APPLICABILITY OF SOLID MICROELECTRODES TO NONAQUEOUS

AMPEROMETRIC TITRATIONS

By

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PREFACE

Polarographic determinations are ordinarily carried out in an aqueous medium using the dropping mercury electrode. Some polarographic work has been done in mixtures of water and organic solvents, while a smaller amount has been done in anhydrous organic solvents. One of the greatest difficulties involved in nonaqueous polarography is the high resistances of the solvents. This problem has been largely solved through the use of the iR- compensator developed by Dr. Paul Arthur.

Electrodes other than the dropping mercury electrode have been used in polarography, one of the more common ones being the rotating solid microelectrode. One of the greatest disadvantages in using this type of electrode is that the materials of which such electrodes are made do not have the high hydrogen overvoltage possessed by mercury. Because of this, their cathodic range in aqueous solutions is severely limited.

The purpose of this research was to examine the behavior of several different types of rotating microelectrodes in nonaqueous solvents. It was hoped that by using anhydrous solvents their cathodic range might be extended and new uses for them found.

The author wishes to express his sincere appreciation and gratitude for the help and guidance extended by Dr. Paul Arthur during the course of the investigation.

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CHAPTER I

INTRODUCTION

Polarography is a branch of electroanalytical chemistry which deals with the measurement and interpretation of current-voltage curves obtained during the electrolysis of a solution containing an electro-oxidizable or electro-reducible substance. The electrolysis takes place between two electrodes, one of which is very small and easily polarized, while the other is a large non-polarizable electrode.

The voltage necessary for the electrolysis indicates the nature of the reacting substance, while the current observed is a function of its concentration.

The apparatus necessary for the basic polarographic circuit consists of four units; (1) a source of electromotive force; (2) a means of varying the potential applied across the cell; (3) the electrolysis cell; and (4) the current-measuring circuit.
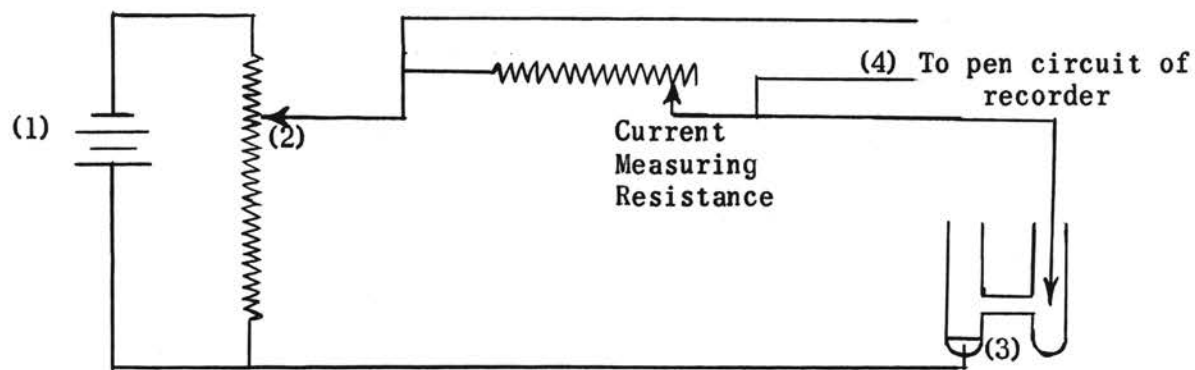
Figure 1. Circuit of Common Recording Polarograph

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In the recording polarograph, the potential across the cell is automatically controlled by a bridge which advances the voltage at a uniform rate of speed.

The electrolysis cell contains the reference electrode and the microelectrode. The most common microelectrode is the dropping mercury electrode (D.M.E.). It consists of a leveling bulb, serving as a mercury reservoir, which is connected by means of rubber tubing to a glass capillary of about 0.05 mm. internal diameter. The level of the bulb is adjusted so that a drop falls every three to six seconds. In use, the tip of the capillary is inserted beneath the surface of the solution to be analyzed and the small mercury drops serve as the electrode at which the electrolysis reaction takes place. Care must be taken to keep the electrode clean in order to obtain reproducible results. In order to maintain a constant rate of flow through the capillary, a constant pressure or head of mercury must be maintained.

The D.M.E. has a number of advantages over other types of microelectrodes. The surface area is reproducible and can be calculated from the weight of the drop. The surface itself is constantly being renewed by the falling away of the old drops and their replacement by new ones. This prevents the electrode from becoming contaminated by electrolysis products.

The most common non-polarizable or reference electrode is the saturated calomel electrode (S.C.E.). It can be used for both anodic and cathodic polarography. A number of other reference electrodes can be used, but the calomel electrode is by far the most popular. Most half-wave potentials which are reported in the literature are reported in terms of the saturated calomel electrode.

The pen circuit of the recorder measures the current as a function of the voltage drop across a standard resistor. The chart on which the pen records the current is arranged so that it advances at a uniform rate along with the bridge. The curves produced by an instrument such as this are linear plots of current versus voltage. A typical polarogram is shown in Figure 2.

As an increasing voltage is applied to the electrolysis cell, a small current begins to flow. This is called the residual current. This current, in the case of the D.M.E., is due in part to the fact that the drop acts as a condenser; and as the drop area grows, current must flow to build up a charge on its surface. This charge increases with increasing applied voltage. The residual current may also be in part due to a small electrocapillary effect produced by ions which lower the interfacial tension between the mercury drop and the solution. The residual current is also partly due to trace impurities which are present even in the best grades of reagents. Oxygen may also be responsible for a portion of this current since it is quite difficult to remove the last traces of dissolved oxygen from the solvent.

As the potential increases across the cell, only the residual current flows until the decomposition potential of a reducible substance is reached. At this point the current rises quite rapidly until the limiting current is reached. The curve then levels off and rises only very slowly. The limiting current represents a state in which the electrode reaction is dependent only upon the rapidity with which ions can diffuse to the electrode. The limiting current represents the sum of the residual current and the so-called diffusion current. The diffusion current itself is the limiting current minus the residual current.
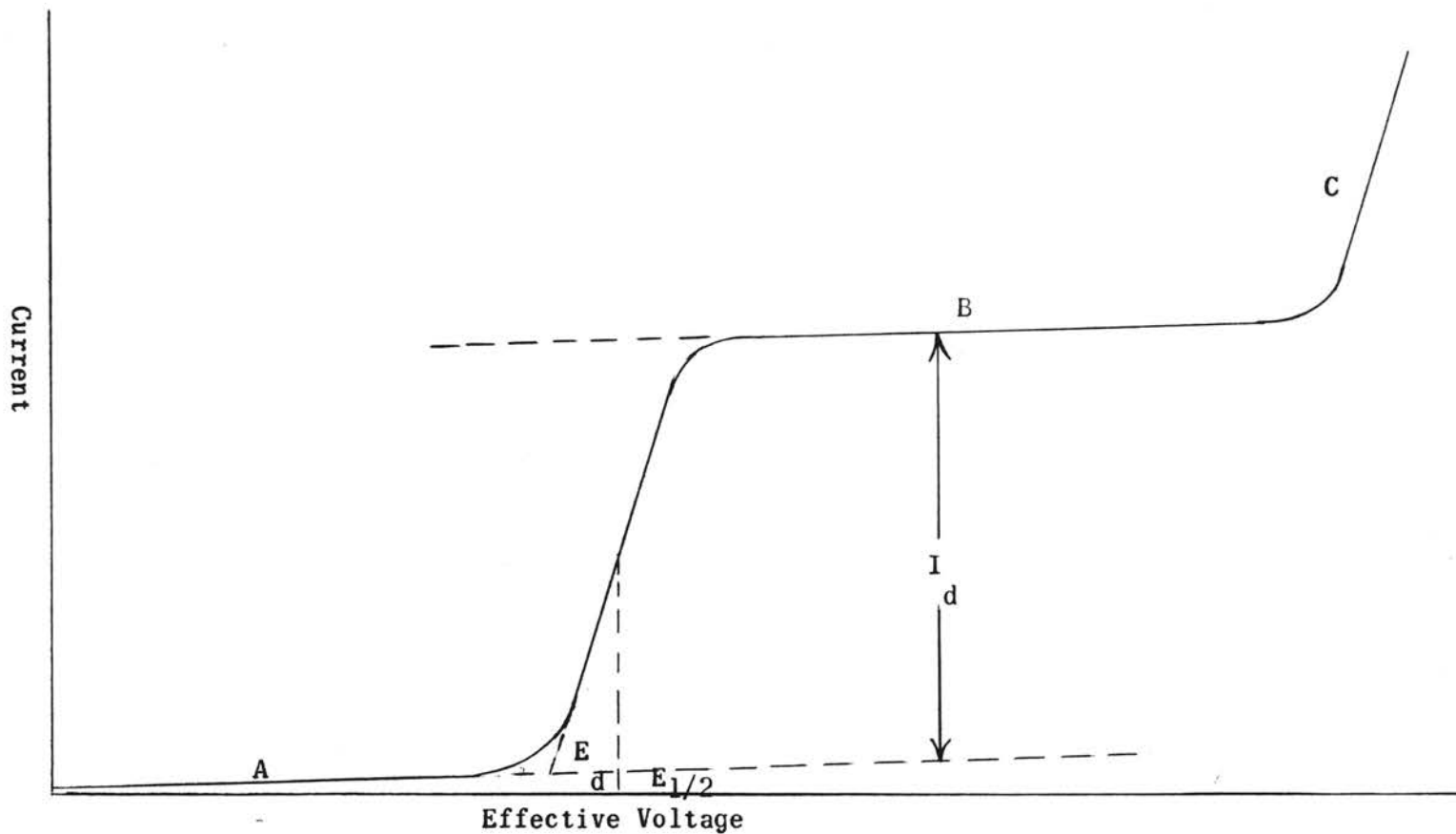
Figure 2. A Typical Polarogram

A. Residual Current Line I_d Diffusion Current
B. Limiting Current Line $E_{1/2}$ Half Wave Potential
C. Carrier Wave E_d Decomposition Potential

It can easily be seen that if only the ions to be reduced were present in the solvent, they would reach the electrode not only by diffusion but by migration. The positively charged ions would be attracted to the negatively charged electrode. In order to minimize this migration of ions, an electrolyte called the supporting electrolyte must be added to the solution in a concentration of from 50 to 100 times that of the ion to be reduced. This supporting electrolyte serves as a source of ions which can be attracted to the surface of the electrode but not discharged. These ions form an oppositely charged cloud of ions around the electrode and serve to neutralize it and prevent it from attracting the reducible ions. Since migration thus is greatly reduced, the ions must reach the electrode almost entirely by the process of diffusion. The rate of diffusion is proportional to the concentration; consequently, the diffusion current is proportional to the concentration of the reducible ion.

The half-wave potential is characteristic of the substance being electrolyzed and gives to polarography its qualitative nature. It can be defined as the point on the current voltage curve which is midway between the projections of the residual current and the limiting current lines. The half-wave potential is a function of the nature of the reduced or oxidized material, of the nature and concentration of the supporting electrolyte, of the reference electrode used, and to a very small extent, the temperature. In certain cases it may also be a function of the concentration of the ion being determined. If the half-wave potentials are to be meaningful, all of these conditions must be reported.

The decomposition potential is located at the intersection of the

extrapolated residual current and wave-front lines.

As the potential across the cell is increased, a point is eventually reached at which the ions of the supporting or carrier electrolyte begin to discharge at the reference electrode. Due to the relatively high concentration of the carrier ions, the current rises quite rapidly with further increases of voltage. In some cases, and particularly at solid microelectrodes, the carrier wave may not actually be due to the electrolysis of the carrier electrolyte, but instead may be due to the electrolysis of solvent molecules.

Amperometric Titrations

The polarographic method can be used as the basis of an electrometric titration. In this case, the voltage applied across the indicator electrode and the reference electrode is kept constant and the current passing through the cell is measured and plotted against the volume of reagent added; hence the name **amperometric titration**.

In amperometric titrations, the current is measured on the diffusion current region of the current-voltage curve. In such a region, the current is largely independent of the potential of the indicator electrode and is proportional to the remaining concentration of diffusing substance in the solution. The currents are measured after each addition of reagent. If a complete polarogram is made after each addition of reagent, a series of waves like the ones in Figure 3 is obtained.

When the volume change is appreciable during the titration, the end point is sometimes less easy to locate due to flattening of the angle of intersection and the curvature of the lines. In such cases

results can be improved by multiplying the individual current readings
by a correction factor.

$$i_{correct} = i_{measured} \frac{(V+v)}{V}$$

where $\underline{V}$ is the original volume of the solution and $\underline{v}$ is the total volume
of titrant added in order to obtain the measured current reading.
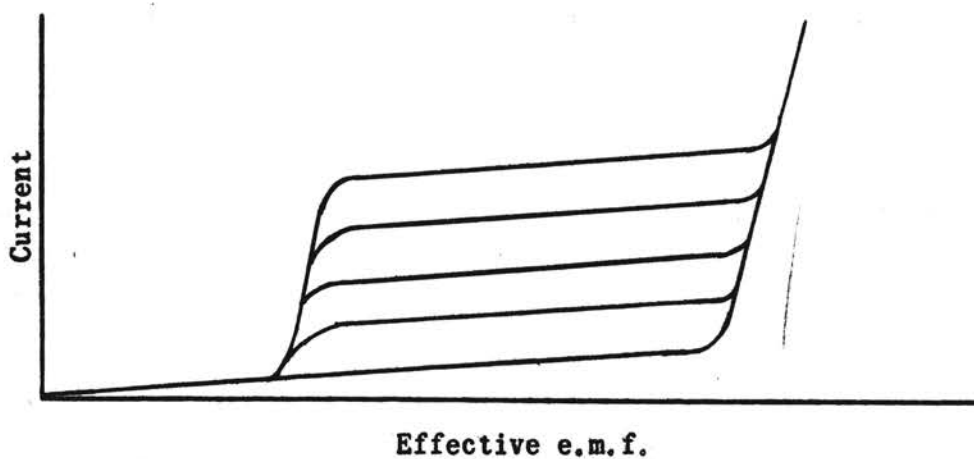
Figure 3.   Illustration of Amperometric Titration

We may distinguish between different types of titration graphs de-
pending upon whether the substance being titrated, or the reagent, or
both are reducible or oxidizable at the applied e.m.f. used.   Consider
the titration of a substance A with reagent B which removes A from the
solution by precipitation, complex formation, oxidation, or reduction.
The following are examples of types of curves obtained.

(a)   Substance A yields a diffusion current while reagent B does
not.   Upon addition of B, the diffusion current decreases continuously
until the equivalence point is reached.   At this point, the curve levels
off and the current remains constant with further addition of B.   The
end point is determined by the point of intersection of the two straight
lines.

(b)   Substance A is not reduced or oxidized at the microelectrode but the reagent B yields a diffusion current. In this case, only a residual current is observed until an excess of B is added. After the equivalence point, the excess B is electrolyzed at the reference electrode and the current rises rapidly. A current is obtained which is proportional to the concentration of the excess B.

(c)   Both substance A and B give diffusion currents at the same applied e.m.f. The diffusion current falls with the addition of reagent B until the equivalence point is reached. At this point the current again begins to rise.

(d)   Substance A gives an anodic diffusion current at the same potential as that at which B gives a cathodic diffusion current. A titration curve of this type is practically a straight line, although a slight change in slope usually occurs at the equivalence point.

Volume of Titrant
(a)

Volume of Titrant
(b)

Volume of Titrant
(c)

Zero current line

Volume of Titrant
(d)
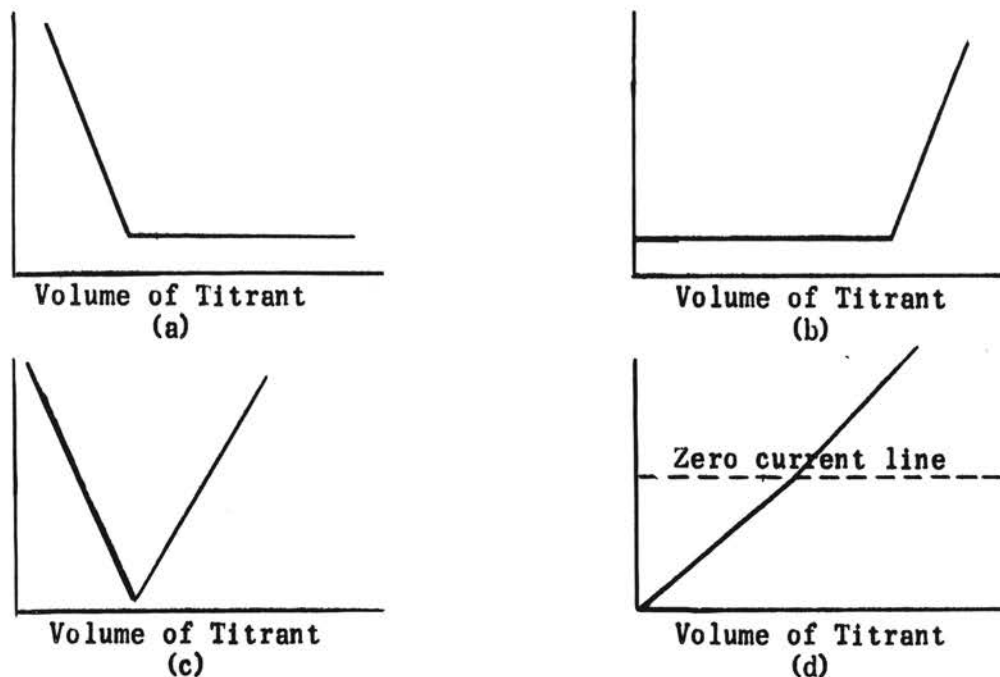
Figure 4. Four Common Amperometric Titration Curves

In some cases, it will be observed that there is a curvature in the current-volume plot in the region of the end point. This is commonly due to the slight dissolving of a very slightly soluble precipitate or to the formation of an unstable complex during the titration. In this case, the end point is determined by the point of intersection of the extrapolated straight line portions of the curve.

CHAPTER II

HISTORICAL

In 1903 Kucera (29) constructed a dropping mercury electrode for the purpose of studying the electrocapillary curve of mercury in various electrolyte solutions. During the course of his investigations, he observed certain peculiar inflections in the curve when a reducible substance was present. It was his suggestion that further studies be made of these peculiarities that prompted Heyrovsky (14, 15) to begin the investigations that led him to the development of the polarograph.

The first polarograms were made by hand plotting but in 1925 Heyrovsky and Shikata (18) constructed an automatic instrument for doing this, calling the instrument a _polarograph_. With their instrument the current-voltage curves were recorded photographically. They named the curves which they obtained _polarograms_.

The principle underlying amperometric titrations was mentioned as early as 1897 by Salomon (47, 48) and later by Nernst and Merriam (43). Salomon described the amperometric titration of chloride with silver nitrate. Heyrovsky and Berezicky (16) used a depolarizing anode and the dropping mercury electrode as an indicator electrode in the titration of barium with sulfate. He suggested the name "polarographic titrations" for this new method of analysis. Majer (39), discussing the titration of lead with sulfate, coined the term "polarometric titrations." In 1939, Kolthoff and Pan (28) reported the titration of lead with

chromate and proposed the now generally accepted name "amperometric ti-
trations."

Nejedly (42) studied the diffusion currents of several metal ions
at the dropping mercury electrode and found that they increased at a
rate of about 2 percent for each degree of temperature rise.

Ilkovic (19) derived an equation, on a purely theoretical basis,
for the diffusion current in terms of the concentration of the reducible
substance, its characteristic diffusion coefficient, the amount of mer-
cury flowing from the capillary per second and the drop time. The fol-
lowing is the original Ilkovic equation.

$$i_d = 0.627 \ nFD^{1/2}Cm^{2/3}t^{1/6}$$

In this equation, the diffusion current is expressed in amperes,
n is the number of faradays of electricity required for the electrore-
duction of one mole of the substance in question, F is the faraday
(96,000 coulombs), D is the diffusion coefficient of the reducible sub-
stance in cm.^{2} sec.$^{-1}$, C is the concentration of the reducible substance
in moles per ml., m is the weight of mercury in grams flowing from the
dropping mercury electrode capillary per second, and t the time in
seconds for the formation of each drop. It was shown that experimental
results were essentially in agreement with the derived equation (33, 37).
The following is a rearranged form of the Ilkovic equation, with I repre-
senting the diffusion current constant.

$$I = \frac{i_d}{Cm^{2/3}t^{1/6}}$$

In spite of the general agreement of the Ilkovic equation with ex-
perimental results, the equation did not account completely for the

observed variations of the diffusion current constant with the character-
istics of the D.M.E. It was found later (34, 50) that the fault of the
equation was due to the neglect of the curvature of the electrode sur-
face in the derivation of the equation.

It is evident from the Ilkovic equation that, with all other factors
constant, the diffusion current of a given reducible substance should
be directly proportional to its concentration.

$$i_d = KC$$

This simple linear relation is the basis of quantitative polaro -
graphic analysis.

Heyrovsky and Ilkovic (17) have shown that the potential at any
point on the rising portion of the polarographic wave is given by the
equation:

$$E_{de} = E_{1/2} - \frac{0.0591}{n} \log \frac{i}{i_d - i} \, .$$

where: E_{de} is the potential of the microelectrode at any point on
           the wave,

        $E_{1/2}$ is the half-wave potential,

        n is the number of electrons per ion taking part in
               the electrode reaction,

        i is the current measured at the potential E_{de},

        i_d is the diffusion current.

It can be seen from the above equation that for a polarographic
wave at 25°C., a plot of E_{de} versus log i/i_d - i should be a straight
line with a slope of -0.0591/n. It can also be seen that the point at
which the log term becomes zero corresponds to the half-wave potential.
One of the most valuable theoretical aspects of this curve is the slope,

since it is possible to calculate from it the value of "n". This is very important since it often explains the nature of the electrode reaction taking place. If the electrode process is irreversible or if the current is controlled by other than diffusion, the "n" values calculated are not whole numbers.

Despite the many advantages of the dropping mercury electrode, there are ways in which other electrodes might be better. The formation of the drop itself, with the current increasing as the drop grows, causes the current-voltage curve to contain oscillations. It is necessary to plot the averages of these oscillations in order to get a smooth polarographic curve. In addition, the oxidation potential of mercury is low which makes it unsuitable for most anodic work.

Many schemes have been tried in an attempt to overcome these disadvantages. Some involve the alteration of the design of the mercury microelectrode, while others use materials other than mercury for the electrode. Salomon (48) used solid silver electrodes in his early amperometric titration work. Nernst and Merriam (43) were the first to describe current-voltage curves obtained with a rotating platinum electrode.

Laitinen and Kolthoff (30), in an attempt to extend the range of the polarographic method in a positive direction, used an electrode consisting of a platinum wire sealed in a glass tube. Although quantitative results could be obtained to an accuracy of 1 percent at the stationary platinum electrode, the waiting time for the diffusion current to become steady constituted a serious disadvantage to the technique. A two-minute waiting period was needed for the current to become constant after each application of a given voltage and the current-

voltage curves had to be plotted by hand. In later work, Rogers (46) produced further experimental evidence showing the unsatisfactory behavior of this type of electrode. Thus, when polarograms for the reduction of silver ions from a 0.1 molar potassium nitrate solution were made automatically, a pronounced maximum in the polarographic wave was observed. It was discovered that a maximum of this type was produced because the rate at which the system reached diffusion equilibrium was slower than the rate of change of the applied potential. To overcome this difficulty, Kolthoff and Laitinen (31) rotated the platinum electrode at a constant speed of about 600 revolutions per minute, finding that with this technique the waiting period which had been required before was no longer necessary. Cooke (10) has reported success in the automatic recording of current-voltage curves of cobalt and cadmium with a rotating amalgamated silver electrode. Lindsey (32) has reported the use of a vibrating platinum electrode in which the electrode vibrates in a vertical plane at constant frequency and with the amplitude greater than its linear dimensions. Kolthoff and Jordan (26) reported that the rotating gold electrode was useful over a wider range of potential than one of platinum. Lord (36) also studied the rotating gold electrode along with other electrodes of platinum and of graphite.

Although the solid microelectrodes have the advantages of greater anodic range and the elimination of the oscillations due to the formation of mercury drops, they also have several disadvantages. One of these disadvantages is their low hydrogen overvoltage which severely limits their cathodic range. Another is the formation of electrolysis products on the surface of the electrode, these deposits often causing erratic results. Miller (40) overcame part of this difficulty by

stripping off any deposited reduction product after each reading. He did this by applying the desired potential and making the measurement and then reversing the potential to clean the electrode before again taking another reading with it.

Although water has been the solvent most commonly used in polarography, a large volume of work has been done using mixtures of organic solvents and water. Kolthoff and Pan (28) suggested an alcohol-water mixture for the amperometric titration of sulfate ion with lead ion, the purpose of the alcohol in this mixture being to suppress the solubility of the lead sulfate formed during the titration. Kolthoff and Harris (25) developed a method for the titration of mercaptans in 95 percent ethanol with an aqueous solution of silver nitrate. Kolthoff and Bovey (24) reported the titration of styrene in a 75 percent methanol solution with potassium bromate, while the titration of olefins with bromine was reported by Braae (9).

In spite of the great deal of work which has been done with mixtures of water and organic solvents, that done in anhydrous organic solvents has been relatively small. Glacial acetic acid was one of the earliest anhydrous solvents used. MacGillavry (38) reported its use as a polarographic solvent in 1936, although the results he obtained were very unsatisfactory. Bachman and Astle (6, 7) later obtained very good polarographic waves for a number of inorganic metal ions in anhydrous acetic acid. They reported that the degassing of the solution was a very critical step with determinations in this solvent. Long periods of degassing with nitrogen were required to prevent interference from dissolved oxygen. Bergman and James (8) also used this solvent to determine a large number of nitro compounds while Arthur and Lyons (4) used it for the

determination of lead and cadmium.

A number of polarographic determinations have been performed using low molecular weight alcohols as solvents. Allison (1) was able to obtain polarographic waves for lead in methanol. He found that the presence of dissolved oxygen in the solution interfered with the determination. This dissolved oxygen could be removed by degassing with nitrogen which had been bubbled through one or more gas washing bottles filled with an alkaline solution of pyrogallic acid. The purpose of this treatment was to remove any oxygen that might be present in the tank nitrogen. Kikichi, Sakagachi and Honda (23) were able to determine p-nitrosodiethylaniline in ethanol, while Hans and von Strum (12, 13) obtained polarographic waves for copper in methanol, ethanol, 1-butanol and 1-pentanol, although it was necessary to plot the curves manually to correct for iR-drop. Vleck (51) was able to make determinations of several strong acids in ethanol, while Zumam, Zumanova, and Soucek (53) used ethanol as a solvent in the determination of CS_2.

A number of other solvents, such as formamide, pyridine, tetrahydrofuran, liquid ammonia, acetonitrile and sulfuric acid, have been used also in polarographic work, mixtures of various organic solvents likewise having been used.

High Resistance Polarography

In ordinary polarography, the current is plotted against the voltage applied to the cell. Actually what should be plotted is the effective voltage, but since the resistance across the cell normally is not high and the currents usually are very small, the conventional technique, applied to aqueous solutions, does not introduce any appreciable error.

As long as the cell resistance is low, the iR-drop is negligible and the difference between applied voltage and effective voltage is insignificant. When the cell resistance is high, on the other hand, a certain amount of error is introduced and the curve obtained is badly distorted. If the cell resistance is known, the curve may be corrected for iR-drop and the effective potential may be determined by the following equation.

$$E_{eff} = E_{app} - iR$$

where i is the current at the applied voltage, R is the resistance of the cell and circuit, and E_{eff} and E_{app} are the effective and applied voltages. If either the cell resistance or the current becomes extremely large, the curve may become so distorted that the polarographic waves are not recognizable.

Several methods have been devised to compensate for iR-drop automatically. Nicholson (44) reported a method of compensation in which an auxiliary bridge, operated by the pen chart circuit, was connected in series with the cell. This device applied to the cell a corrective voltage which was equal and opposite to the iR-drop. Arthur (3, 35) approached the problem by devising a polarograph which plots the current against the actual effective voltage. Jackson and Elving (20) have reported a compensator in which a standard resistor is placed in series with the polarographic cell and the iR-drop across the resistor is made equal to the iR-drop across the cell by amplification. The amplifier output is placed in series with the applied voltage from the bridge and thereby compensates for the iR-drop within the cell. Sawyer, Pecsok and Jensen (49) have reported the development of an iR-compensating polarograph which is similar in principle to the instrument developed by Arthur. Kelly (22) and Oka (45) have also reported instruments which

compensate for iR-drop.

Recently Arthur (5) has developed a compensator which can be used with almost any conventional polarograph. This compensator requires the use of a polarographic cell containing two calomel electrodes and the usual microelectrode. One of the calomel electrodes serves as the electrolysis reference electrode (E.R.E.) while the second calomel electrode serves as a stable reference electrode (S.R.E.). It is this second reference electrode against which the effective voltage of the microelectrode is measured. The following is a schematic diagram of a polarograph using this type of compensator.
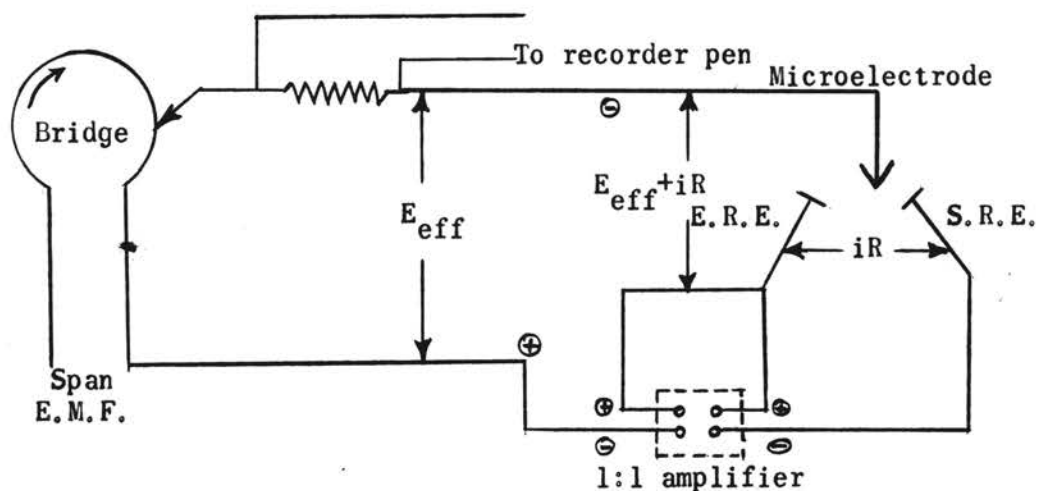
Figure 5. Schematic Diagram of High Resistance Polarograph

As can be seen from the diagram, the potential difference between the electrolysis reference electrode and the microelectrode is equal to the effective voltage plus the iR-drop. The difference of potential between the stable reference electrode and the microelectrode is equal to the effective voltage. It is apparent then that the potential difference between the S.R.E. and the E.R.E. is numerically equal to the iR-drop within the electrolysis branch of the cell.

The two reference electrodes are connected, as shown, to a 1:1 amplifier of very high input impedance. The output of this amplifier is connected in series with the E.M.F. applied by the bridge of the polarograph. Since the output from this amplifier is equal and opposite to the $i\underline{R}$-drop within the cell, compensation is achieved.

CHAPTER III

SCOPE OF INVESTIGATION

The purpose of this investigation was to study the behavior of rotating solid microelectrodes in nonaqueous solvents. It was hoped that by using anhydrous alcohols in place of the usual aqueous medium, an extension of the useful cathodic range might be obtained. Another purpose of this investigation was to study the nature and behavior of polarographic waves obtained in nonaqueous solvents with these electrodes.

The investigation was mostly of an exploratory nature since no studies of this type have previously been reported.

CHAPTER IV

APPARATUS

The polarograph used in this investigation was a Sargent Model XXI.
All work was performed using the $\underline{iR}$-compensator developed by Arthur (5)
and described in Chapter II.

The polarographic cell used in this work was designed by Doctor
Arthur and is shown in Figure 6. The electrolysis reference electrode
(E.R.E.) and the stable reference electrode (S.R.E.) were both aqueous
saturated calomel electrodes. The salt bridges, contained in the cell,
consisted of small asbestos fibers sealed in the glass between the calo-
mel cells and the electrolysis cell. The resistance of these salt
bridges was found to be about 30,000 ohms each. It was found that as
long as the liquid level in the electrolysis cell was kept above that
of the reference electrode cells, no diffusion was observed to take place
into the electrolysis cell.

As is shown in Figure 7, the calomel electrodes are separate units
from the polarographic cell itself. With this arrangement, it was pos-
sible to completely degas the solution before any liquid was added to
the calomel cell holders. To connect the calomel cells it was then
only necessary to add a small amount of saturated KCl to the calomel
cell holders and insert the cells. The purpose of the additional satu-
rated KCl was to make electrical contact with the salt bridges. The
calomel cells were never inserted until just before the polarograms

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$\dfrac{45}{50}$ Standard taper

$\dfrac{24}{40}$ Standard taper

Openings for gas dispersion tube, thermometer, and burette

$\dfrac{29}{42}$ Standard taper

Asbestos fiber salt bridges
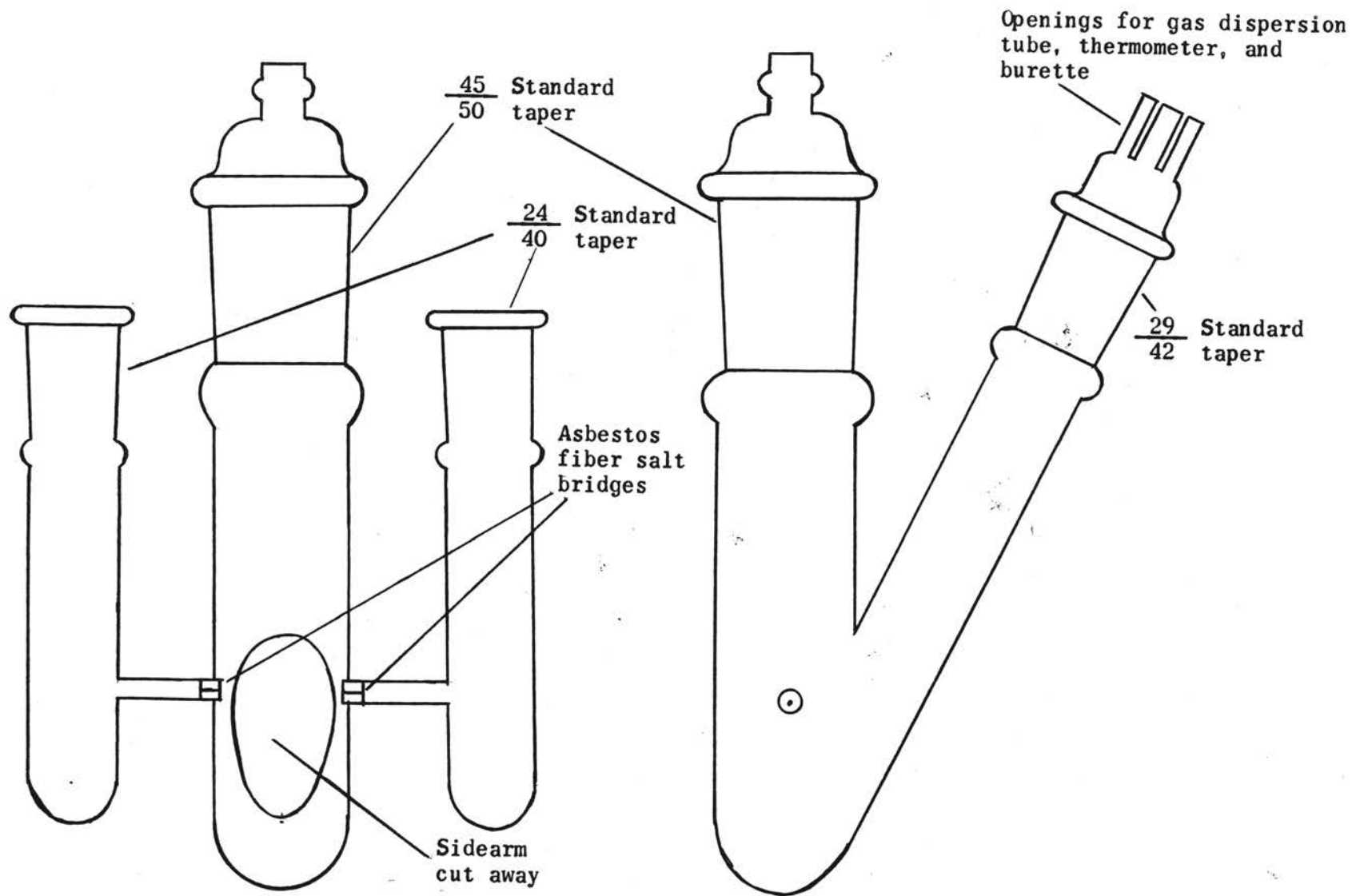
Sidearm cut away

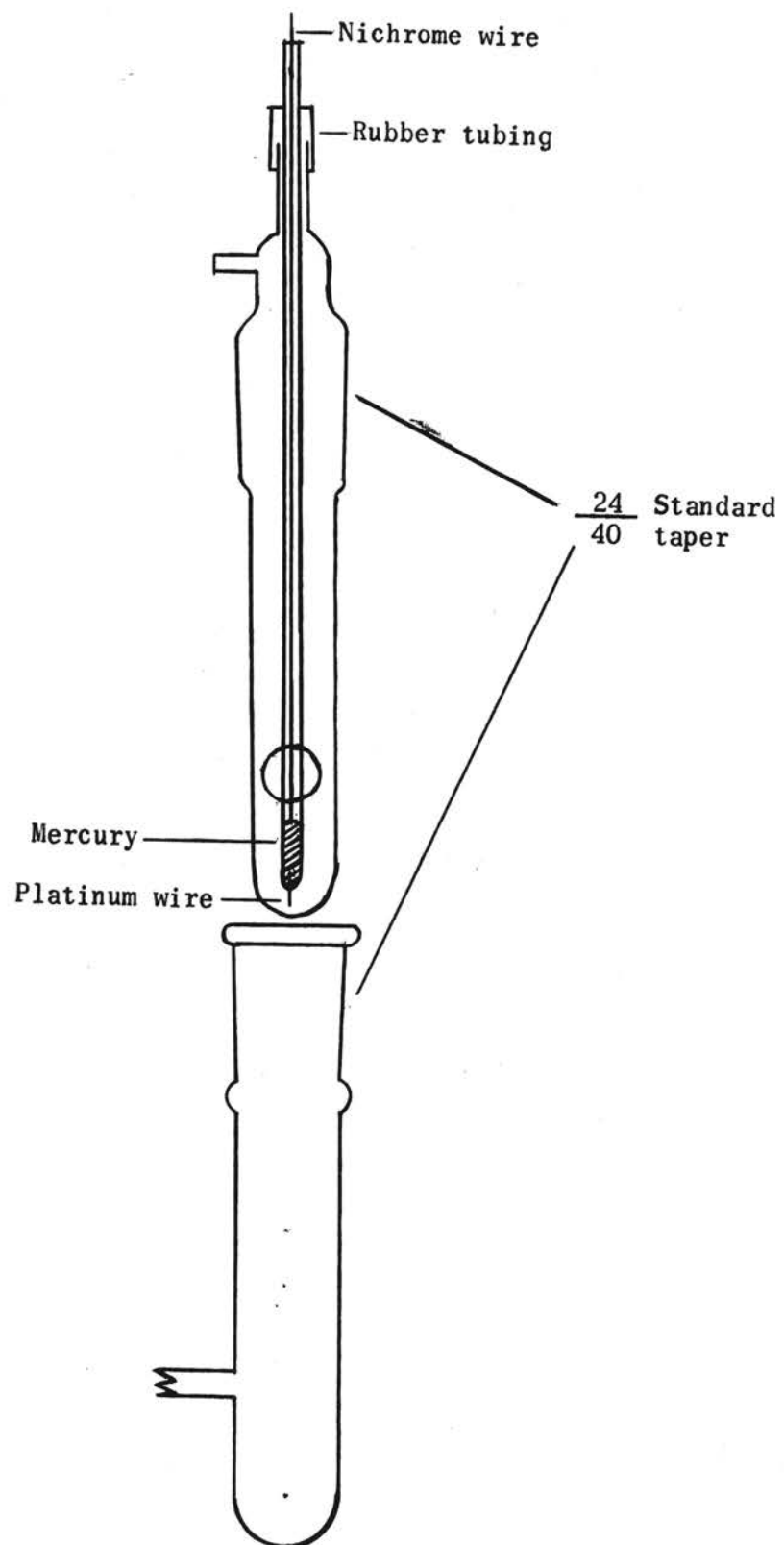Figure 6. Polarographic Cell

Figure 7. Calomel Cell and Cell Holder

were made. By following this procedure, any diffusion which might have taken place was held to an absolute minimum.

A Beckman pH meter, Model H2, was used for determining the end point in a number of acid-base standardization titrations.

Two microburettes were used in the amperometric titrations. The larger had a capacity of 10 ml. and was graduated every .02 ml. The smaller held only 2 ml. and was graduated every .01 ml. It was possible, with the smaller burette, to estimate to the nearest .001 ml.

A Sargent potentiometer, Catalog Number S-30260, was used for accurate checks of the potential being applied by the bridge of the polarograph. The potentiometer was calibrated against a standard cell contained in the potentiometer itself.

Several types of microelectrodes were employed in this investigation. These included platinum, gold, gold amalgam, and silver amalgam. All electrodes were prepared by sealing short pieces of wire, of the desired material, into the side of a piece of soft glass tubing. The electrodes were carefully annealed, then the glass tubes were mounted on the rotating electrode shaft as shown in Figure 8 and sealed to the shaft with a small amount of ceresin wax.

The gold electrode was about 1 mm. in diameter and extended for about .5 mm. from the glass tube in which it was sealed.

The platinum electrode was about .4 mm. in diameter and extended for 1 mm. from the wall of the glass tube.

The gold amalgam electrode was prepared by electroplating a layer of gold onto the platinum electrode. The electrode was then amalgamated by electroplating a layer of mercury from a mercuric chloride solution.

The silver amalgam electrode was made by sealing a silver wire, which
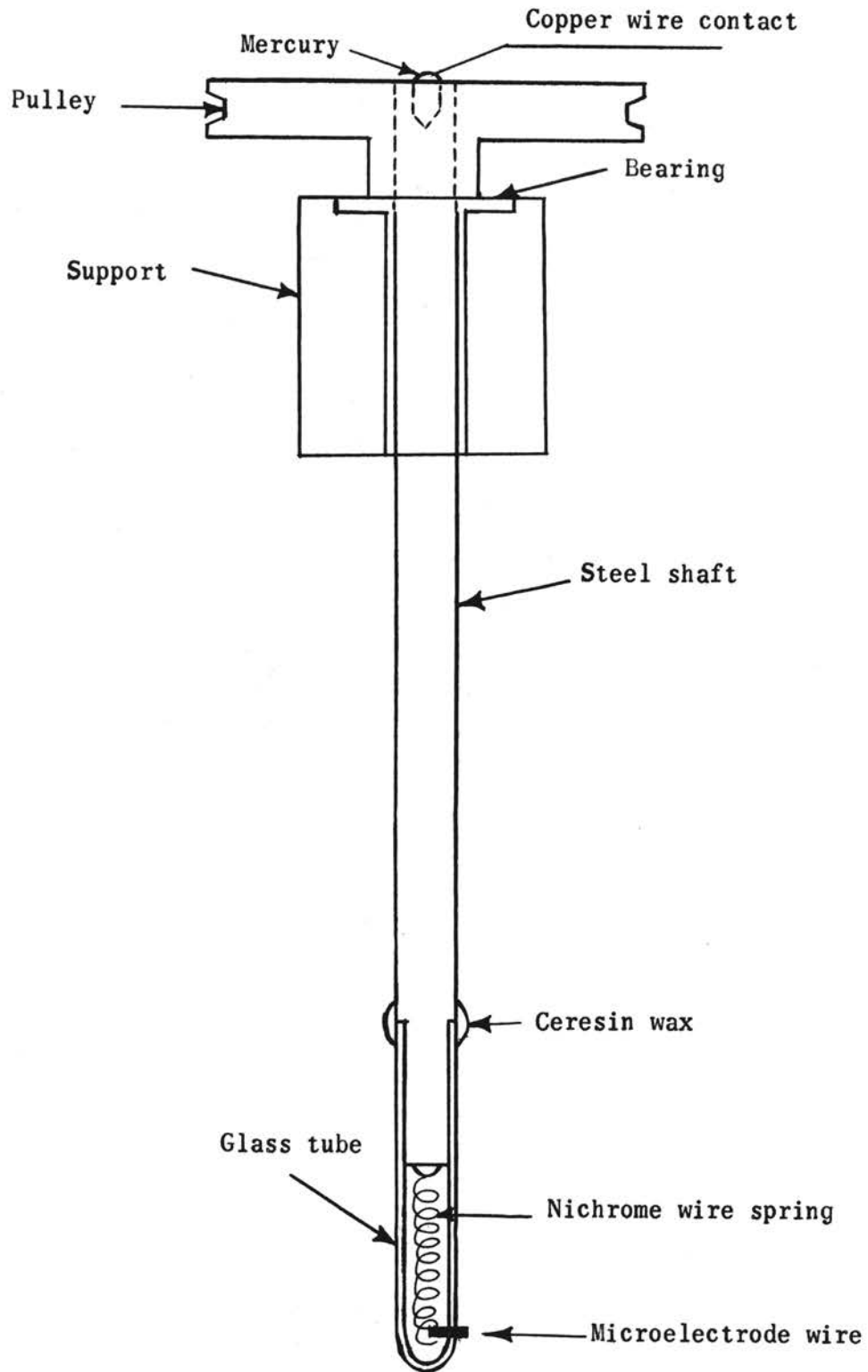
Figure 8. Rotating Microelectrode Assembly

was about .4 mm. in diameter, into the side of a piece of soft glass tubing. This electrode, which extended about 1 mm. from the side of the tube, was then amalgamated by dipping it into a small amount of mercury. This method of amalgamation had been previously recommended by Cooke (10).

The shaft, on which the glass tube was mounted, was rotated at a speed of 600 r.p.m. by a 0.05 h.p. Delco motor. The motor speed of 1725 r.p.m. was reduced to the desired 600 r.p.m. by appropriate pulleys.

CHAPTER V

REAGENTS

Acetic Acid - DuPont reagent grade was used without further purification.

Ammonia - Anhydrous Matheson reagent grade was used without further purification.

Benzil - Matheson, Coleman and Bell white label grade was used without further purification.

n-Butyl Alcohol - Fisher Scientific reagent grade was used after being redistilled in the presence of KOH.

n-Butylamine - Fisher Scientific reagent grade was used without further purification.

Cadmium Chloride - Baker and Adamson reagent grade was used without further purification.

Cetyldimethylethylammonium Bromide - Matheson, Coleman and Bell Tech. grade was used without further purification.

Chromic Sulfate - Mallinckrodt analytical reagent grade $Cr_2(SO_4)_3 \cdot XH_2O$ was used without further purification.

Copper Metal - Baker and Adamson reagent grade was used without further purification.

Cupric Chloride - Baker and Adamson reagent grade was used without further purification.

Ethanol - U. S. Industrial Chemicals Co. reagent grade was used after being redistilled in the presence of KOH.

Ethylamine Hydrochloride - Eastman Kodak white label grade was used without further purification.

Ferric Nitrate - Merck reagent grade was used without further purification.

n-Hexyl Alcohol - Eastman Kodak practical grade was used after being redistilled in the presence of KOH.

Iodine - Fisher Scientific reagent grade was used after being resublimed in the presence of potassium iodide.

Lead Chloride - Fisher Scientific reagent grade was used without further purification.

Lithium Chloride - Mallinckrodt analytical reagent grade was used after being dried in oven at $115^{o}C$.

Lithium Iodide - Mallinckrodt white label was used after being dried in the oven at $115^{o}C$.

Lithium Nitrate - Fisher Scientific reagent grade was used after being dried in the oven at $115^{o}C$.

Mercuric Chloride - Merck reagent grade was used without further purification.

Mercurous Chloride - Fisher Scientific reagent grade was used without further purification.

Methyl Alcohol - Fisher Scientific reagent grade was used after being redistilled in the presence of KOH.

Methylamine Hydrochloride - Eastman Kodak white label grade was used without further purification.

Methyl Orange - Baker and Adamson reagent grade was used without

further purification.

2-Naphthalenesulfonic acid — Eastman Kodak white label grade was used without further purification.

Nitrogen — Linde laboratory grade nitrogen was used after being passed through two towers of chromous sulfate-sulfuric acid-amalgamated zinc, a column of glass wool, a column of calcium sulfate drying agent, and a presaturator tower filled with the solvent system. The chromous sulfate scrubbers are similar to those described by Altieri (2). The exact method of their preparation has been described by Jones (21).

n-Octanol — Eastman Kodak white label grade was used after being redistilled in the presence of KOH.

2-Pentanone — Matheson, Coleman and Bell white label grade was used after being redistilled in the presence of KOH.

Potassium Carbonate — Fisher Scientific reagent grade was used without further purification.

Potassium Chloride — Fisher Scientific reagent grade was used with-further purification.

Potassium Hydroxide — Fisher Scientific reagent grade was used without further purification.

Potassium Iodide — Baker and Adamson reagent grade was used without further purification.

2-Propanol — Fisher Scientific reagent grade was used after being redistilled in the presence of KOH.

Quinone — Fisher Scientific reagent grade was used after being twice recrystallized from hot water.

Silver Carbonate — Fisher Scientific reagent grade used without further purification.

Silver Nitrate - Mallinckrodt analytical reagent grade was used without further purification.

Sodium Borate - Mallinckrodt analytical reagent grade was used without further purification.

Sodium Hydroxide - Fisher Scientific reagent grade was used without further purification.

Sodium Iodide - Mallinckrodt analytical reagent grade was used without further purification.

Sodium Thiosulfate - Mallinckrodt white label grade was used without further purification.

Stannic Chloride - Merck reagent grade was used without further purification.

Sulfuric Acid - Fisher Scientific reagent grade was used without further purification.

Tenamene 60 - This Eastman Kodak product was used without further purification.

Tetra-n-butylammonium Iodide - From stock on hand prepared by Lloyd (35) was used without further purification.

Tetramethylammonium Chloride - Matheson practical grade was used after being recrystallized from an acetone-methanol solution.

Thallium Nitrate - City Chemical Corporation C.P. grade was used without further purification.

Urea - Merck reagent grade was used without further purification.

Zinc Chloride - Mallinckrodt analytical reagent grade was used without further purification.

Zinc Metal - Fisher Scientific (mossy) reagent grade was used without further purification.

CHAPTER VI

EXPERIMENTATION AND DISCUSSION

Cathodic Range. Although a great deal of work has been done with rotating microelectrodes, their application to nonaqueous polarography has been very limited. One purpose of this investigation was to determine if the cathodic range of the rotating solid electrodes might be extended through the use of nonaqueous solvents. It was also desired to study the behavior of polarographic waves obtained under these conditions.

When the rotating platinum electrode is used in aqueous solutions, its cathodic range is much less than that of the dropping mercury electrode. This is due to the fact that hydrogen is evolved at a much lower potential from platinum than from mercury. Due to the unusually large overvoltage of hydrogen at mercury surfaces, when the dropping mercury electrode is used the supporting electrolyte is usually electrolyzed before any electrolysis of the solvent takes place. It was hoped that by using certain alcohols as solvents, low-voltage evolution of hydrogen at the platinum electrode might be prevented.

The first step in this investigation was to determine the cathodic range of the rotating platinum electrode in a 0.1M solution of $LiNO_3$ in 2-propanol. The range was determined by measuring the decomposition potential of the solution. The decomposition potential was found to be greater than for an aqueous solution, but when duplicate runs were

attempted variations in the curves were observed, no two duplicate runs being exactly alike. As the number of duplicate runs increased, the magnitude of the irregularities grew larger. These irregularities consisted of a rather pronounced bump in the residual current line at about + 0.1 volts and a small wave just preceding the carrier wave.

When the platinum electrode was replaced with a gold electrode and the runs repeated, it was found that these irregularities were still present.

It was observed that the bump in the residual current line was not present in the first run made after the electrode had been cleaned with nitric acid. On any subsequent runs it was present, providing the previous run had been allowed to continue into the carrier wave. If the polarograph was stopped just before the curve started upward on the carrier wave, duplicate runs could be made without the bump occurring; consequently it appears that this behavior is due to some product collecting on the electrode during the formation of the carrier wave.

An attempt was then made to determine the nature of the small wave that occurred just before the carrier wave. The thought occurred that it might be due to a trace of water in the alcohol. To check this a portion of 2-propanol was shaken with K_2CO_3 and allowed to stand overnight in its presence. It was then redistilled and used for a series of runs. The drying of the alcohol had no effect on the behavior of the polarographic curve. A small amount of water was then added to the solution. This addition failed to give any increase in the height of the wave.

An attempt was then made to determine if the wave was due to impurities in the supporting electrolyte. A small portion of $LiNO_3$ was

recrystallized from hot water, filtered, and dried. This material was then used to prepare a 2-propanol solution which was 0.1M in $LiNO_3$. The curves obtained using this solution exhibited the same irregularities.

LiCl was then substituted for the $LiNO_3$ as the supporting electrolyte. It was found that this eliminated both the small wave and the bump in the residual current line, these results indicating that the small wave which preceded the carrier wave probably was due to an impurity in the $LiNO_3$ which was quite difficult to remove.

Tests with a rotating gold microelectrode indicated that the gold microelectrode was superior to the platinum electrode in two different ways: (1) the curves obtained with it were much less erratic than those obtained with the platinum electrode, and (2) the cathodic voltage range of the gold was somewhat greater. A gold electrode, therefore, was used in a series of runs on a number of different alcohols, each being made 0.1M with LiCl. For each alcohol solution the decomposition potential was determined, as was also the potential at which the current had risen 0.1 μ A. above the extrapolated residual current line. These values are an indication of the useful cathodic voltage range of each solvent. Table I gives the results obtained.

From the decomposition potentials obtained it can be seen that the carrier waves usually begin at more negative potentials with increased molecular weight of the alcohols.

An attempt was made to determine the decomposition potentials of these same alcohols using the rotating gold amalgam electrode. It appeared that the cathodic voltage range was greater than for the gold electrode, but after being used for a short time this electrode exhibied

erratic behavior and had to be re-plated. After the electrode had been re-plated it was found that the decomposition potentials obtained with it were different from those obtained previously. Since a single electrode could not be used for repeated runs, and electrodes could not be prepared whose behavior was the same, there was no point in trying to determine decomposition potentials for a series of solutions.

TABLE I

DECOMPOSITION POTENTIALS AND 0.1 μA POINTS
OF VARIOUS SOLUTIONS OF 0.1M LiCl

Solvent	Decomposition Potential	0.1 μA Point
Water	– 1.46 volts	– 1.27 volts
Methanol	– 1.53 volts	– 1.19 volts
Ethanol	– 1.68 volts	– 1.44 volts
2-Propanol	– 1.68 volts	– 1.51 volts
1-Propanol	– 1.67 volts	– 1.44 volts
1-Butanol	– 1.67 volts	– 1.45 volts
1-Hexanol	– 1.73 volts	– 1.52 volts
1-Octanol	– 1.85 volts	– 1.66 volts

A silver amalgam electrode was then prepared and used to determine the decomposition potential of a 0.1M solution of LiCl in 2-propanol. It was observed that the decomposition potential shifted in a negative direction with repeated runs. This shift was still taking place after twelve duplicate determinations had been made. The silver amalgam electrode was than allowed to stand for twenty four hours in hopes that

the electrode behavior might stabilize. When the tests were then repeated with this electrode, the same behavior was observed. Attempts to determine decomposition potentials with this electrode were then abandoned.

In the first experiment, a polarogram of 0.1M solution of tetramethylammonium chloride in 2-propanol was made. The decomposition potential of this solution was found to be -2.08 volts -- a large increase over the value obtained for a 0.1M solution of $LiNO_3$ in 2-propanol. This seemed to indicate that the supporting electrolyte is responsible for the carrier wave.

Three solutions of LiCl in 2-propanol, at concentrations of 0.01, 0.1, and 1.0 molar, were then prepared. When polarograms were made of these solutions, it was found that the decomposition potentials decreased with increased concentration of supporting electrolyte. This is further evidence that the carrier wave is the result of the reduction of the supporting electrolyte.

Additional evidence was obtained by making polarograms of 0.1M solutions of NaI, LiI, and tetrabutylammonium iodide in 2-propanol. Potassium iodide would have been included but was found to be too insoluble to prepare a solution of this concentration. The following decomposition potentials were obtained for the three solutions.

NaI - - - - - - - - - - - - - - - - - - - 1.51 volts

LiI - - - - - - - - - - - - - - - - - - - 1.77 volts

Tetrabutylammonium iodide - - - - - - - - - 1.96 volts

As can be seen, these decomposition potentials fall in the order in which the respective cations are normally reduced.

Although there is a great deal of evidence that the carrier wave is largely a result of the reduction of the supporting electrolyte,

the fact remains that the type of solvent also influences the decomposition potential. It seems possible that this might be due to the cations of the supporting electrolyte forming different solvation products in the different alcohols. These differently solvated cations would be expected to have different decomposition potentials.

Cathodic Waves for Various Substances. In this part of the research, a study was made of the polarographic waves obtained for a number of substances in 2-propanol with various rotating microelectrodes.

It was found that $PbCl_2$ was too insoluble in 2-propanol to dissolve in quantities large enough to produce polarographic waves. Lead nitrate was also found to be insoluble.

Polarographic waves for 10^{-3}M solutions of $CdCl_2$ in 2-propanol, 0.1 M with LiCl, were obtained at platinum, gold amalgam, and silver amalgam electrodes. It was found that the rotating platinum electrode produces a well-formed polarographic wave up to the point at the top of the cadmium wave where the curve normally begins to level off. At this point, the diffusion current begins to decrease rapidly with increased voltage. Repeated runs with this electrode, in the same solution, produced progressively smaller wave heights as if some sort of reduction product were forming on the surface of the electrode and partly blocking the electrode reaction.

The gold amalgam electrode was found to have a tendency to produce two distinct polarographic waves for cadmium, this type of behavior being especially pronounced in ethanol. In ethanol the first wave was well formed and had a half-wave potential of -0.68 volts. The second wave, however, was rather erratic and not very reproducible and ex-

hibited the same type of dip as that which was observed previously for cadmium at the platinum electrode.

With the silver amalgam electrode, it was observed that after the occurrence of the characteristic cadmium wave, the limiting current line failed to level off and began to rise rapidly. This behavior makes it impossible to determine the diffusion current of the wave.

Polarographic waves for stannic and thallous ions were also obtained with the rotating platinum electrode. A solution of 0.1M LiCl in 2-propanol was used as the solvent, the sources of the stannic and thallous ions being stannic chloride and thallium nitrate, respectively. In both cases, dips in the waves very much like the ones observed for cadmium were observed. It was found likewise that if the voltage was held constant after a point on top of the wave was reached, the diffusion current decreased as a function of time. This is further evidence that the dip observed is the result of the formation of reduction products on the surface of the electrode.

The rotating platinum electrode was used to obtain a polarographic wave for copper. Copper waves were obtained in both 2-propanol and methanol. The source of the cupric ion was $CuCl_2 \cdot 2H_2O$. In these studies it was necessary to use 0.1M $LiNO_3$ as the supporting electrolyte, since the half-wave potential of the copper occurs at such a positive potential that the chloride ions from the LiCl might be oxidized at the microelectrode. In 2-propanol, the cupric ion gave two distinct waves. The half-wave potential of the first was + .48 volts while that of the second was about -.30 volts. Two copper waves were also observed in methanol, but the half-wave potentials in this case were a great deal different, that for the first wave being + .20 volts while that for the second was about

- .25 volts. This large shift in the half wave potential seems to indicate that a different complex or solvated form of the cupric ion is responsible for the waves in each case.

In order to study the nature of the electrode reaction, the equation on page 12 was used to calculate the number of electrons per ion taking part in the first step of the electrolysis of the cupric ion. The value of "n" calculated for the reduction of the cupric ion to the cuprous state was 0.506 electrons. This intermediate value indicates that the electrode reaction is not purely diffusion controlled, but is either a rate controlled process or is thermodynamically irreversible.

Polarographic waves were also obtained for copper in 2-propanol using the gold electrode. It was found that in this case the first wave was rather poorly formed and indistinct, while the second wave was quite normal. If the voltage was held constant just after the upper plateau of the second wave was reached, it was found that the diffusion current did not decrease to any extent with time unless the concentration was greater than 6×10^{-4} M. Above this concentration a certain amount of decrease in the diffusion current did take place.

A polarographic wave for silver was also obtained using the rotating gold electrode in a solution of 0.1M LiNO$_3$ in 2-propanol. The half-wave potential of the silver wave varied a great deal with the condition of the gold electrode. Thus the first polarographic wave obtained had a half-wave potential of + .33 volts; but as duplicate runs were made, the half-wave potential shifted slowly to a value of + .28 volts. When the electrode was cleaned with nitric acid and a second run made, the half-wave potential obtained shifted back to + .37 volts. The waves obtained, however, were quite well formed, and when the voltage was held constant

on top of the wave, only a slight decrease in diffusion current was observed.

An electrode coating effect was observed in all waves which were the result of a metal ion being reduced to its metallic state. In some cases this decrease in diffusion current with time was only noticeable with higher concentrations. Up to a concentration of about 6×10^{-4}M the cupric and silver ions produced polarograms of normal appearance, but all other cations tested exhibited definite dips in their polarographic waves before their concentrations were this high.

Polarographic waves were obtained for iodine with both the platinum and gold electrodes. These waves were obtained in a 2-propanol solution which was 0.1M with $LiNO_3$. It was found that the iodine wave always possessed an anodic portion. This is probably due to some of the iodine being reduced to the iodide after it is added to the solution, for it was observed that the anodic portion of the wave became larger as the age of the solution increased. A small amount of Ag_2CO_3 was added to one of the iodine solutions in hopes that the iodide present might be precipitated as AgI and the anodic portion of the wave eliminated. It was found, however, that this removed not only the iodide but also the iodine.

Different types of waves were observed when gold and platinum electrodes were used with iodine. The platinum electrode produced a single smooth wave which included both cathodic and anodic portions. The gold electrode produced two distinct waves. One wave consisted of the anodic portion of the wave, while the other consisted of the cathodic portion, a very distinct break occurring between the waves. This separation of the iodide-iodine wave by the gold electrode indicates that under these

conditions an irreversible electrode reaction takes place.

Attempts were made also to obtain polarograms of organic compounds.
Benzil was found to produce a very good wave with a half-wave potential
of - 1.00 volts at the rotating gold electrode. The solvent used was
2-propanol and the supporting electrolyte 0.1M LiCl.

A polarographic wave for quinone was also obtained, using a rotat-
ing platinum electrode in a 2-propanol solution which was 0.1M with
$LiNO_3$. At a concentration of $3 \times 10^{-3}M$, the quinone wave was found to
have a half-wave potential of - .27 volts, but the half-wave potential
seemed to shift in a negative direction with increased concentration.
It was observed that if repeated polarograms were made with the same
electrode in the same solution, the wave height steadily decreased, and
that the carrier wave, which would normally occur at about - 1.1 volts,
was completely absent in solutions in which quinone was present. All
these observations are explainable in terms of the formation of insolu-
ble quinone reduction products on the surface of the microelectrode.

A very peculiar behavior was observed in solutions which contained
quinone when cadmium ions were added. When a small amount of $Cd(NO_3)_2$
was added to a solution containing quinone, the quinone wave was com-
pletely eliminated, while the cadmium which was added also failed to
produce a polarographic wave, even when present in very large excesses.
This appears to be an extreme case of electrode coating since even the
residual current is practically eliminated.

The rotating gold microelectrode was used to obtain a polarographic
wave for 2-naphthalenesulfonic acid. The solvent used was 2-propanol
which was 0.1M with LiCl. The half-wave potential of the wave obtain-
ed was found to be partially dependent upon the concentration of the

acid. It was found to vary from - .85 volts for a 1×10^{-4}M solution to - .97 volts for a solution that was 9×10^{-4}M. In this range of concentration, the diffusion current was directly proportional to the concentration.

When LiCl was used as the supporting electrolyte in a 2-propanol solution, it was found that the cathodic range was insufficient to give a complete zinc wave. In an attempt to obtain a complete polarographic wave for zinc, tetramethylammonium chloride was used as the supporting electrolyte. When an anhydrous standard solution of $ZnCl_2$ was added to the solvent and supporting electrolyte, however, a white precipitate quickly formed. It was also found that precipitates were obtained when $CuCl_2$, $CdCl_2$, or $Co(NO_3)_2$ were added to anhydrous solutions of tetra-methylammonium chloride in 2-propanol. These precipitates were solids which could be filtered and dried in the oven at 110°C. Each precipi-tate had a characteristic color. The solid copper complex was yellow, the cadmium and zinc were white, and the cobalt was blue.

It was observed that if a few drops of water were added to the cop-per complex, the precipitate quickly dissolved and the solution took on a green color. This indicated that the complexes were not as stable in aqueous solutions as in the alcoholic medium.

Upon further investigation, it was found that a solid complex of copper had previously been prepared in a similar manner by Wheatly, Bier, and McCormick (52). They reported the formula for this complex to be $\left[(CH_3)_4N\right]_2CuCl_4$.

It seems possible that the formation of the complexes, in anhydrous solutions, might be made the basis of an amperometric titration. A large number of metal ions might be titrated by this method. This point is one

which needs further investigation.

During the course of this investigation, it was observed that the gold electrode sometimes developed erratic behavior which was very difficult to eliminate. This behavior could sometimes be corrected by soaking in nitric acid or by scraping; in other cases it was found that neither of these treatments helped. A method was finally found which very satisfactorily eliminated all erratic behavior which was associated with the electrode itself. This method consisted of connecting the electrode to the positive terminal of a 1½ volt battery and using it for the electrolysis of a concentrated solution of nitric acid. The electrolysis was carried out for about one minute, then the electrode was disconnected and washed carefully. This method was found to be both quick and effective.

Amperometric Titrations

Since a great deal of work had previously been done by Moran (14) and Jones (21) on the amperometric titration of sulfonic acids in nonaqueous solvents, an investigation was made to determine the possibility of using the rotating gold electrode for this type determination. The solvent used was 2-propanol, which was 0.1M in LiCl. In these titrations, 2-naphthalenesulfonic acid was titrated with a standard solution of KOH in 2-propanol. The acid solutions were degassed for one hour before each titration while the titrant was degassed and handled by the method described by Jones (21).

The results obtained were rather unsatisfactory. It was found that no polarographic wave was obtained until the acid concentration had reached about 1×10^{-4}M as if the solvent had neutralized a certain amount of acid. The amount of acid seemingly neutralized was determined by

titrating a standard solution of the sulfonic acid into a solution of the solvent and supporting electrolyte, the diffusion current being determined after each addition of titrant and plotted against the volume of titrant. The line obtained was then extrapolated back to zero current. By this means, it was found that the concentration of supporting electrolyte had no effect on the amount of acid apparently neutralized and that the acid, therefore, was not being neutralized by impurities in the supporting electrolyte.

An attempt was then made to destroy any alkalinity in the alcohol by redistilling it in the presence of a small amount of 85 percent phosphoric acid. This was found to reduce the apparent acid loss, but did not eliminate it entirely.

It was observed that if the concentration of the 2-naphthalenesulfonic acid was above about 5×10^{-4}M, a constant diffusion current could not be obtained. When the voltage was held constant at a point on top of the acid wave, a gradual decrease in diffusion current took place. This behavior severely limits the maximum concentration range of the titration.

Even if the apparent neutralization of the acid could be eliminated, the range of concentrations which could be determined would be very limited. It would be necessary to know the approximate concentration of the sample beforehand in order to adjust its concentration for the titration and this limitation would make the titration impractical in many cases. Since the gold electrode appeared definitely inferior to the dropping mercury electrode used by Jones and Moran for this type of determination, work on this titration was discontinued.

Another amperometric titration which appeared promising was the

titration of amines with silver ion. It had been found previously that
a satisfactory polarographic wave could be obtained for silver. An at-
tempt was first made to standardize the titrant, a solution of $AgNO_3$ in
2-propanol. An amperometric titration was chosen for this standardiza-
tion, the $AgNO_3$ being titrated against a known amount of lithium chloride
dissolved in a 0.1M solution of $LiNO_3$ in 2-propanol. Since the titration
was carried out at an applied E.M.F. of 0.0 volts, no degassing was nec-
essary.

The titration was unsuccessful due to the fact that there was no
distinct break in the titration curve, a smooth curved line being obtain-
ed. It seems possible that this behavior may be due to AgCl, which is
formed during the titration, being somewhat soluble in 2-propanol.

It was then decided to find out if an amperometric titration of
n-butylamine was possible before further attempts were made to standard-
ize the reagents. An approximately 4×10^{-4}M solution of $AgNO_3$ was ti-
trated with a 0.01M solution of n-butylamine in 2-propanol, silver ni-
trate being dissolved in 2-propanol containing 0.1M $LiNO_3$. A complete
polarogram was made after each addition of titrant.

It was found that the height of the silver wave was not reduced by
the addition of the n-butylamine. The only result which was observed
was a slight shift of the half wave potential in a negative direction.
Since a similar shift was observed when repeated runs were made on sil-
ver solutions alone, this shift cannot be used as indicative of complex
formation although normally such an interpretation might be made. In
any case, the results indicated that an amperometric titration of this
type is not possible.

Since amines have already been shown to complex with cupric ion, a

study was undertaken to determine the possibility of titrating them with a solution of $CuCl_2$. Moran (41) had previously reported the titration of Tenamene 60 with $CuCl_2$ in a nonaqueous medium at the dropping mercury electrode. Tenamene 60 is an 80 percent solution of disalicylal propylene di-imine in toluene, advertised by Eastman Kodak as a "copper deactivator."

An attempt was made to perform the same type of titration with the rotating gold electrode. The solvent and supporting electrolyte chosen were 2-propanol and $0.1M$ $LiNO_3$, respectively. In this study, the $CuCl_2$ was titrated with a solution of Tenamene 60. Each solution was degassed for one hour before the titration and diffusion current measurements were made at a constant E.M.F. of $-.42$ volts, a value corresponding to a point just on top of the second copper wave.

In the first titration, a solution which was about $1 \times 10^{-3}M$ with $CuCl_2$ was titrated with a solution of Tenamene 60 in 2-propanol. The titration curve obtained (see Figure 9) was somewhat distorted.

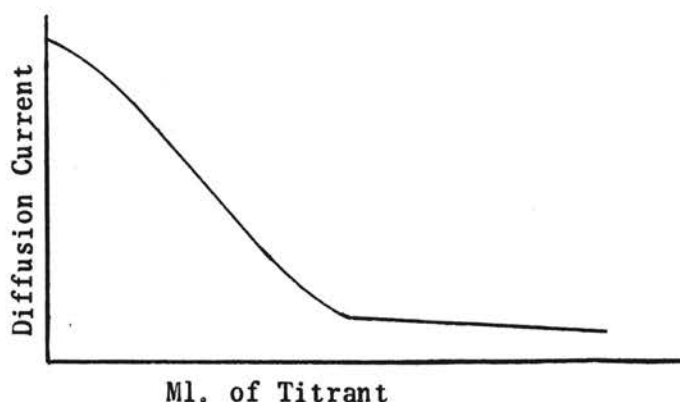Figure 9. Titration Curve of 100 ml. of $1 \times 10^{-3}M$ $CuCl_2$ in a Solution of 2-Propanol, $0.1M$ with $LiNO_3$, with a Solution of Tenamene 60 in 2-Propanol.

This same type of curve was also obtained for the titration of a 3×10^{-4}M solution of $CuCl_2$.

In an attempt to determine the cause of this distortion, polarograms were made of the copper wave and of the complexed copper wave. These polarograms showed a certain amount of overlapping of these two waves. It was found that at the $- .42$ volts used, diffusion current was being recorded from both the copper wave and the copper complex wave. This overlapping of the two waves was probably responsible for at least part of the peculiar distortion of the titration curve. The curve may also be distorted by a certain amount of electrode coating during the early part of the titration.

Due to the unsatisfactory titration curves obtained and to the fact that it was desired to perform amperometric titrations of simple amines, no further work was done on Tenamene 60.

Owing to the relationship of ammonia to the amines, an amperometric titration of ammonia was performed using $CuCl_2$ as the titrant and 2-propanol which was 0.1M with $LiNO_3$, as the solvent. A stock solution of ammonia was prepared by passing anhydrous ammonia through a solution of 2-propanol and this solution then standardized by titrating it with a standard aqueous solution of HCl, the end point for this titration being determined by means of a pH meter. A titration curve was first obtained by plotting milliliters of titrant against pH; then from this curve the pH at the equivalence point was determined. Later determinations were made by titrating to this known pH. In this case 5.6 was the pH at the equivalence point.

Special precautions had to be taken during the standardization to prevent escape of the NH_3 from the 2-propanol solution. A rough titration

was first made to determine the approximate end point. On subsequent titrations a volume of standard HCl solution, just slightly less than that required to neurtalize the aliquot of ammonia solution, was added to a beaker. The ammonia solution was then drained directly into the standard HCl, the tip of the pipette being held beneath the surface of the liquid during the transfer. The titration was then completed in the usual way. It was found that if this procedure was followed, duplicate checks could be obtained, otherwise, it was impossible to get consistent results.

A standard copper solution was prepared by dissolving enough $CuCl_2 \cdot 2H_2O$ in 2-propanol to make a 0.02M solution. A standard solution of sodium thiosulfate was prepared and standardized by the iodimetric method outlined by Hall (11); then the copper solution was standardized by the iodimetric method against the standard thiosulfate solution. The copper solution was found to be 0.01992M, which is very close to the value calculated from the weight of the dissolved salt.

The solutions to be titrated were prepared by adding the required amount of stock ammonia solution to the solvent and supporting electrolyte, just prior to the titration. Because of the tendency for the NH_3 to escape from solution, the solutions could not be degassed, and when the voltage was set at a point on top of the second copper wave, interference from dissolved oxygen resulted. Because of this it was necessary to make readings of diffusion currents at a point on top of the first copper wave. All measurements were made at 0.0 volts applied potential.

It was observed that if the voltage was held at a constant value on top of the first copper wave, the diffusion current decreased

slightly with time. To minimize any error which might result from this, the voltage across the cell was applied for only the few seconds required to make the readings.

The titration curves obtained were similar to the one shown in (b) of Figure 4. It was found that in order to obtain points which fell on a uniform straight line, it was necessary to wait one or two minutes between the addition of the titrant and the making of the reading, for apparently the formation of the copper complex is not a reaction which takes place instantaneously. The results of a series of five amperometric titrations are summarized in Table II.

TABLE II

TITRATION OF AMMONIA IN 100 ML. OF 0.1M LITHIUM NITRATE IN 2-PROPANOL
WITH A STANDARD SOLUTION OF CUPRIC CHLORIDE IN 2-PROPANOL

Titration of 1.143×10^{-4} Moles of Ammonia with 0.01992M Cupric Chloride

Sample	End Point (ml.)	Deviation	Deviation^2
1	2.68	0.00	0.0000
2	2.78	0.10	0.0100
3	2.66	0.02	0.0004
4	2.71	0.03	0.0009
5	2.60	0.08	0.0064
Mean	2.68	0.05	0.0035

Standard Deviation = (Mean of Squared Deviations)$^{1/2}$ = 0.059

$\dfrac{\text{Standard Deviation}}{\text{Mean of End Points}}$ = 0.0220 = 2.20%

Apparent Coordination No. = $\dfrac{\text{Moles of Amine}}{\text{Moles of CuCl}_2}$ = 2.14

As can be seen in Table II, the apparent coordination number is not a small whole number. This is probably due to a mixture of complexes being formed during the titration. Such is not surprising, for it is known (27) that in aqueous solutions cupric ion forms a series of different ammonia complexes from $Cu(NH_3)^{++}$ to $Cu(NH_3)_5^{++}$. The proportions of the various complexes are dependent upon the concentration of the excess ammonia. It seems quite reasonable to assume that a mixture of complexes might also be formed in nonaqueous solutions.

It appears that in aqueous solutions this type of titration would not be possible due to the multiplicity of forms involved in the equilibrium. An aqueous titration of this type might well result in a curved line with no distinct break.

At first it might seem strange that the titration is successful in nonaqueous solutions. In spite of this, the curves obtained in 2-propanol solutions were quite normal and the titration curves obtained indicate little or no equilibrium shift taking place.

The answer to this strange behavior may lie in the fact that a precipitate is formed during the titration. The precipitate appears to be quite insoluble and is observed as a slight cloudiness early in the titration. If one particular complex predominates in the precipitate, its formation would explain the results obtained and its most probable formula would correspond to two amines per cupric ion.

A $CuCl_2$ solution was also used to perform a series of titrations of methylamine. The same solvent and supporting electrolyte were used as with the ammonia solution.

A stock solution of methylamine was prepared by passing methylamine gas through a 2-propanol solution. The gas was prepared by the action

of NaOH on methylamine hydrochloride and dried by passing it through a drying tube filled with NaOH, after which it was bubbled through a 2-propanol solution. The solution was standardized by the same method used for the ammonia. Since methylamine is a gas, the same precautions had to be taken.

The amperometric titrations were performed in exactly the same way as those for ammonia. Again it was necessary to make diffusion current measurements at 0.0 volts applied potential. This was necessary not only because of interference from dissolved oxygen, when a point on the second copper wave was used, but also because of interference from the slightly soluble copper complexes formed. The results of this series of five amperometric titrations are shown in Table III.

TABLE III

TITRATION OF METHYLAMINE IN 100 ML. of 0.1M LITHIUM NITRATE IN 2-PROPANOL
WITH A STANDARD SOLUTION OF CUPRIC CHLORIDE IN 2-PROPANOL

Titration of 1.224×10^{-4} Moles of Methylamine with 0.01987M Cupric Chloride			
Sample	End Point (ml.)	Deviation	Deviation^2
1	3.80	0.00	0.0000
2	3.82	0.02	0.0004
3	3.75	0.05	0.0025
4	3.85	0.05	0.0025
5	3.79	0.01	0.0001
Mean	3.80	0.03	0.0011

Standard Deviation = (Mean of Squared Deviation)$^{\frac{1}{2}}$ = 0.032

$\dfrac{\text{Standard Deviation}}{\text{Mean of End Points}}$ = 0.0084 = 0.84%

Apparent Coordination No. = $\dfrac{\text{Moles of Amine}}{\text{Moles of CuCl}_2}$ = 1.62

As can be seen, the reproducibility of the results for methylanine is much better than for ammonia. The plots for the titration curves were also much more regular.

A series of amperometric titrations was next undertaken for ethylamine. Since the ethylamine is also a gas, the stock solution was prepared and standardized in the same way as for methylamine. To prevent escape of the ethylamine, the polarographic solution was not degassed and all measurements of diffusion current were again made at 0.0 volts. The results of a series of five amperometric titrations of ethylamine are shown in Table IV.

TABLE IV

TITRATION OF ETHYLAMINE IN 100 ML. OF 0.1M LITHIUM NITRATE IN 2-PROPANOL
WITH A STANDARD SOLUTION OF CUPRIC CHLORIDE IN 2-PROPANOL

Titration of 1.432×10^{-4} Moles of Ethylamine with 0.01987M Cupric Chloride			
Sample	End Point (ml.)	Deviation	Deviation^2
1	4.45	0.04	0.0016
2	4.46	0.03	0.0009
3	4.50	0.01	0.0001
4	3.38	0.01	0.0001
5	4.57	0.08	0.0064
Mean	4.49	0.03	0.0018

Standard Deviation = (Mean of Squared Deviation)$^{1/2}$ = 0.043

$\frac{\text{Standard Deviation}}{\text{Mean of End Points}}$ = 0.0095 = 0.95%

Apparent Coordination No. = $\frac{\text{Moles of Amine}}{\text{Moles of CuCl}_2}$ = 1.61

As can be seen, the apparent coordination number decreases in going from ammonia to ethylamine. It appears that this may possibly be due to a certain amount of steric hindrance from the aliphatic group of the amine. If this were the case, it would appear that an amine with a larger aliphatic group might have an even smaller apparent coordination number. In order to study this, a series of amperometric titrations on n-butylamine was performed.

A stock solution of approximately 0.02M n-butylamine was first prepared. This was done by adding a weighed amount of redistilled n-butylamine to the proper volume of 2-propanol. The solution was then standardized against a standard HCl solution. Again the pH meter was used to obtain a titration curve from which the pH at the equivalence point was determined. The end point was then determined by titrating to this known pH. Since the n-butylamine was a liquid, it was not necessary to take special precautions to prevent it from escaping from the 2-propanol solution.

The solutions to be titrated were prepared by adding a measured amount of the standard n-butylamine solution to the solvent and supporting electrolyte.

Preliminary studies were made to determine if it might be possible to perform the titrations at a voltage on top of the second copper wave, the second wave being preferred not only because of the added diffusion current obtained, but also because of the absence of electrode coating effects. It was found that the second wave was quite satisfactory for this purpose and gave very satisfactory titration curves. All measurements of diffusion current were made on top of this wave at an applied E.M.F. of - .50 volts.

The solutions were degassed for 30 minutes prior to each titration. This shorter period of degassing was found to be sufficient to eliminate interference from dissolved oxygen. Since the volume of titrant was very small, and oxygen interference very slight at this applied potential, the titrant was not degassed. This appeared to cause no ill effects.

The titration curves obtained for n-butylamine were even more satisfactory than those for the previously titrated amines. Again, as with all the other amines, it was necessary to wait for about one minute after adding the titrant before making the readings. A series of five amperometric titrations was again performed, the results of the titrations being as shown in Table V.

TABLE V

TITRATION OF n-BUTYLAMINE IN 100 ML. OF 0.1M LITHIUM NITRATE IN 2-PROPANOL
WITH A STANDARD SOLUTION OF CUPRIC CHLORIDE IN 2-PROPANOL

Titration of 9.72×10^{-5} Moles of n-Butylamine with 0.01987M Cupric Chloride

Sample	End Point (ml.)	Deviation	Deviation^2
1	3.27	0.00	0.0000
2	3.25	0.02	0.0004
3	3.26	0.01	0.0001
4	3.27	0.00	0.0000
5	3.29	0.01	0.0001
Mean	3.27	0.01	0.0001

Standard Deviation = (Mean of Squared Deviation)$^{\frac{1}{2}}$ = 0.010

$\dfrac{\text{Standard Deviation}}{\text{Mean of End Points}}$ = 0.0031 = 0.34%

Apparent Coordination No. = $\dfrac{\text{Moles of Amine}}{\text{Moles of CuCl}_2}$ = 1.49

An attempt was next made to perform an amperometric titration upon n-butylamine at a much lower concentration, a 9.73×10^{-5}M concentration being chosen for this series of titrations. The solutions to be titrated were prepared by adding the required amount of standard solution to a 0.1M solution of $LiNO_3$ in 2-propanol.

An attempt was made to calculate the expected end point. This calculation was made using the apparent coordination number obtained at the higher concentration.

After the first few titrations, it was apparent that the end points were somewhat higher than expected. Because of this, a series of blank determinations was made. The blank determinations were performed exactly like an amperometric titration, except that no n-butylamine was added to the solvent and supporting electrolyte. Three determinations were made in this way and the average blank so obtained was subtracted from the volume of titrant required for the titration of the n-butylamine.

After subtracting the volume of the blank, the resulting volume was found to be somewhat less than the calculated value. This is in part due to the fact that a blank should also have been subtracted from the higher concentration titration from which the apparent coordination number was obtained. Even at this higher concentration, the neglect of the blank would result in an appreciable error. If the value of the blank were subtracted from the earlier titration, the apparent coordination number would become 1.54. When this value is used to calculate the end point at the lower concentration, the calculations are in much better agreement with the experimental results. The results obtained seem to indicate that it would be possible to perform successful amperometric titrations of this amine if proper precautions were taken. If it was

desired to perform amperometric titrations for other amines, it would be necessary to determine the apparent coordination number constant for each individual case.

The results of a series of five titrations of a 9.72×10^{-5}M solution of n-butylamine are summarized in Table VI.

TABLE VI

TITRATION OF n-BUTYLAMINE IN 100 ML. OF 0.1M LITHIUM NITRATE IN 2-PROPANOL
WITH A STANDARD SOLUTION OF CUPRIC CHLORIDE IN 2-PROPANOL

Titration of 9.72×10^{-6} Moles of n-Butylamine with 0.00993M Cupric Chloride			
Sample	End Point (ml.)	Deviation	Deviation^2
1	0.819	0.027	0.000729
2	0.800	0.008	0.000064
3	0.785	0.007	0.000049
4	0.798	0.006	0.000036
5	0.760	0.032	0.001024
Mean	0.792	0.016	0.000380

Mean Volume of Blank = 0.170 ml.

Mean of End Points - Mean Volume of Blank = 0.622 ml.

Standard Deviation = (Mean of Squared Deviation)$^{1/2}$ = 0.019

$\dfrac{\text{Standard Deviation}}{\text{Mean of End Points - Blank}}$ = 0.0305 = 3.05%

Calculated End Point* = 0.636

$\dfrac{\text{Actual End Point}}{\text{Calculated End Point}}$ = 97.8%

*Calculation based on assumption that one mole of $CuCl_2$ combines with 1.54 miles of n-butylamine.

From the results obtained from this titration, it appears that corrections for blanks should also be made for all previous amine titrations. A list of corrected apparent coordination numbers is given in Table VII. In the calculation of these corrected figures, the blanks are assumed to be the same as for the previous titration.

TABLE VII

CORRECTED APPARENT COORDINATION NUMBERS FOR AMMONIA, METHYLAMINE
ETHYLAMINE AND N-BUTYLAMINE WITH CUPRIC ION IN A 0.1M
SOLUTION OF LITHIUM NITRATE IN 2-PROPANOL

Ammonia	2.21
Methylamine	1.64
Ethylamine	1.64
n-Butylamine	1.54

CHAPTER VII

SUMMARY AND CONCLUSIONS

It was hoped at the beginning of this investigation that the cathodic range of the solid microelectrodes might be extended by using non-aqueous solvents. This was found to be the case. Alcohol solutions had higher decomposition potentials than the corresponding aqueous solutions and the decomposition potentials increased generally with increased molecular weight of the alcohol.

It was observed that the decomposition potential was also dependent upon the nature of the supporting electrolyte. Studies of different supporting electrolytes, at different concentrations, indicated that the carrier wave was the result, at least in part, of the electrolysis of the supporting electrolyte.

One of the greatest disadvantages in using the alcohols as polarographic solvents, with the rotating microelectrodes, is the erratic electrode behavior which often is encountered. This erratic behavior is apparently caused by the formation of electrolysis products on the surface of the electrodes.

It was found that a large extension of the cathodic range was obtained by using the quaternary ammonium salts as supporting electrolytes. These salts have the one great disadvantage that at least certain metal ions form insoluble complexes with them in anhydrous alcoholic solutions. In spite of this, it appears that they may be useful in organic nonaqueous polarography and in the determination of certain non-complexing metals.

A series of amperometric titrations was performed. Although silver ion was found to be unsuitable for the titration of the amines, cupric ion was found to be quite satisfactory.

It was found, from the amperometric titrations, that the apparent coordination number of cupric ion with the amines was not a small whole number. This indicated that a mixture of complexes was being formed during the titration. The apparent coordination number observed was found to be characteristic of the amine being titrated. In spite of the apparent formation of a mixture of complexes, the titration curves obtained were quite normal.

From the results of the titrations, it appears that amines may be determined with reasonable accuracy by this method. In a titration of this type, it would, of course, be necessary to know the apparent coordination for each amine. It is also quite probable that this coordination number is effected by the nature of the polarographic solvent. It would be best, therefore, to standardize all solutions using the same solvent systems and techniques as those to be used in the actual analysis.

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