degassed in the usual manner, and a series of polarograms made. The first two polarograms were normal cadmium waves with half wave potentials of -0.63 volts versus the mercury pool. The third polarogram gave a definite second wave, and this second wave was accompanied by a decrease in the height of the Cd^{++} wave that was proportional to its own height. This solution was now degassed for an additional one-half hour and additional polarograms were then run. The first two of these gave only normal Cd^{++} waves, and the next three contained, in addition to the Cd^{++} wave, the second wave which increased in wave height with each run. The increase in height of the second wave was again accompanied by a proportionate decrease in the height of the Cd^{++} wave.

A polarogram of 0.002 M lead acetate in 1 M lithium chloride in ethanol was made. Although the lead acetate was poured into the ethanol solution containing a large excess of chloride ion, the solution turned cloudy due to the precipitation of lead salts. A smooth, regular polarographic wave for Pb^{++} was obtained, with a half wave potential of -0.36 volts versus the mercury pool anode.

Acetic Acid

A polarogram of 0.1 M lithium chloride in glacial acetic acid was made. Owing to the high resistance of this solution, it was found necessary to make these runs with the tip of the dropping mercury electrode lowered to within 0.6 cm of the surface of the mercury pool. A flat residual current line was obtained up to a potential of -1.2 volts, at which point the slope of the residual current line increased sharply, to give another straight line.

A 0.001 M cadmium chloride solution in acetic acid that was 0.1 M in lithium chloride gave a somewhat flattened wave for Cd^{++} with a half wave potential of -0.76 volts versus the mercury pool after correction for i R drop through the cell. This flattened effect was also noted in the waves reported by Bachman and Astle[3] in glacial acetic acid.

In order to demonstrate the necessity for close electrode spacing in solutions of high electrical resistance, consecutive polarograms were run on a 0.001 M cadmium chloride solution in acetic acid containing 0.1 M lithium chloride, first with a 0.6-cm electrode spacing, and then with 5-cm electrode spacing. Although the wave with a spacing of 0.6 cm was somewhat flattened, it was still recognizable as a definite polarographic wave, while the wave with a 5-cm spacing was so flattened and drawn out as to be useless for polarographic work. (Fig. 3)

Pyridine

A solution containing 0.1 M lithium chloride was prepared in pyridine that had previously been distilled over NaOH and stored over the same chemical. A series of three polarograms was made. A flat residual current line to about -1.1 volts was obtained, at which point the slope increased quite sharply, and the current became somewhat erratic. Repeated runs, both on this sample, and other samples of untreated pyridine gave the same results. (Fig. 4)

A series of polarograms was made on a 0.005 M cadmium chloride solution in 0.1 M lithium chloride in pyridine. Very erratic waves resulted. There was evidence of a Cd^{++} wave, but it was of too poor a quality for any measurements to be made. The diffusion current was extremely irregular. (Fig. 4)

Acetone

The major part of this investigation was done in acetone solution. In addition to lithium chloride other carrier electrolytes were tried in this solvent in an attempt to extend the negative voltage range. Tetramethylammonium chloride was found to be too insoluble in acetone to be

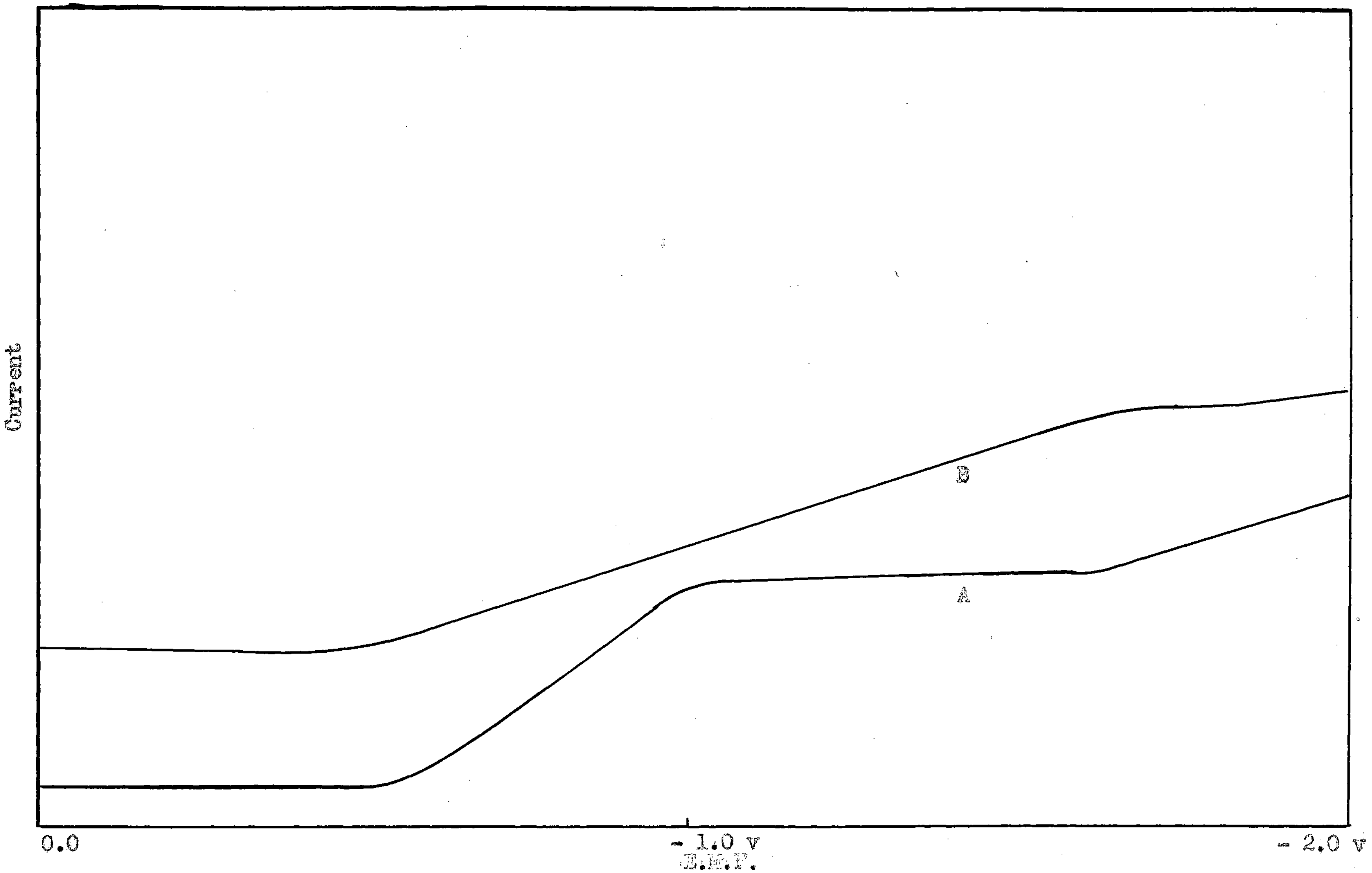

Fig. 3 Effect of Electrode Spacing on Cadmium Chloride Wave in Acetic Acid

A - 0.6-cm spacing

B - 5.0-cm spacing

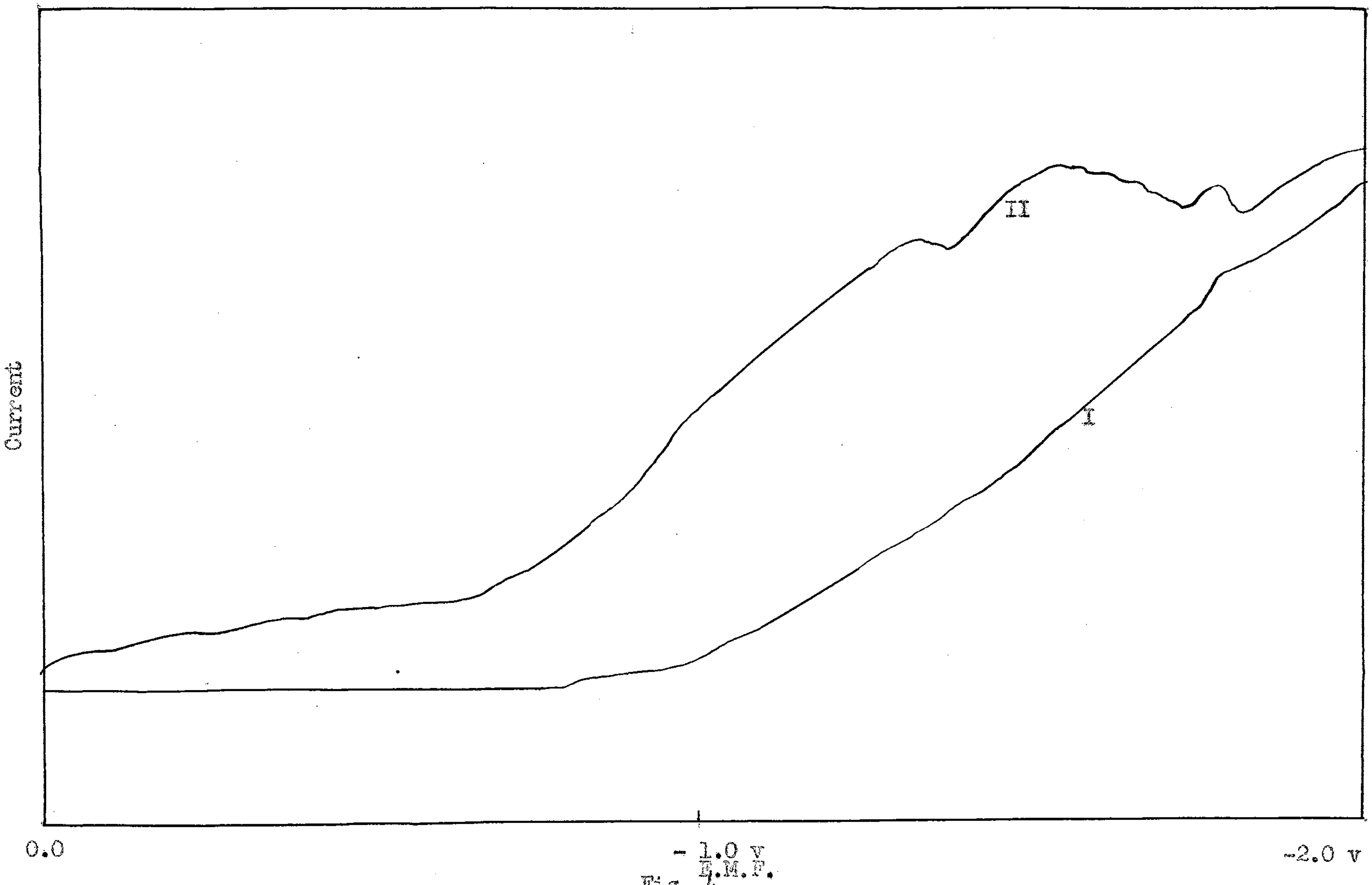

Fig. 4

I - 0.1 M LiCl in Pyridine
II - 0.005 M $CdCl_2$ in Pyridine containing 0.1 M LiCl

of practical value. The same lack of solubility eliminated tetraethylammonium bromide and tetraethylammonium iodide. Tetra-n-butylammonium iodide was found to be of sufficient solubility to be of practical value.

A 0.1 solution of tetra-n-butylammonium iodide was found to give a flat residual current line out to -1.9 volts while a saturated lithium chloride solution (approx. 0.09 M) gave a flat residual current line out to -1.65 volts.

A polarogram of 0.001 M cadmium chloride in acetone containing 0.1 M tetra-n-butylammonium iodide gave a rounded maximum on top of a small wave at -0.31 volts, and a suggestion of another wave at about -1.8 volts. Since this possible second wave coincided with the carrier wave, it was not possible to make certain of its existence, or to make any measurements.

In order to check on the above results, a 0.002 M solution of cadmium iodide was prepared in a 0.1 M acetone solution of tetra-n-butylammonium iodide. Two successive polarograms were made on this solution with somewhat anomalous results. What appeared to be a double wave appeared at about -0.30 volts, with the half wave potential being difficult to measure with any degree of accuracy due to the two waves appearing to run into each other. The diffusion current on the first run was much larger than on the second, and both runs showed the same type of rounded maximum that was noted in the preceding experiment. There was also definite evidence of a second wave at -1.54 volts. (Fig. 5)

A series of experiments on cadmium chloride in acetone solutions containing 0.09 M lithium chloride was run to compare with the above results. In anhydrous acetone, a solution containing 0.001 M cadmium chloride was found to give no wave at the usual potential for a Cd^{++} wave, but to give what appeared to be a definite wave at much more

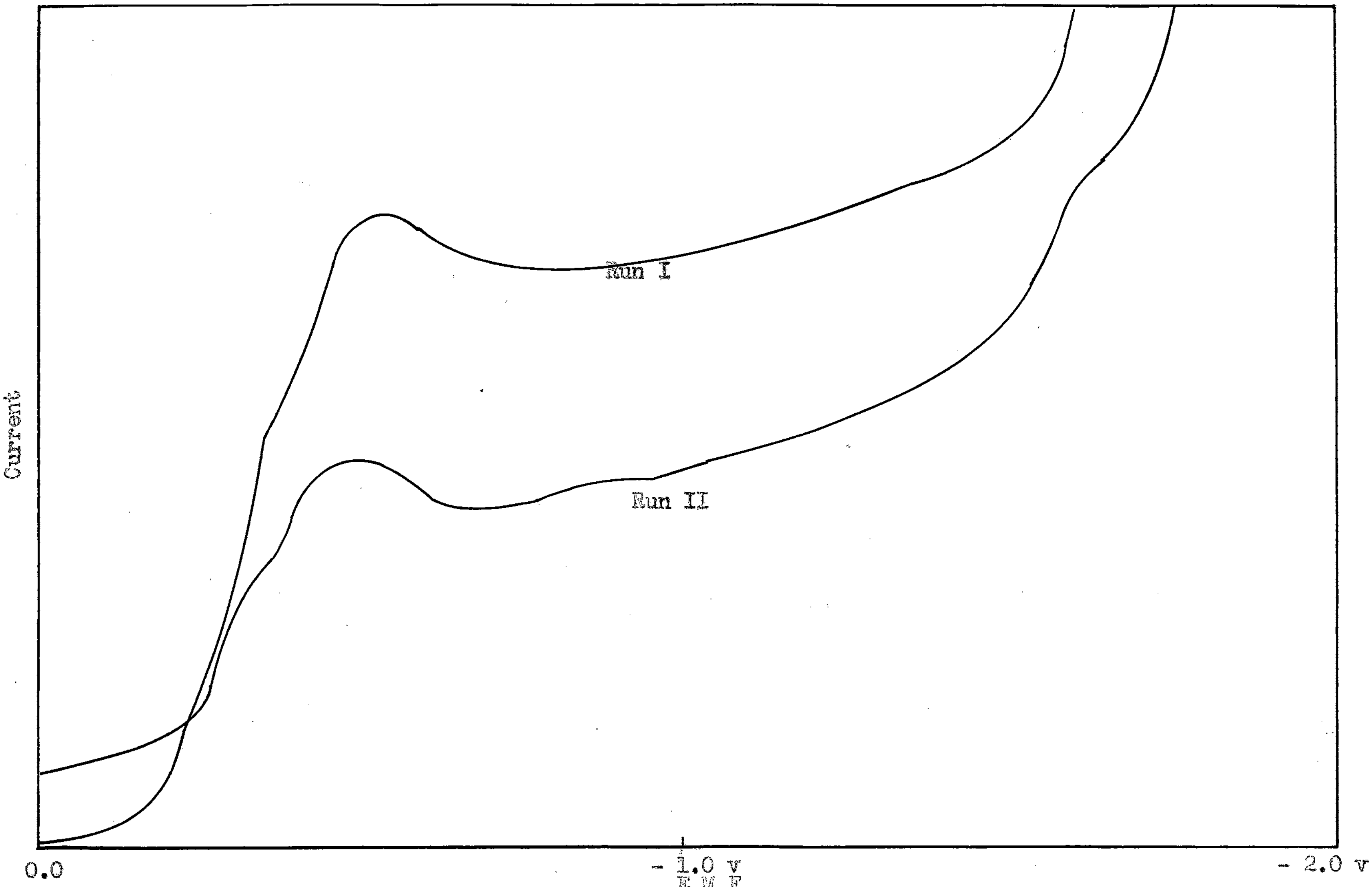

Fig. 5 - 0.002 M CdI_2 in 0.1 M $N(C_4H_9)_4I$ in Acetone

negative potentials. More experiments showed that this wave shifted in half wave potential with concentration. With more concentrated cadmium chloride solutions, this wave showed a definite maximum. On the addition of small quantities of water, this wave was observed to shift to more positive potentials.

Since the preceding results strongly indicated the formation of cadmium halide complexes in anhydrous acetone solution, it was decided to investigate whether there was any polarographic evidence of similar complex formation in aqueous solutions in which a very large excess of halide ion was present.

As a control, a polarogram was made of an aqueous solution containing 0.09 M lithium chloride and 0.001 M cadmium chloride. This solution gave a characteristic wave with a half wave potential of -0.70 volts versus the mercury pool anode. This value could be changed to correspond to the usual values reported in the literature, that is, versus the saturated calomel electrode, by measuring the difference in potential between the pool and the saturated calomel electrode, and algebraically subtracting this difference from the observed potential. Since a 0.1 N calomel electrode (which is essentially what the mercury pool represents in this case) is + 0.089 volts with respect to the S.C.E., the corrected half wave potential would be -0.611 volts, which corresponds to the value usually given.

A saturated aqueous solution of lithium chloride containing 0.001 M cadmium chloride was run on the polarograph. This polarogram showed a greatly reduced diffusion current for the Cd^{++}, the half wave potential being -0.66 volts versus the mercury pool anode. The carrier wave occurred much earlier than usual, going off scale at - 1.8 volts. There was no sign of a second wave.

The effect of the addition of controlled amounts of water on the cadmium wave in acetone was next investigated.

A solution containing 95% of acetone and 5% water by volume exhibited a very slight wave at - 0.69 volts versus the mercury pool anode, and a large second wave with a small maximum at - 1.5 volts.

A solution containing 90% acetone and 10% water by volume gave a small cadmium wave at - 0.76 volts versus the mercury pool, and a large second wave with a maximum whose peak occurred at - 1.7 volts versus the same reference as above.

An 85% acetone solution had a small wave with a half wave potential of - 0.64 versus the mercury pool anode, and a very sharp maximum, but no true wave at - 1.6 volts.

The 80% acetone solution exhibited a half wave potential that seemed to shift with time. The first run had a fairly large cadmium wave, with a half wave potential of - 0.66 volts and a small maximum, the peak of which occurred at - 1.58 volts, both measurements being against the mercury pool. The second run had a somewhat smaller cadmium wave, with a half wave potential of - 0.69 volts, and a much larger maximum but no second wave. If there is cadmium halide complex formation in acetone, a possible explanation of this shift in half wave potential and diminishing of the Cd^{++} diffusion current in 80% acetone might be that equilibrium is reached comparatively slowly in this medium.

The 75% acetone solution seemed to react much like an aqueous solution, having a large cadmium wave with a half wave potential of - 0.66 volts versus the mercury pool anode, and a flat diffusion current line, with no maxima or carrier wave in the two volt span.

Typical curves of cadmium chloride in the various acetone-water solutions tested are presented in Fig. 6.

The shift in half wave potentials using tetra-n-butylammonium iodide as a carrier electrolyte with a mercury anode reference, the work with acetone-water solutions, and the doubt, in general, of the stability of the mercury pool as a reference, led to a study of various standard reference electrodes, by which measurement might be made directly, or by which the mercury pool potential might be ascertained and its stability determined.

The standard reference electrode in polarography is the saturated calomel electrode, although other standard reference electrodes have been used from time to time. There are several obvious difficulties in using a conventional standard calomel electrode to measure potentials against an anhydrous acetone system. The diffusion of water into the acetone, and vice versa, itself, would present a problem, and would make the maintenance of anhydrous conditions in the system under study extremely difficult. In addition, a considerable liquid junction potential of unknown magnitude might be expected to exist. For these reasons, the idea of using a conventional saturated calomel electrode as a reference was not pursued experimentally.

The first reference electrode that was tried was a Ag/AgI electrode. It was reasoned that if this electrode was feasible, it would allow the use of tetra-n-butylammonium iodide as a carrier, and since the electrode could be inserted directly into the electrolysis cell, it would eliminate any liquid junction.

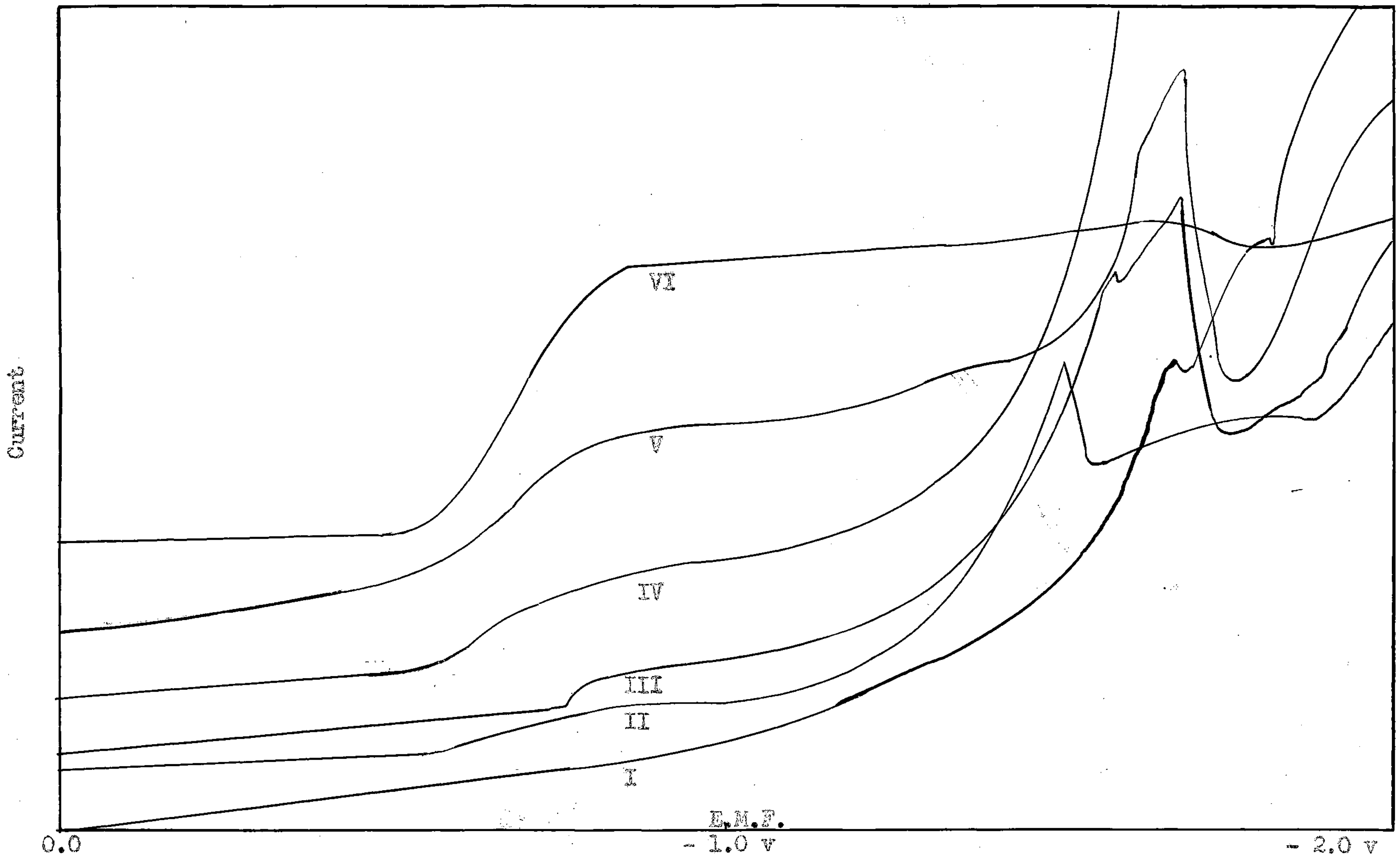

Fig. 6 - $CdCl_2$ in Various Acetone-Water Solutions

I - 100% Acetone
II - 95% Acetone
III - 90% Acetone
IV - 85% Acetone
V - 80% Acetone
VI - 75% Acetone

Two rectangular pieces of silver foil were thoroughly cleaned, and platinum wire leads were spot welded to each. The silver foil electrodes were made the cathode, and a platinum wire, the anode, in a solution of K-Ag cyanide, and a current of 2 milliamperes was passed for 5 hours. The electrodes at this point had a uniform white silver coating of freshly deposited silver. They were rinsed thoroughly in distilled water, and then made the anode in a solution of approximately 1 N HI with a platinum wire cathode. A current of 6 milliamperes was passed for 30 minutes, at the conclusion of which time the electrodes had acquired a light yellow color. They were placed in distilled water after thorough washing, and allowed to stand overnight. In the morning the electrodes had turned purple. They were washed again, and set in distilled water.

As a first step in determining the reversibility of the electrodes, they were tested in aqueous 0.1 N NaI solution. The electrodes were shorted together for one hour in the sodium iodide solution, separated, and the potential between them determined with a type K potentiometer while they were still immersed in the solution. The potential was 2.5 millivolts. The electrodes were then washed in distilled water, and placed in fresh 0.1 N NaI solution, and a current of 100 microamperes passed for 30 minutes between one of the Ag/AgI electrodes as cathode and a platinum wire as anode. The second Ag/AgI electrode was immersed in the solution, but not made a part of the electrical circuit. At the end of the 30 minutes, there was no detectable E.M.F. between the two Ag/AgI electrodes as measured with a student type potentiometer.

The same Ag/AgI electrode that had previously been the cathode was made the anode in a fresh 0.1 N NaI solution, a platinum wire was made the cathode, while the second Ag/AgI electrode was again placed in the solution, but not made a part of the electrical circuit. A current of 100 microamperes was passed for 30 minutes, after which time the potential between the two Ag/AgI electrodes was measured with a student potentiometer, and no detectable E.M.F. noted.

The two Ag/AgI electrodes were placed in distilled water in the dark for 16 hours, and then air dried and placed in a solution of 0.1 N NaI in anhydrous acetone. The potential between the electrodes was measured and found to be 0.8 millivolt. A current of 100 microamperes was then passed for one half hour between a Ag/AgI electrode as cathode and a platinum wire anode, while the other Ag/AgI electrode was immersed in the solution. At the end of this time, it was noted that the acetone solution was quite yellow. The potential between the two Ag/AgI electrodes in the acetone solution was measured and found to be very erratic, varying from 2 to 10 millivolts.

Two Ag/AgCl electrodes were next prepared. Two rectangular pieces of silver foil were silver plated in the same manner as the Ag/AgI electrodes previously prepared. The electrodes were then washed and made the anode, with a platinum cathode in a 0.1 N HCl solution, and a current of 6 milliamperes passed for one hour. At the end of this time the electrodes had assumed a purplish hue. They were thoroughly washed, and placed in distilled water.

The two Ag/AgCl electrodes were placed in an acetone solution that was 0.09M with respect to LiCl, and the potential between the two electrodes was measured. At first the potential varied widely and erratically, but the variations gradually lessened to a constant potential of 0.5 millivolt. The decrease in variation of the potential was found to be accompanied by a fading of the purplish AgCl color, and when the potential had become constant, the electrodes were examined and found to resemble pure silver electrodes. It was decided that the solubility of AgCl in acetone was too great for this electrode to be used as planned.

Since most of the polarographic work in acetone was done with a saturated (approx. 0.09 M) lithium chloride solution, it seemed logical to prepare the acetone analog of a saturated calomel electrode and to determine its reversibility.

Two acetone saturated calomel electrodes were constructed, using two tubes with a platinum wire sealed in the bottom of each, the tubes being connected with each other by a ground glass standard taper joint that was packed with glass wool and which served as a salt bridge. The electrodes were constructed in the usual manner with a layer of mercury on the bottom, a paste of mercury, mercurous chloride and saturated lithium chloride solution overlaying the mercury, and a saturated lithium chloride solution overlaying the paste, and serving as the bridge electrolyte between the two similar electrodes.

A current of 50 microamperes was passed between the electrodes for one hour, after the E.M.F. between the two electrodes had first been measured and found to be zero. At the conclusion of the electrolysis, the potential between the two electrodes was again measured and found to be zero. The same procedure was repeated, with the current being passed in the opposite direction, and again the potential between the electrodes remained at zero after the electrolysis.

An "H" cell was constructed, one leg of which was an acetone analog of the saturated calomel electrode while the other contained a layer of mercury covered by an acetone solution saturated with lithium chloride.

This cell was used to study the deviation of the potential of the mercury anode pool from that of the acetone analog of a saturated calomel electrode (0.09 M LiCl), both at the start of a polarogram, and after current had been passed.

The potential between the electrodes was measured before any current had been passed and found to be 0.320 volts. A current of 15 microamperes was then passed through the cell for one hour and the potential at the end of this time was found to remain at 0.320 volts. A current of 25 microamperes was then passed for an additional hour, and the potential between the electrodes was then checked and found to be 0.312 volts. Enough calomel was then added to the anode pool to saturate the solution, and the potential between the electrodes was measured and found to be zero within the limits of accuracy of the measurements (0.001 volt).

A saturated solution of lithium chloride and calomel in acetone was prepared, let stand at room temperature, and the solid lithium chloride and calomel removed by filtration.

This solution was placed in one arm of an "H" cell over a layer of mercury, and the dropping mercury electrode was introduced into this compartment. The other arm consisted of the acetone analog of the S.C.E. Two polarograms were run, one with the polarograph being connected across the dropping mercury electrode and the S.C.E., and the other, with the polarograph across the dropping mercury electrode and the mercury pool anode. The polarogram taken across the dropping mercury electrode and the S.C.E. resembled the results obtained when an extremely high resistance was placed across the polarograph terminals. The polarogram made across the dropping mercury electrode and the mercury pool anode showed a very large current, starting from zero applied voltage, and rising steeply and going off scale, even with a 1000 sensitivity setting of the Ayrton shunt. These results were taken to indicate that calomel is sufficiently soluble in acetone to give an extremely large wave from zero applied voltage, and therefore must not be permitted to be present in any appreciable amounts in the cell containing the material being examined.

The next attempt was to use an "H" cell with the acetone analog of the S.C.E. in one arm, and the mercury pool anode and a saturated solution of lithium chloride in acetone in the other (dropping mercury electrode) compartment. The bridge of this "H" cell has a fritted glass disc, and in addition was packed with pyrex glass wool to minimize diffusion. Despite all these precautions, including connecting the two electrodes at the very last moment before making the polarograms, experiments showed that there was enough diffusion of mercurous ion into the test cell within a few minutes to make this scheme impractical.

In order to definitely minimize diffusion from the S.C.E. to the electrolysis cell, a more elaborate apparatus was prepared. (Fig. 7.) The electrolysis cell itself was a Sargent No. S-29306 polarographic cell, to which a side arm and a male 10/30 standard taper joint had been sealed. The acetone analog of the S.C.E. was equipped with a fritted glass disc in a side arm, at the end of which was a female 10/30 standard taper joint. In between the two was placed an intermediate unit as illustrated. It was constructed so that if diffusion were still encountered when used as a stationary liquid junction, it could be converted to a flowing liquid junction by slightly opening the two stopcocks. The solution to be examined was placed in the Sargent cell, which also had a sealed female cap for the standard taper joint so that it could be used for degassing before assembly. Part of the solution was also placed in

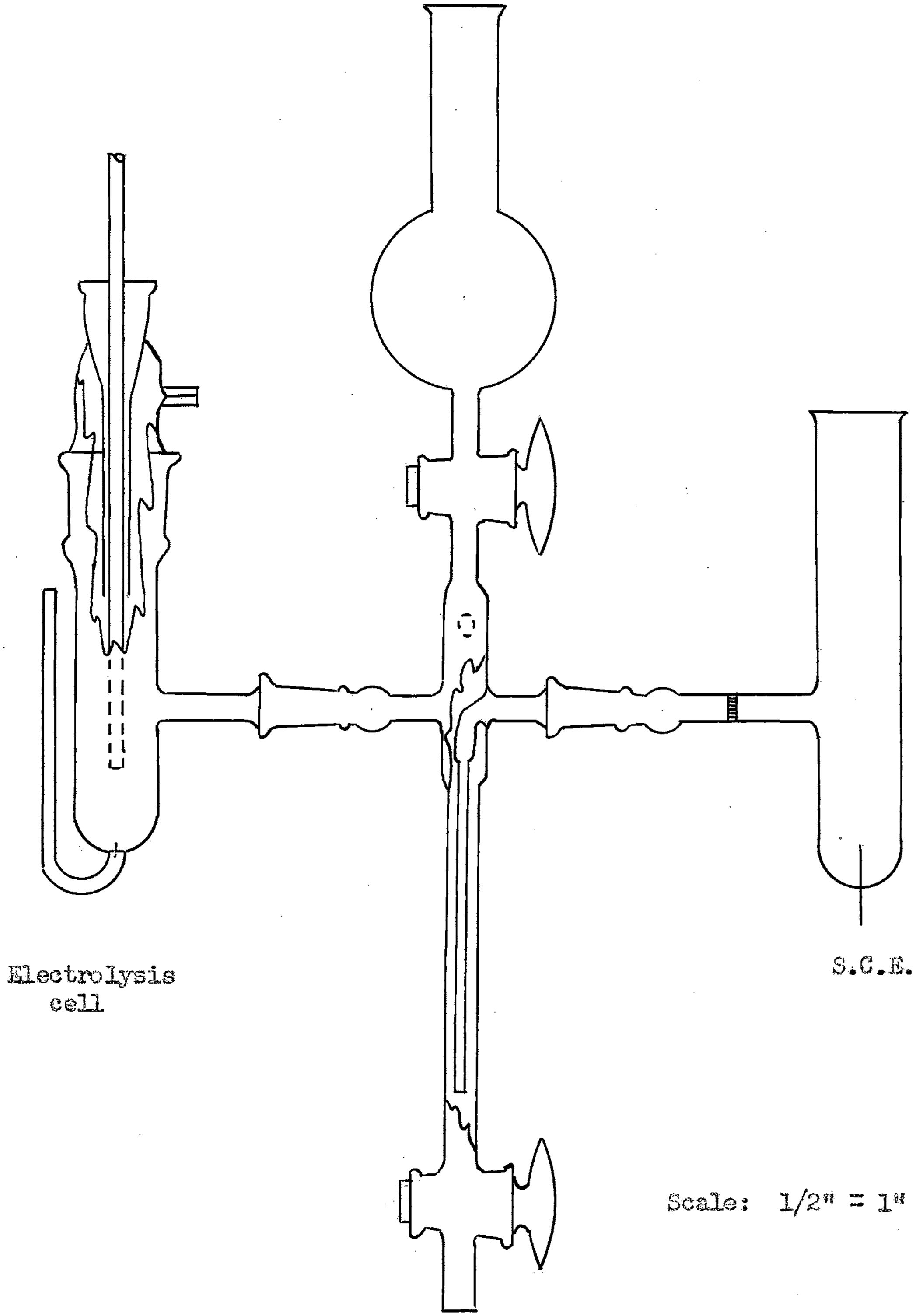

Fig. 7 - Apparatus to Prevent Diffusion Between S.C.E. and Electrolysis Cell

the 100 ml. flask sealed on top of the junction apparatus, and the solutions were degassed for the usual length of time. The three pieces were then assembled and the upper stopcock opened so as to allow the solution to run down and completely fill the center portion of the apparatus and the side arms. A vent, not plainly shown in the illustration, was sealed into the upper part of the center portion for the release of the trapped air.

This apparatus was first tested by making a polarogram of a saturated solution of lithium chloride in acetone. Due to the high electrical resistance between the dropping mercury electrode and the S.C.E., it was found necessary to make the polarograms across the dropping mercury electrode and the mercury pool anode, and then determine the potential of the anode against the S.C.E. at various applied voltages, and make the appropriate correction to obtain half wave values in terms of the S.C.E. By following this method, it was possible to obtain flat residual current lines for the solution of lithium chloride in acetone, with no sign of diffusion of mercurous ion into the electrolysis cell. The potential of the pool was then checked against the S.C.E. at applied voltages varying from zero to -2.0 volts and in each case, the potential was found to be 0.272 volts. The mercury pool was negative with respect to the S.C.E.

The constancy of the mercury pool anode was checked repeatedly, using saturated lithium chloride solutions in acetone containing cadmium chloride and various acid halides and found to be constant, at least to the second decimal place, under the conditions under which the polarograms were run.

In order to more accurately interpret the polarograms obtained, it was thought pertinent to determine at least the order of magnitude of the cell resistance, both between the dropping mercury electrode and the mercury pool anode, and also between the dropping mercury electrode and the S.C.E. in the apparatus which had been constructed to minimize diffusion. A Kohlrausch slide wire and a decade resistance box were used in the bridge circuit, with a 1000-cycle audio oscillator and a set of earphones as a null indicator. It was attempted to take the readings as far as possible during the maximum size of the mercury drop, so that the resistance would be at a minimum. The resistance between the dropping mercury electrode and the mercury pool in a saturated solution of lithium chloride in acetone at room temperature (32°C) was found to be approximately 7500 ohms at an electrode distance of 0.6 cm — the usual electrode spacing in this work. In order to determine the effect of small changes in electrode spacing, the resistance was determined at 0.85 cm and found to be 8,200 ohms. The resistance between the dropping mercury electrode and the S.C.E. was found to be very high and could only be measured to a very rough approximation, the results being of the order of 90,000 ohms.

Acid Halides

Since there is no mention in the literature of polarographic waves from organic acid halides, and since here seemed to be a good example of a case where non-aqueous polarography might apply and where aqueous solutions could not be used, it was decided to investigate the polarographic behavior of these substances in acetone.

An approximately 0.005 M solution of acetyl chloride in a saturated acetone solution of lithium chloride was prepared, degassed thirty minutes, and a polarogram made.

A very good wave (Fig. 8) was obtained, with a half wave potential (corrected for i R drop) of - 1.03 volts versus the mercury pool anode. The potential of the mercury pool versus the saturated calomel electrode

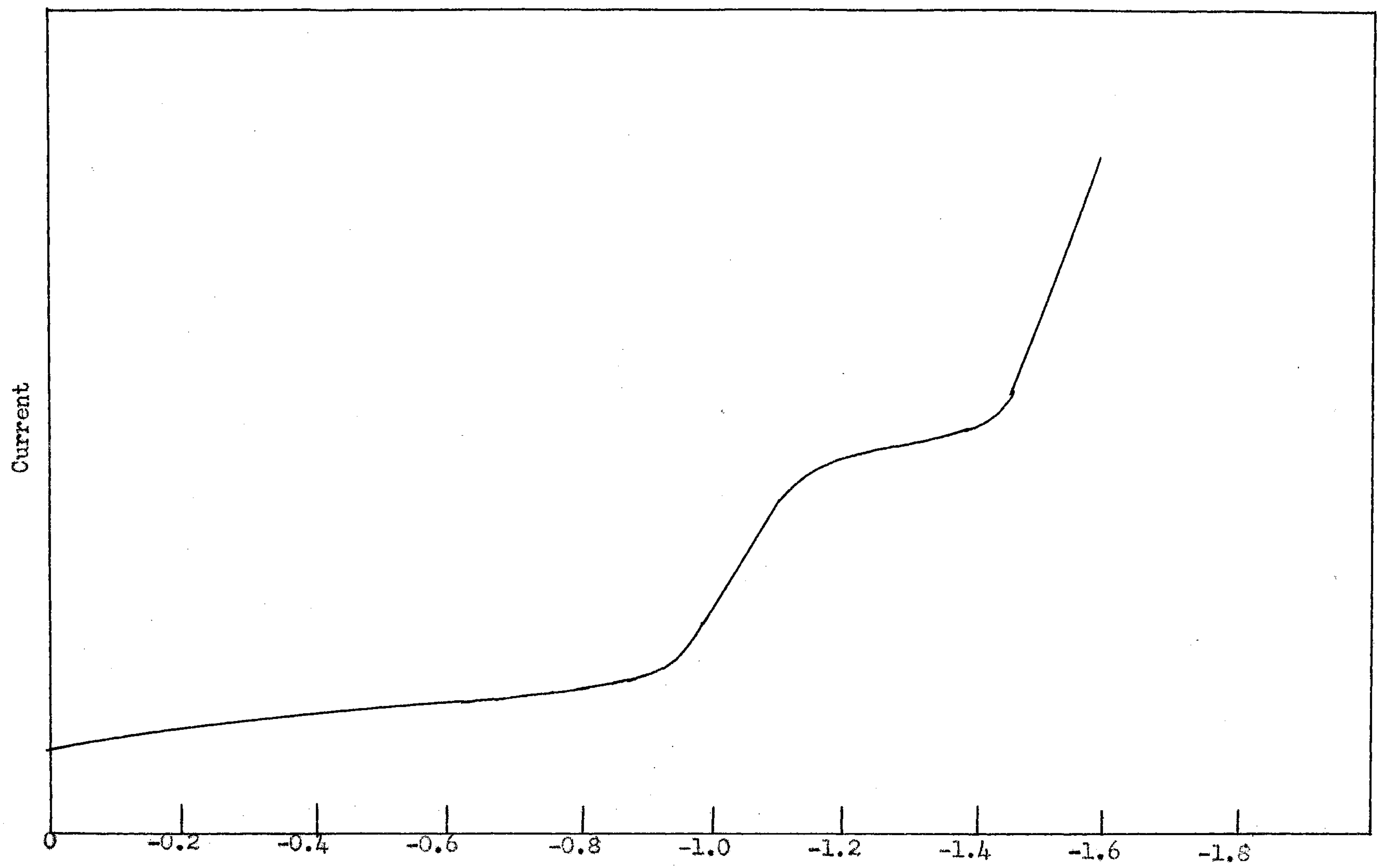

Fig. 8 - Acetyl Chloride in Saturated LiCl-Acetone

was checked and found to remain constant at - 0.27 volts throughout the run.

These results were checked on another sample of acetyl chloride from a previously unopened bottle and the same type of waves were obtained, with the same half wave potential.

In order to determine whether acetic acid from a possible hydrolysis of the acetyl chloride might be responsible for the wave, a polarogram was made from 0.005 M acetic acid in acetone saturated with lithium chloride, and no wave was obtained. A drop of concentrated HCl was added and another polarogram run again with no wave appearing. The above experiments were repeated with a few drops of acetic anhydride in the solution, followed by the addition of glacial acetic acid and a drop of concentrated HCl. No wave resulted from any of these tests.

Attempts were then made to follow the same technique as for acetyl chloride, and to extend the study to other acid halides. All early attempts to obtain a wave from benzoyl chloride were unsuccessful, as a flat residual current line would be obtained up to about - 1.0 volt, and then a very steep current line would go off scale, even when the most insensitive galvanometer settings were used. On reducing the benzoyl chloride concentration to approximately 10^{-4} M, something approaching a wave was obtained, but of too poor quality for measurements to be made.

Experiments were then made with propionyl chloride. As a rough experiment, a saturated solution of lithium chloride was degassed, the residual current line recorded, and then a drop of propionyl chloride was added to the solution in the electrolysis cell, and a polarogram made. The polarogram showed a definite wave with a very slight maximum at the peak of the wave. The maximum made it difficult to accurately measure the half wave potential, but it was approximately - 1.04 volts versus the mercury pool anode.

An 0.007 M propionyl chloride solution in acetone containing 0.09 M lithium chloride was degassed for 30 minutes, and three consecutive polarograms made. Before the third run a few drops of acetic anhydride were added to the solution. Three definite waves resulted, all similar, and all having a fairly large maximum at the peak of the wave, with the top of the maximum coming at about - 1.15 volts versus the mercury pool. The acetic anhydride apparently had no effect on the wave.

Two drops of acetyl bromide were added to a degassed solution of lithium chloride in acetone, the solution was degassed an additional five minutes, and a series of polarograms was made. All of these polarograms showed a wave with a large maximum that made measurement of half wave potentials impossible.

A series of experiments was run with common maximum suppressors such as methyl red in an attempt to suppress the acetyl bromide maximum, but none were successful.

Polarograms were run on acetyl chloride in glacial acetic acid containing a trace of acetic anhydride, but no wave was obtained. Propionyl bromide was also tested in glacial acetic acid containing a trace of acetic anhydride, but it, too, failed to give a wave.

An experiment was next run to determine whether quinhydrone would give a wave in anhydrous acetone solutions saturated with lithium chloride. Since the reduction of quinhydrone involves hydrogen, it was thought that the appearance of a wave would be evidence that there is a source of hydrogen in the acetone solution, and this evidence might be of value in postulating theories concerning the nature of the reduction reaction undergone by acid halides at the dropping mercury electrode. A well defined wave for quinhydrone was obtained, and when checked on the Sargent Model XXI polarograph, anodic and cathodic waves were obtained similar to those given by quinhydrone in unbuffered aqueous solution.

Since inspection of polarograms run in previous experiments on acid halides had given some evidence that the diffusion current height changed with time, a somewhat different technique was adopted in an attempt to obtain results which might be interpreted more quantitatively.

The following runs were made in acetone, freshly distilled over anhydrous potassium carbonate just prior to use. The Sargent electrolysis cell was calibrated so as to give the volume of solution it contained to the nearest ml. The lithium chloride in acetone solution was degassed in the cell. Just prior to the running of the polarogram, the acid halide was quickly weighed out into a glass stoppered weighing bottle, and transferred with the aid of a small quantity of lithium chloride-acetone solution to the electrolysis cell where degassing was continued for about 10 seconds, the final volume of the solution recorded, and the polarogram made.

A 0.003 M solution of benzoyl chloride was prepared in this manner, and two successive polarograms were recorded. The first polarogram showed a definite wave with a half wave potential of - 0.83 volts versus the mercury pool. This wave had no sign of a maximum, and a regular diffusion current up to about - 1.3 volts was obtained. Above this, however, the current became very erratic. The second polarogram showed no wave at all, but a fairly flat residual current line to - 1.0 volt, and then a very steep current line going off scale, and similar to previous results obtained with benzoyl chloride.

In order to investigate the cause of this phenomenon, the previous run was repeated, but just prior to the addition of the benzoyl chloride a small amount (0.005 gms) of benzoic acid was added to the solution. Two successive polarograms were recorded, with an addition of about 1% of acetic anhydride to the solution before the second run. In all cases, the same odd type of wave appeared -- i.e., one that suddenly went off scale at - 1.0 volt.

Using the technique that had given a good polarographic wave with benzoyl chloride, polarograms were then made of 0.006 M propionyl bromide. The first wave was a fairly good polarographic wave, with a half wave potential of - 0.97 volts (iR correction insignificant) versus the mercury pool. The second polarogram had a definite maximum, and was of too poor a quality for measurements to be made.

Two polarograms were made on a 0.009 M acetyl bromide solution. Both of these showed very sharp maxima and were thus unsuitable for measurement of the half wave potential. A polarogram was then made of an 0.004 M acetyl bromide solution, and this time a polarographic wave with no maximum was obtained, with a half wave potential versus the mercury pool of - 0.94 volts (i R correction insignificant).

Several polarograms were then made using various concentrations of n-butyryl chloride, but all of these were of poor quality and showed erratic diffusion currents. Since there was reason to believe that at least part of the erratic results were due to stray electrical leaks in the Sargent Model XII polarograph due to a long period of consistently high humidity, all other qualitative investigations of half wave potentials of acid halides that follow were recorded on the Sargent Model XXI visible recording polarograph.

Using the same technique as previously, a run on the Sargent Model XXI polarograph on n-butyryl chloride again gave very erratic results, and it was decided to further modify the technique in an attempt to obtain polarographic waves of good enough quality for measurements to be made.

The method followed in the succeeding runs was to thoroughly degas the acetone-lithium chloride solution in the cell, thermostated at 25°C, for 30 minutes, add the mercury pool, degas an additional five minutes, and then while the nitrogen was still bubbling, add two drops of the substance to be studied, shut the gas off, and immediately run the polarogram.

n-Butyryl chloride gave a good wave by this technique, with a half wave potential of - 1.00 volts versus the mercury pool (corrected for iR drop).

Similar experiments on other acid halides gave the following half wave potentials versus the mercury pool. All were corrected for iR drop, where this correction was significant.

Propionyl chloride	- 1.01 volt
β-Phenylpropionyl chloride	- 1.00 volt
Iso-valeryl chloride	- 1.01 volt

Despite all methods tried, a good wave for benzoyl bromide was never obtained. This acid bromide seemed to greatly affect the characteristics of the capillary so that it was not possible to maintain a suitable drop time. In fact at about - 1.2 volts, the mercury was dropping in an almost continual stream.

The effects of changes in concentration were studied, using the technique of weighing the acid halide in a closed weighing bottle, and rinsing it into the cell just prior to the running of the determination. As two representatives of this group, acetyl chloride and propionyl bromide were chosen for quantitative studies.

The "m" value of the capillary was determined by immersing it in an acetone solution saturated with lithium chloride, and collecting 50 drops of mercury while noting the time required. The mercury was collected in a tared weighing bottle, the acetone decanted, the mercury washed with distilled water, and then dried and weighed. The "m" value was calculated to be 2.19 mg/sec. mercury.

The following quantitative runs were made in a cell that was thermostated at 30°C in a mineral oil bath. Diffusion current measurements were made at - 1.30 volts versus the mercury pool where $m^{2/3}\ t^{1/6}$ was 2.13 for the acetyl chloride, and at - 1.40 volts for the propionyl bromide where $m^{2/3}\ t^{1/6}$ was 2.11. The following results were obtained:

Table I

Acetyl Chloride	Molarity	I_d(microamps)	I_d(microamps)/m mol
	0.014	14.3	1.02
	0.011	5.1	0.46
	0.0097	12.7	3.70
	0.0034	3.7	1.08
Propionyl Bromide	0.017	17.1	1.00
	0.010	7.8	0.78
	0.007	6.0	0.83
	0.005	3.9	0.78

The above results, especially with acetyl chloride, indicate that the method in its present form will, at best, give only an approximate quantitative estimation. On different days, especially under varying conditions of humidity, etc., these results could not be duplicated within better than

10% of the values on a straight line drawn through the average of the above points.

In order to determine the number of electrons involved in the reduction of acid halides, the value of "n" was calculated from the waves obtained on propionyl chloride and iso-valeryl chloride at 30°C. The method used was to plot the function log $\frac{I}{I_d - I}$ versus voltage, and to take the reciproval of the slope. If "n", the number of electrons, were equal to one, the theoretical slope would be 0.0601 at 30°C. The slope for propionyl chloride was 0.066 volts, a definite indication of a one-electron change. It should be noted that this slope was constant for only about half the curve.

For iso-valeryl chloride, the slope was found to be 0.081 volts. (Fig. 9.) Although this differs from the value expected for a one-electron change, it is even further from the value (0.03) which would indicate a two electron change. Such a difference is not surprising if one considers the fact that the reaction is probably irreversible, the lack of symmetry in the wave indicating this to be the case.

In closing this description of the experimental part of the work, a few words should be said about the constancy of the half wave potential. In a series of runs during the quantitative study of propionyl bromide, all of which were made on the same day, the half wave potential remained constant at - 1.01 volts, versus the mercury pool anode. On a polarogram made on a different day, using a concentration of the same order of magnitude as above, the half wave potential was found to be - 0.97 volts. This is the largest variation that was found, although other half wave potentials of acid halides seemed to vary one or two hundredths of a volt on different days.

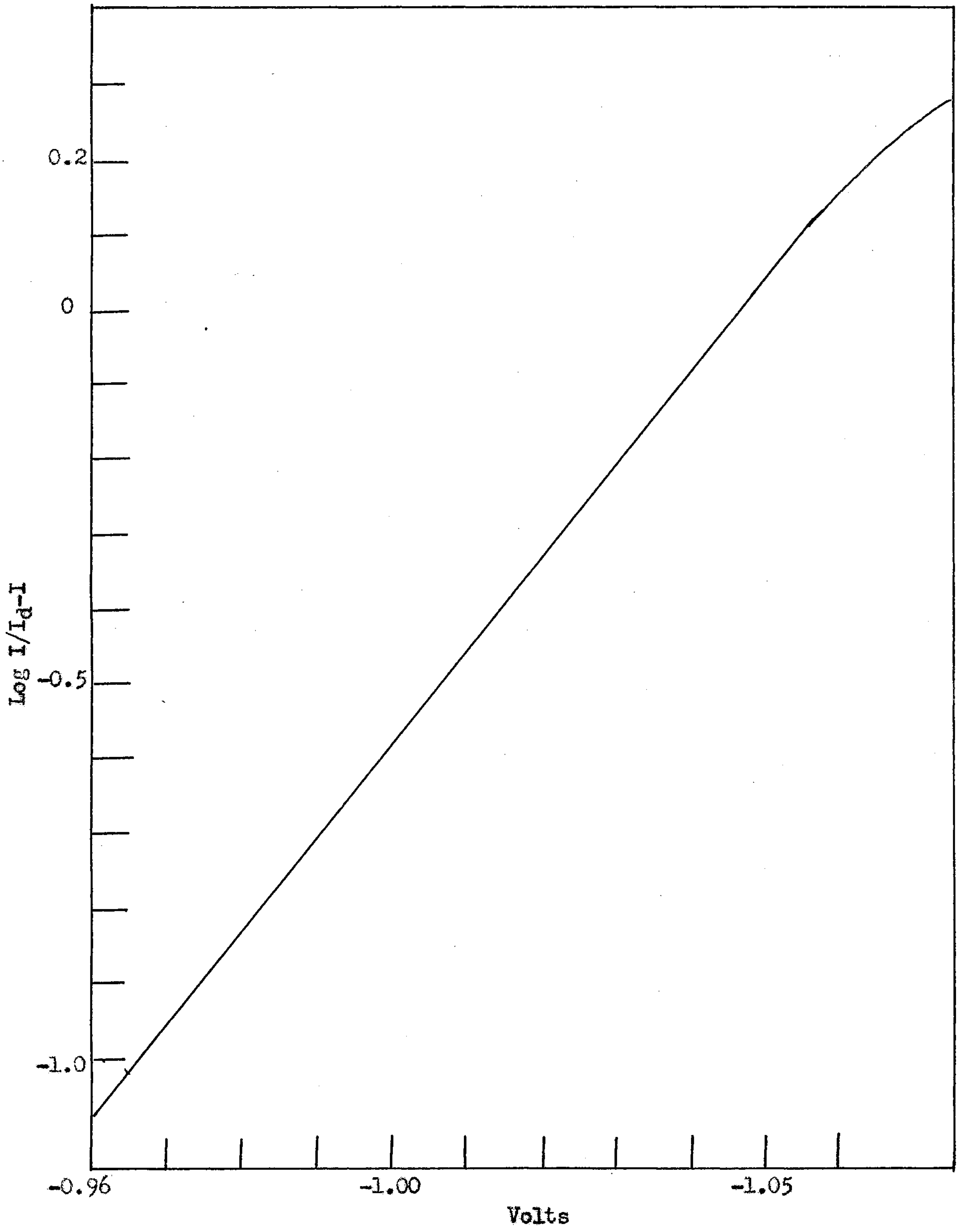

Fig.9- Determination of "n" for Iso-valeryl Chloride

Results and Discussion

Early in this research it became very apparent that if good results are to be obtained in polarographic work in anhydrous organic solvents, care must be taken (1) to degas the solution before mercury is brought into contact with it, (2) to degas the solution much more thoroughly than would be normally required for aqueous solutions, and (3) to decrease the spacing between the electrodes (to as little as 0.6 cm) in those cases where the high resistance of the solution results in a flattening of the wave.

It would be unwise to attempt to explain, on the basis of evidence now available, the peculiar effect of degassing in the presence of mercury. It is possible, however, that either the organic solvents themselves, or traces of water yet remaining in these solvents may act in a manner similar to that reported for aqueous solutions.[13] If mercury is added to aqueous solutions before the oxygen is removed, the metal reacts more or less rapidly with the oxygen and water to form H_2O_2 and mercurous salts. Mercurous ions are reduced rapidly at zero applied voltage while H_2O_2 is reduced at about - 1.0 volt. If a similar reaction could take place in the organic solvents studied, this might explain the irregulatities encountered.

The results of this research indicate that polarograms can be made successfully in methanol, ethanol, acetic acid, acetone and probably in pyridine, using halides of lithium or quaternary ammonium salts as carrier electrolytes. Table II gives typical results obtained for cadmium and lead in the above solvents. The half wave potentials for lead and cadmium are somewhat different than those found in aqueous solutions, as can be seen by comparing the values of - 0.485 for lead, and - 0.688 for cadmium, each versus the quiet mercury pool, in aqueous solutions containing 0.1 N

KCl with the values reported in Table II. This is to be expected since not only the form in which these ions exist in the organic solvents, i.e., as solvated ions, as molecules, etc., but also the potential of the reference pool electrode might be expected to be different.

Table II

Cation	Carrier	Solvent	$E_{\frac{1}{2}}$* vs pool
Pb^{++}	LiCl	CH_3OH	- 0.36 volt
Pb^{++}	LiCl	C_2H_5OH	- 0.36 volt
Cd^{++}	LiCl	CH_3OH	- 0.66 volt
Cd^{++}	LiCl	C_2H_5OH	- 0.63 volt
Cd^{++}	LiCl	$HC_2H_3O_2$	- 0.76 volt
Cd^{++}	LiCl	C_5H_5N	- 1.0** volt

* iR drop correction made when significant

** The wave in this case was so poorly formed that accurate measurements of either the half wave potential or the diffusion current were impossible. The value given here, is at best, an approximation.

The waves obtained for these substances were, with the exception of the pyridine solutions, well formed, and, except for a flattened effect noted in the cadmium waves in acetic acid, very similar to those obtained in water.

The results of attempts to obtain polarographic waves from solutions of acid halides in acetone saturated with lithium chloride are summarized in Table III.

Table III

Acid Halide	$E_{\frac{1}{2}}$ vs pool	$E_{\frac{1}{2}}$ vs acetone-S.C.E.	I_d(microamps) m mol
Acetyl chloride	- 1.03 volts	- 1.275 volts	0.85
Propionyl chloride	- 1.01 volts	- 1.273 volts	-
Butyryl chloride	- 1.00 volts	- 1.272 volts	-
Iso-valeryl chloride	- 1.01 volts	- 1.273 volts	-
Benzoyl chloride	- 0.83 volts	- 1.102 volts	0.82
β-Phenylpropionyl chloride	- 1.00 volts	- 1.272 volts	-
Acetyl bromide	- 0.94 volts	- 1.212 volts	0.66
Propionyl bromide	- 1.01 volts	- 1.273 volts	0.85

The I_d/m mol values given above are subject to the same quantitative errors as have been discussed previously in dealing with the quantitative aspects of the waves, and hence are given as an estimate of the order of magnitude only.

One of the important questions encountered in the study of the polarographic behavior of these compounds was that dealing with the nature of the electrode reaction. It was at first thought that each acid halide should be reduced to the corresponding aldehyde, with or without the possibility of further reaction to form condensation products. The simple single wave obtained indicates a single electrode reaction. Unfortunately for the aldehyde theory, however, is the fact that the direct reduction to aldehyde would require a source of hydrogen and would be a two-electron reaction. While it is conceivable that the organic solvents used might provide hydrogen or that traces of water present might do so, the graph obtained by plotting $\log \frac{I}{I_d - I}$ versus the voltage was definitely that of a one electron reaction. This leads to the conclusion that the electrode reaction products are most probably acyl free radicals and halide ions.

The amount of water present in the "anhydrous" acetone was determined by means of a Karl Fischer titration through the courtesy of Dr. Paul Yates of these laboratories, and found to be approximately 0.11%. Although it was at first thought that the trace of water might be necessary for the reaction, consideration of the fact that propionyl chloride gives the same type of wave in the usual acetone and in acetone to which a small quantity of acetic anhydride had been added to remove water, indicates that the presence of water probably is not essential.

The rapid deterioration in the quality of the wave with time indicates the necessity for making the polarograms as rapidly as possible after preparation of the final solution. The fact that the best results were obtained when freshly distilled acetone was used also points up the care in handling that is necessary for good results. It seems most probable that moisture reacting with the acid halide is at least the chief cause of this difficulty.

A technique that might be expected to give at least fair quantitative results would be to use freshly distilled acetone, to degas thoroughly before introducing the acid halide, to weigh the acid halide in a sealed ampoule, to break the ampoule after it is in the acetone solution, and to run immediately after a ten-second nitrogen degassing and mixing period. With the exception of the fact that a small weighing bottle was used instead of the ampoule, this is essentially the technique which first gave useful results in this research. The placing of the entire polarographic cell assembly in a "dry box" should make the determination more convenient and accurate.

Any future work on the polarography of acid halides in acetone should certainly include an investigation of various methods for obtaining more thoroughly dried acetone, and the comparison of the I_d/m mol values obtained under these conditions with those indicated in this study.

Conclusions and Summary

This work has demonstrated that it is entirely feasible to obtain good polarographic results in many organic solvents, if certain procedures are followed.

A very thorough degassing of the solution with treated nitrogen in order to remove oxygen is necessary. The mercury pool should not be added until the solution is degassed. The maintenance of anhydrous handling conditions is important in order for reproducible results to be attained especially in those cases where the material being analyzed is unstable in the presence of water. The advantages of super drying have not been studied; there is some indication (e.g. in the case of benzoyl chloride) that traces of water are beneficial. In order to follow changes, if any, in the pool potential when using organic solvents, it proved very convenient to prepare the organic solvent analog of the saturated calomel electrode. This electrode in acetone saturated with lithium chloride proved to give excellent results.

Polarography in acetone solution may be applied to the detection of acid halides, but will not differentiate between the various members of this series. It is believed that with proper calibration and technique, this method should give quantitative results of reasonable accuracy.

BIBLIOGRAPHY

(1) Adkins, H. and Cox, F., J. Am. Chem. Soc., 60, 1157 (1938)

(2) Allison, B., Polarographic Studies of Lead in Methanol Solution, Unpublished M.S. thesis, Oklahoma A. and M. College (1950)

(3) Bachman, G. B. and Astle, M. J., J. Am. Chem. Soc., 64, 1303 (1942)

(4) Bachman, G. B. and Astle, M. J., J. Am. Chem. Soc., 64, 2177 (1942)

(5) Black, H., Polarographic Studies in Organic Solvents, Unpublished M. S. thesis, Oklahoma A. and M. College (1948)

(6) Gentry, C. H. R., Nature, 157, 479-480 (1946)

(7) Heyrovsky, J., Chem. Listy., 16, 256 (1922)

(8) Heyrovsky, J., Trans. Faraday Soc., 19, 785 (1924)

(9) Heyrovsky, J., Phil. Mag., 45, 303 (1923)

(10) Heyrovsky, J. and Ilkovic, D., Coll. Czech. Chem. Commun., 7, 198 (1935)

(11) Heyrovsky, J. and Shikata, M., Rec. trav. chim., 44, 496 (1925)

(12) Kolthoff, I. M. and Lingane, J. J., Chem. Rev., 24, 1-94 (1939)

(13) Kolthoff, I. M. and Lingane, J. J., Polarography, p. 111, Interscience, (1941)

(14) Kolthoff, I. M. and Lingane, J. J., Polarography, p. 144, Interscience, (1941)

(15) Kucera, G., Ann. Physik., 11, 529 (1903)

(16) Laitenen, H. A., and Wawzonek, S., J. Am. Chem. Soc., 64, 1765 (1942)

(17) Leeds and Northrup Co., Bibliography of Polarographic Literature, E-90(1), (1950)

(18) Lewis, W. R., Quackenbush, F. W., and De Vries, T., Anal. Chem., 21 762 (1949)

(19) Lingane, J. J., J. Am. Chem. Soc., 61, 2099 (1939)

(20) Lingane, J. J. and Loveridge, B. A., J. Am. Chem. Soc., 66, 1425 (1944)

(21) Lingane, J. J. and Loveridge, B. A., J. Am. Chem. Soc., 72, 438 (1950)

(22) Müller, O. H., Physical Methods of Organic Chemistry, A. Weissberger, Editor, 2nd Edition, Part 2, 1776-1884 (1949) (Interscience)

(23) Page, J. E. and Robinson, F. A., J. Chem. Soc., 133-135 (1943)

(24) Parks, T. D. and Hansen, J. A., Anal. Chem., 22, 1268 (1950)

(25) Peracchio, E. and Meloche, V., J. Am. Chem. Soc., 60, 1770 (1938)

(26) Sanko, A. M. and Manussowa, F. A., J. Gen. Chem., 10, 1171 (1940)

(27) Schulman, J. H., Battey, H. B. and Jelatis, D. B., Rev. Sci. Instruments, 18, 226 (1947)

(28) Semerano, G., Gazz. chim. ital., 62, 518 (1932)

(29) Shikata, M., Trans. Faraday Soc., 21, 42 (1925)

(30) Shikata, M., Mem. Coll. Agr. Kyoto Imp. Univ., Ser. No. 4, 1 (1927)

(31) Smith, L. I., Kolthoff, I. M., Wawzonek, S. and Ruoff, P. M., J. Am. Chem. Soc., 63, 2341 (1941)

(32) Strehlow, H. and von Stackelberg, M., Z. Elektrochem., 54, 51 (1950)

(33) Strnad, F., Coll. Czech. Chem. Commun., 11, 391 (1939)

(34) Taylor, J. K., Anal. Chem., 19, 368 (1947)

(35) Vitek, V., Coll. Czech. Chem. Commun., 7, 537 (1935)

(36) Wawzonek, S. and Laitenen, H. A., J. Am. Chem. Soc., 63, 2341 (1941)

(37) Weissberger, A. and Proskauer, E., Organic Solvents, p. 143, Oxford (1935)

THESIS TITLE: POLAROGRAPHY IN ANHYDROUS ORGANIC SOLVENTS

NAME OF AUTHOR: HAROLD LYONS

THESIS ADVISER: DR. PAUL ARTHUR

The content and form have been checked and approved by the author and thesis adviser. "Instructions for Typing and Arranging the Thesis" are available in the Graduate School office. Changes or corrections in the thesis are not made by the Graduate School office or by any committee. The copies are sent to the bindery just as they are approved by the author and faculty adviser.

NAME OF TYPIST: Mrs. J. O. Richardson