ACID-BASE ELECTRODE BEHAVIOR IN
2-PROPANOL-WATER SOLUTIONS

By

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PREFACE

Although a great many substances possess acidic or basic character, many do so to so slight a degree that they cannot be titrated in water. Since their strength may often be increased by changing to another solvent, analyses that are impossible in water can be performed in nonaqueous solvents.

The amperometric method is rapid and particularly suited for use with solutions of low concentrations. The high resistance polarograph and the iR compensator invented by Dr. Paul Arthur make possible direct determinations of electroactive materials in solutions of very high resistance.

The purpose of this research was to investigate the nature of, and some potentialities of acid-base behavior in nonaqueous solutions with emphasis on amperometric titrations and high resistance polarography.

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CHAPTER I

INTRODUCTION

Introduction to Polarography

When two electrodes are placed in a solution and an increasing voltage is impressed across them, a potential will be attained which causes the decomposition of the solution and an accompanying increase in current due to electrolysis. Following the attainment of the decomposition potential, an additional increase in voltage will bring about an increased current level to values of large magnitude. However, if one of the electrodes is small and easily polarized, other current-voltage relationships are observed.

The polarograph, itself, is an instrument in which a continuously varying voltage is applied across two electrodes. One electrode, due to its large size,its nature, and the fact that it does not encounter large currents in polarography, is not easily polarized. On the other hand, the other electrode which is much smaller and has less surface area is easily polarized. The current is constantly measured by means of a strip chart recorder, the chart movement of which is synchronized with the operation of a motor driven linear voltage divider within the polarograph itself.

The small polarizable electrolysis electrode is usually a dropping mercury electrode (D.M.E.). Basically, it is a glass capillary tube about 10 centimeters long which has a mercury reservoir attached to its upper end, with a head of mercury of 30 to 40 centimeters. The internal diameter of the tube is such that the mercury will form mercury droplets at the distal end of the tube at a determined rate of from 3 to 8 seconds per droplet. The large, nonpolarized or reference electrode is usually the saturated calomel type. Figure 1 illustrates the basic polarographic circuit.

To comprehend fully the current-voltage relationships that are observed in polarography, the various parts of a polarogram should be considered. (Figure 2).

As the voltage increases at _A_, a small current commences to flow. This current is a condenser current due to the adsorption of ions on the surface of the mercury droplet. This current is also attributed to the small amounts of oxygen and mercury ions in the solution itself. At point _B_, there is a rapid increase in current with a small increase in voltage as the oxidizable or reducible species begin to decompose.

The current which flows through the cell is dependent upon the concentration of the various types of ions in solution. In a solution where the cation concentration contains 99% A^+ ions and 1% B^+ ions, the A^+ ions will essentially surround the D.M.E. Thus, the B^+ ions have little or no effect on the migration current, which is due to electrostatic attraction. Under such extreme conditions of polarization of the D.M.E. together with the fact that the B^+ ions are only discharged at voltages greater than _B_, the greater amount of current from _B_ to _D_ can be attributed to the discharge of B^+ ions. At _C_, the B^+ ion concentration will be near zero in the polarized solution surrounding the D.M.E. and therefore the limiting current, _CD_, is dependent upon the diffusion of the B^+ ions into the electrode. The rate of diffusion of

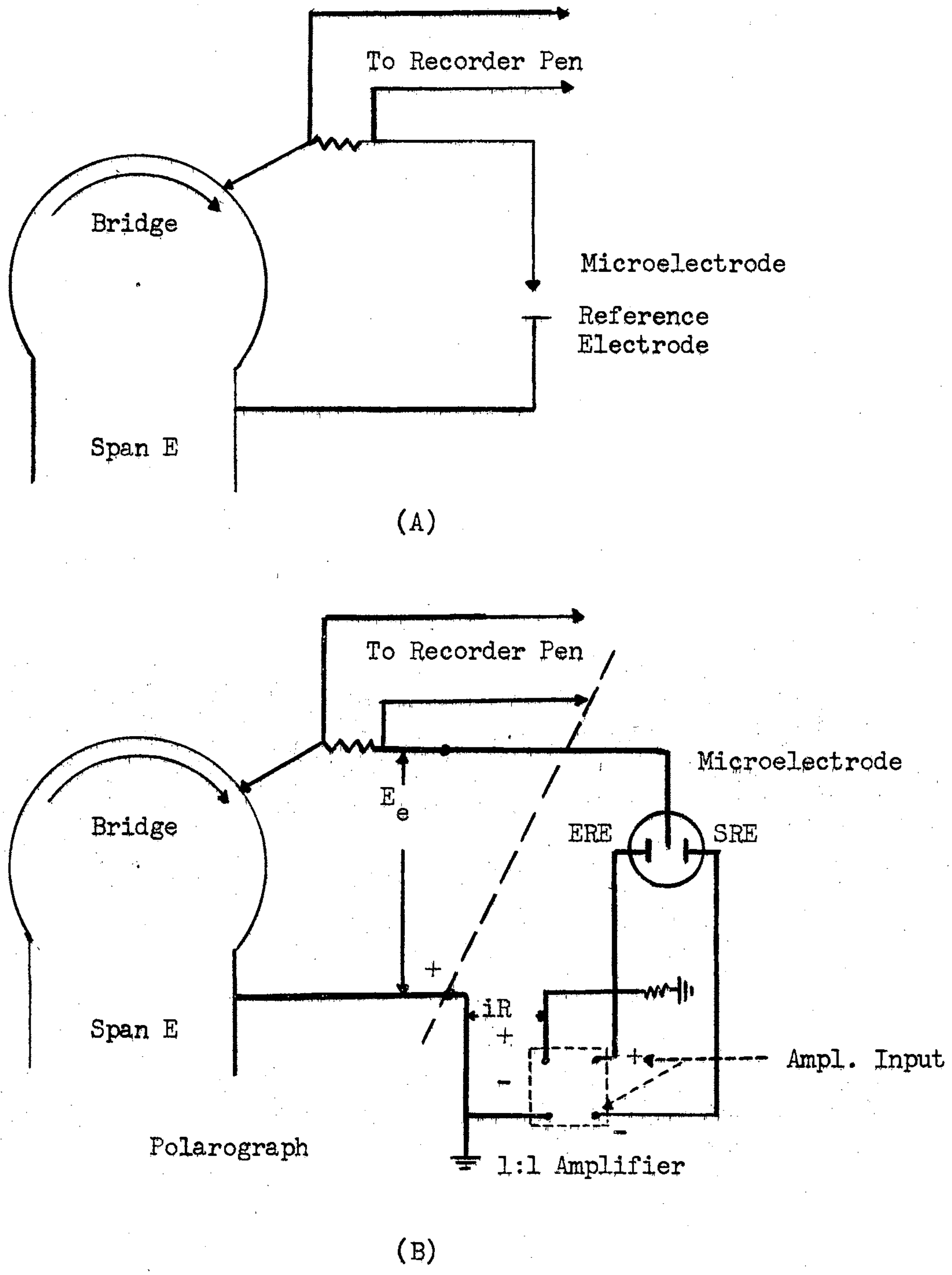


Figure 1. (A) A Schematic Standard Polarographic Circuit.
(B) A Schematic Circuit for Polarography in High-Resistance Solutions.

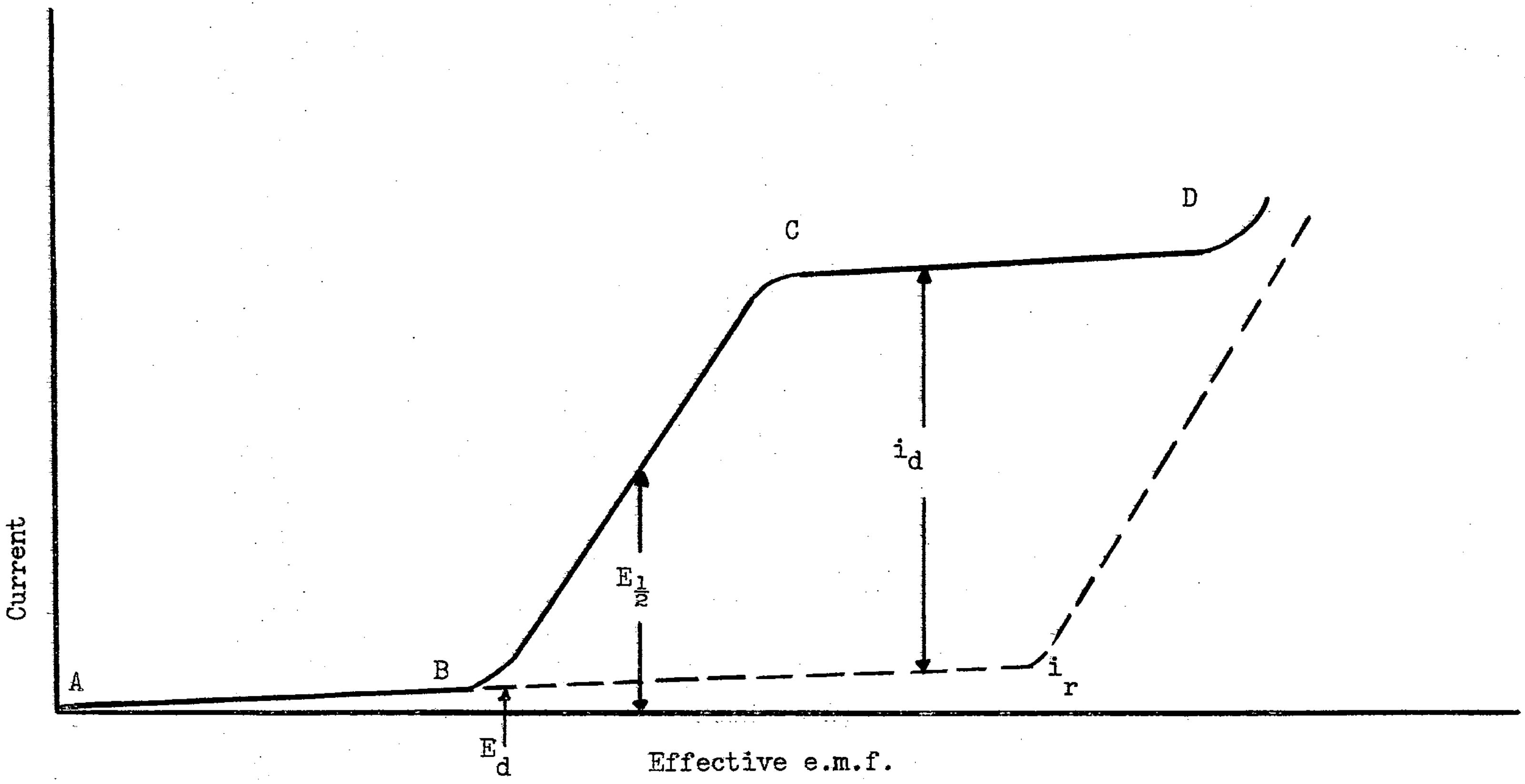


Figure 2. Normal Polarogram

the B^+ ions between the surface of the D.M.E. and the bulk of the solution is dependent upon concentration; consequently the current along the line CD will be a function of the concentration of B^+ ions in the solution. An increase in voltage gives little increase in current until point D is reached. At this point, the potential becomes great enough to initiate the decomposition of the A^+ ions provided by the carrier electrolyte.

The difference between the limiting current and the residual current i_r is called the diffusion current, i_d, a function which is directly proportional to the concentration of the ions being reduced.

$E_{\frac{1}{2}}$ is known as the half-wave potential and is observed as a point of inflection of the current-voltage curve, half way between the limiting current plateau and the residual current. This may be used for identification purposes because of the fact that it is characteristic for most given oxidizable and reducible species under controlled conditions.

The theoretical equation of Ilkovic demonstrated the dependence of the diffusion current on many quantities (20, 21). The original equation was

$$i_d = 607\ nD^{\frac{1}{2}}Cm^{2/3}t^{1/6}.$$

In this, i_d denotes the average current in microamperes during the immediate life of the drop, n is the number of faradays needed per mole of oxidizable or reducible species, D is the diffusion coefficient of the oxidizable or reducible ion or molecule in $cm^2\ sec^{-1}$, C denotes the concentration in millimoles per liter, m is the rate of flow of mercury from the D.M.E. in mg sec^{-1}, and t is the drop time from the D.M.E. in seconds. From this equation and by results determined experimentally, it is essentially agreed that for a given electroactive substance when using a given capillary tube, the diffusion current is proportional to the concentration of the electroactive substance.

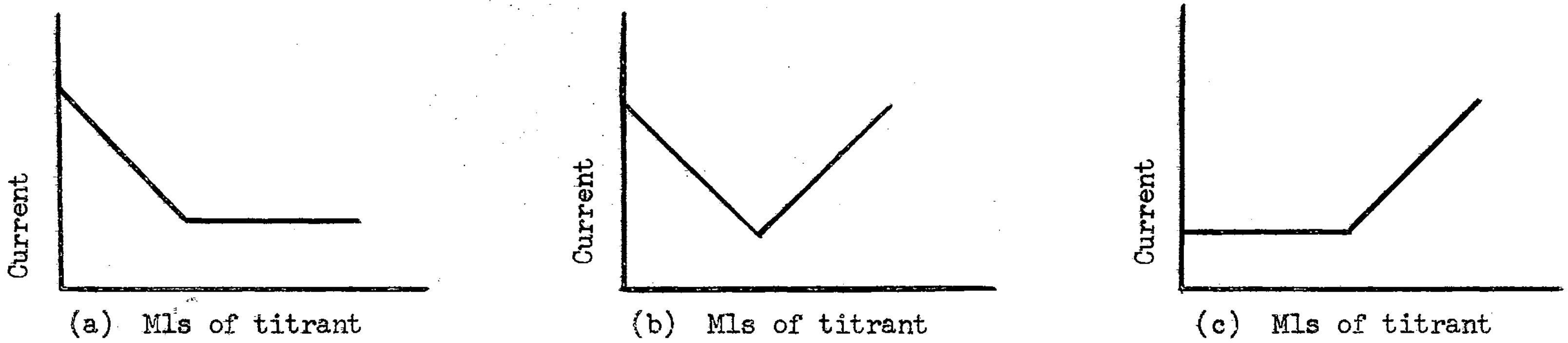
Amperometric Titrations

Polarographic principles can be used as the basis for an electrometric titration. This method, which has been termed "amperometric titration," consists of a selected voltage being applied across a polarographic cell while changes in current due to changes in concentration are brought about by the addition of a suitable reagent to the unknown surrounding the microelectrode. This current is plotted against the volume of the titrant being added to the solution.

To best illustrate that amperometric titrations are of a polarographic nature, let us consider what happens to a given substance X, which produces a polarographic wave when titrated with aliquots of substance Y. Suppose substance Y is a reagent which will remove substance X from solution. Suppose also that Y itself gives no polarographic wave and that there are no products formed which are electroactive at the voltage being used.

As aliquots of substance Y are added to the solution, changes will be observed in the diffusion current, thus affecting the height of the wave. If the observed current is plotted against the volume of the titrant being added, a curve like that in Figure 3a will be observed, the change in slope occurring at the end point.

In amperometric titrations, a fixed voltage is chosen so the current measured will be on the limiting plateau. Current measurements are taken following the addition of each aliquot of titrant being added



(a) Mls of titrant

(b) Mls of titrant

(c) Mls of titrant

Figure 3. Common Amperometric Curves

to the solution. By this method, points of the plot are conveniently obtained.

In similar titrations, but where titrant Y is electroactive at the selected voltage, a curve similar to Figure 3b would be observed. This is explained by the fact that addition of titrant _Y_ beyond the end point would result in an increase in the current due to reaction of the excess of titrant _Y_ at the electrode.

A curve similar to Figure 3c is also observed in amperometric titrations. In this particular case, the ion being titrated is not reducible and therefore there is practically no current produced before the end point is attained. The titrant _Y_ is reducible, however; consequently, after the end point is reached, the diffusion current produced by reaction of _Y_ at the electrode will increase following each addition of excess titrant.

If there are significant changes in volume during titration, corrections must be made in the plotting of the amperometric curve.

By using the techniques of high resistance polarography, commensurate amperometric titration can be extended to nonaqueous solution.

This fact was demonstrated first by the work of Moran (41) who used solutions of copper (II) chloride in 2-propanol to titrate high molecular weight amines in mixtures of 2-propanol and hydrocarbons and Tenamene 60 (a commercial copper deactivator, disalicylal propylene di-imine) in a similar solvent system. Moran also titrated 2-naphthalenesulfonic acid in 2-propanol-hydrocarbon mixtures using potassium hydroxide in 2-propanol, while Jones (23) similarly titrated solutions of hydrogen chloride and of 2-naphthalenesulfonic acid. The results obtained by these two indicated, however, a need for further studies of nonaqueous acid-base titrations particularly from the standpoints of improving standardization techniques and of extending the procedure to other acids and bases.

CHAPTER II

HISTORY

The beginning of polarography was first suggested in 1903, by Kucera (34) and was developed by Heyrovksy (14, 15). Kucera, while studying the electrocapillary curve, observed that deflections in the curve were obtained when reducible substances were present. Heyrovksy, following Kucera's recommendation, further pursued and investigated these curves. Following the determination of the proper diffusion conditions, Heyrovksy was able to produce reproducible currents.

Salomon (47, 48) showed that currents obtained were proportional to the concentration of the reducible substances present. Salomon's procedure was termed "Galvanometric Titration." Following the work of Nernst and Merriman (43) who had shown possible uses for amperometric titrations, Fresenius (11) attempted to determine hydrogen ion concentration by this method. In 1925, Heyrovksy and Shifata (18) developed an automatic recording device for their new procedure and introduced the terms of "Polarography" and "Polarogram." One application of this method was to titrations in which current flows between two depolarized electrodes until after the end point, whereupon one electrode becomes polarized and the current falls to zero or near zero.

In 1934, polarography became theoretically significant. At this time, Ilkovic presented the original derivation of the Ilkovic equation (20, 21). This derivation was completely theoretical; however, later experiments verified the validity of his equation. Later, Heyrovksy and Ilkovic showed the theoretical significance of the polarographic wave and in doing so changed polarography from an empirical technique to a theoretically well-founded branch of electrochemistry.

Antweiler, (2) in 1937, demonstrated that a stirring effect in the solution near the dropping electrode accompanies the maxima which are often observed with polarographic waves. Peracchio (46) studied diffusion currents of alkali ions in alcohol-water, ethylene glycol-water, glycerol-water, and dioxane-water mixtures. Their results showed that diffusion currents were less in these solvent systems than in pure water.

Lingane and Kolthoff (35) did exhaustive studies as to the basic principles and theories of polarography. The validity of Ilkovic's equation had been tested by only two simple polarographic systems. Lingane and Kolthoff made extensive efforts to prove or disprove Ilkovic's postulation. After extensive testing, they concurred with Ilkovic and agreed that his equation for polarographic diffusion currents was essentially correct. They also studied the characteristics of limiting currents and later prepared a comprehensive review concerning the studies of the dropping mercury electrode (36, 29).

In 1950, Strehlow and von Stackelberg (51) developed a new equation for the diffusion current. These men explained that the failure of Ilkovic's original equation to explain small observed variations was due to neglect of the curvature of the electrode surface. Their new equation was

$$i_d = 607\ nCD^{\frac{1}{2}}m^{2/3}t^{1/6}(1 + AD^{\frac{1}{2}}m^{-1/3}t^{1/6})$$

with A being evaluated as 17 at 25°C. Lingane and Loveridge (37) found similar results and their conclusions concurred with those of Streklow and von Stackelberg. Their equation was similar to that of Streklow and von Stackelberg with the exception that A was evaluated as 39 at 25°C.

More recently, Macero and Rulfs (39) have demonstrated that the correct value for A should be 31.2 ± 1.6.

High Resistance Polarography

Many problems have arisen with solutions of high resistance, and several techniques and procedures have been applied in order to solve the problems encountered. Nicholson's (44) application was the modification of an ordinary polarograph whereby the recorder pen stylus drives an auxiliary bridge whose output is wired in a series with the polarograph and gives iR compensation.

The apparatus described by Oka (45) and by Kelley et al. (25) are designed to give compensation not only for iR drop but also for changes of potential at the electrolysis reference electrode. Both employ an auxiliary reference electrode against which the microelectrode potential is controlled. That of Oka used an amplifier to drive a motor-driven bridge to supply compensation and is designed to be used as an attachment to a conventional polarograph.

The instruments described by Kelley et al. are designed to provide iR and voltage compensation. Although the use of their apparatus with a conventional polarograph would require major modifications in the circuit of the latter, their circuit reportedly provides compensation not only for iR drop and potential within the cell, but also a correction for these within the circuit of the polarograph.

An iR compensator for application to the conventional polarograph has been described by Jackson and Elving (22). In this, the iR drop of a small resistor connected in series with the electrolysis cell is amplified to make it equal to the iR drop, then fed back into the circuit. Using somewhat similar applications as those found in the Arthur iR compensator (3, 4, 38), Sawyer, Pecsok, and Jensen (49) have described an automatic recording polarograph with two reference electrodes.

The compensator described by Arthur and VanderKam (4) is a completely electronic apparatus employing a three-electrode cell and designed for use as an attachment for any conventional polarograph, manual or automatic. It provides no compensation for iR drop within the polarograph itself but gives excellent compensation for iR drop within the cell and for any changes in potential of the electrolysis reference electrode.

Kolthoff and Pan (32) were the first to use the term, "Amperometric Titration." They related that in this type of titration a current is measured as a function of concentration.

Many of the analysis which were first used with this new procedure were precipitation titrations. The titration of sulfate ion with lead ion was observed and investigated by Kolthoff and Pan. It was their opinion that alcohol-water mixtures should be used for such titrations in order to lower the solubility of the precipitates formed.

In 1946, amperometric titrations were first used for the determination of mercaptans in alcoholic ammoniacal media (28). Kolthoff and Bovey titrated styrene with potassium bromate (27). By using a solvent of 75% methanol, they obtained low, but satisfactory, results.

In 1950, an amperometric technique was introduced for the analysis of soluble mercapto group materials (5). This procedure employed a rotating platinum microelectrode in a solvent of 80% ethyl alcohol.

Kolthoff and Medalia, using a similar type of electrode, obtained good titration curves from ferrous ion in 70 to 80% acetone (31). Since that time, amperometric end points have been utilized to determine iodine values for fatty acids and oils (8). Also titrations of fluoride with ferric chloride in 50% alcohol have been obtained. Acetone-water mixtures have also been used as solvent systems in the determination of thallium with iodide and with dichromate (24).

The titration of oxalic acid with ammonium hexanitratocerate in glacial acetic acid was accomplished by Hinsuark and Stone (19). Mixtures of 90% acetone with water have been utilized to lower the solubility of silver chloride so chlorides can be successfully titrated at very low concentrations (7).

Recently, potassium bromate has found application to the determination of total phenolic groups in epoxy resins (9). A mixture of methanol and dimethylformamide was used as the solvent, with 0.5M HCl as supporting electrolyte.

Southworth et al. (50) noted that at potentials greater than -1.90 volts versus S. C. E., solution traveled up the capillary, reaction took place in the capillary, and disruption of the mercury drop took place, the drop being dispersed into small droplets throughout the solution. These observations appear to supply the explanation for the erratic behavior which many observers have noted at high negative potentials.

CHAPTER III

APPARATUS

All polarographic work was done with a Model XXI Sargent Polarograph. The preliminary experiments were performed with the iR-compensator used by Arthur and VanderKam (4). However, the majority of the work was performed with a Sargent Model A iR-compensator which is a commercial version of the iR-compensator developed by Arthur. The cells used were of the double-H type developed by Dr. Paul Arthur for use in the three electrode system of the iR-compensator. Asbestos fiber was used as the salt bridges between the electrode compartments of the cell. One cell was obtained from Sargent, the other was fabricated in the Oklahoma State University glass shop. Both reference electrodes were aqueous saturated calomel half cells. (Figure 4).

The dropping mercury electrode assembly was similar to that described by Lloyd (38) but employed surgical rubber tubing in place of tygon. Between runs, the D. M. E. was stored in 2-propanol.

The mercury was purified with a type G mercury oxifier and vacuum still from the Bethlehem Apparatus and Gaertner Scientific Companies, respectively.

All potentials were measured with a Sargent millivolt potentiometer. All experimental measurements utilizing the electrolysis cell were made at a temperature of 25.0 ± 0.1°C, which was maintained in a light mineral

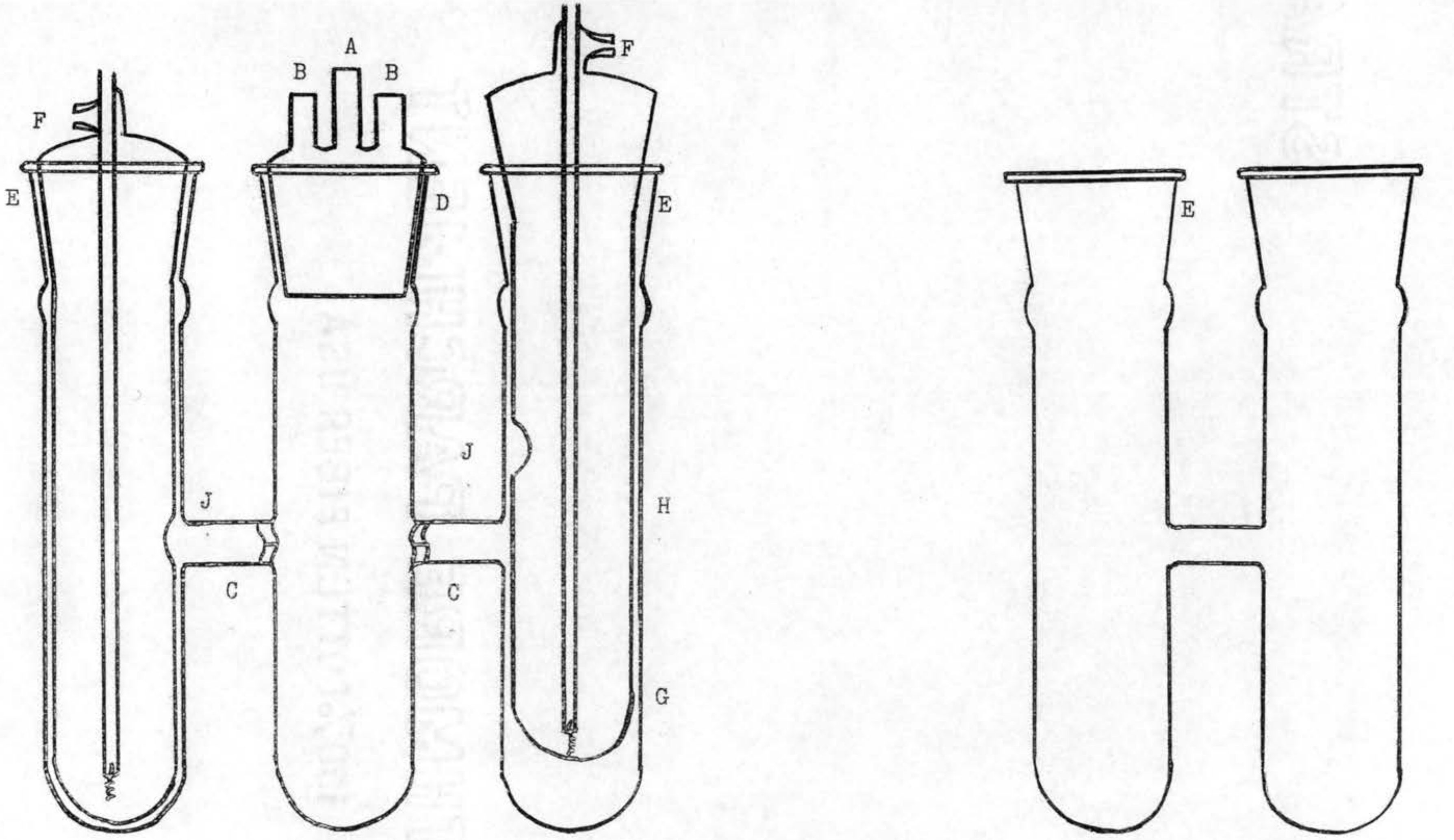


Figure 4. Cell and Electrode Storage

A. DME inlet
B. Inlets for thermometer and gas dispersion tube
C. Asbestos fiber salt bridge
D. Standard taper 34/28 joint

E. Standard taper 24/40 joint
F. Air vent
G. Platinum wire
H. Calomel (or other) electrode
J. Inlet to electrode

oil constant temperature bath.

The microburets with capacities of five milliliters were calibrated in 0.01 milliliters. The burets were supplied with teflon stopcocks. The microburets were filled by means of nitrogen pressure within a system protected from the atmosphere by ascarite.

A Beckman pH meter, Model H2, was used for all pH measurements.

CHAPTER IV

REAGENTS

Acetic acid - Dupont reagent grade was used without further purification.

2-Amino 2(hydroxymethyl) 1,3-propanediol - Fisher reagent grade was used without further purification.

Bacto-agar - "Difco" standardized grade prepared by the Difco Laboratories was used without further purification.

Bromcresol purple - Solid, unlabelled stock from the Oklahoma State University chemistry storeroom was used without further purification.

Chromium (III) sulfate $Cr_2(SO_4)_3 \cdot x\ H_2O$ Fisher certified reagent was used without further purification.

2,5-Dimethylbenzenesulfonic acid - Eastman Kodak white label was used without further purification.

1,3-Diphenylguanidine - Eastman white label was used without further purification.

Ethyl acetate - NF absolute Fisher certified reagent was used without further purification.

Hydrochloric acid - Baker analyzed ACS specification was used without further purification.

Hydrogen chloride - Matheson anhydrous C.P. grade was used without further purification.

Lithium acetate $LiC_2H_3O_2 \cdot 2H_2O$ (crystals) - Matheson Coleman and

Bell reagent ACS specifications was used without further purification.

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

Mercurous chloride - Mallinckrodt analytical reagent grade was used without further purification.

Mercury - was oxified and vacuum distilled in this laboratory.

Mehtanol - Fisher certified reagent was used without further purification.

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

Nitrogen - Linde H. P. dry was purified in a manner described by Jones (23).

Potassium carbonate - Fisher certified reagent, anhydrous, was used without further purification.

Potassium chloride - Fisher scientific reagent grade was used without further purification.

Potassium hydroxide (pellets) - Fisher Scientific certified reagent was used without further purification.

Sodium tetraborate $Na_2B_4O_7 \cdot 10H_2O$ - Mallinckrodt analized reagent ACS specification was used without further purification.

Sulfamic acid - Brothers Chemical was used without further purification.

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

Tetramethylammonium chloride - Matheson (practical) was recrystallized from methanol and washed with ethyl acetate until it was polarographic pure.

CHAPTER V

EXPERIMENTATION AND DISCUSSION

While making high-resistance polarograms of oil additives, Moran (41) noted the presence of a strong acid wave whenever sulfonic acids were present. Jones (23) used a newly developed iR-compensator to perform amperometric titrations of 2-naphthalenesulfonic acid and hydrochloric acid, doing both with potassium hydroxide, at -1.17 v., in a 2-propanol-2, 2,4-trimethylpentane solvent system. With the ability to make conventional polarograms in high-resistance systems with the iR-compensator, it seemed desirable to further investigate the characteristics of the acid wave in a nonaqueous medium.

Since considerable work done in this laboratory had shown that 2-propanol solutions are easily prepared and are relatively stable, this solvent was chosen for subsequent work. Adequate presaturation of the nitrogen used for degassing prevented any large evaporative changes in the volume of the solvent during an experiment. Jones reported that simple distillation was sufficient to make the 2-propanol satisfactorily pure, with the possible exception of carbon dioxide picked up from the atmosphere. Therefore, to eliminate the interference of carbonates, the 2-propanol was pretreated with potassium hydroxide pellets before distillation.

During distillation, nitrogen was bubbled through the 2-propanol into the apparatus which was a closed system protected from the atmosphere by a potassium hydroxide-2-propanol trap that was connected to the receiver. Potassium hydroxide solutions made with 2-propanol treated in this manner showed no visible indications of the formation of the carbonates reported by Jones (23), even on long standing.

The carrier electrolyte was dissolved in the solvent. Occasionally this would take two to three hours of mechanical shaking, the time seeming to depend on the physical condition of the carrier electrolyte. Since tetramethylammonium chloride and lithium nitrate are very hygroscopic, they were stored in an oven at 110°C until needed. After the carrier electrolyte had dissolved, a measured amount of the reagent to be used was added. This was usually done by adding an aliquot of a more concentrated solution that had been previously prepared.

If the electrolytic cell had not been in use for some time, it was necessary to pre-soak the asbestos fibers with distilled water. Subsequent pre-soaking was not necessary for the remainder of the series. The stable reference electrode and electrolysis reference electrode compartments were filled to within one-half an inch below the arms of the cell with saturated potassium chloride solution. Following this procedure, the cell was placed in a constant temperature bath containing light mineral oil. Forty-six milliliters of test solution were added from a buret to the center compartment of the electrolysis cell, bringing the surface of the solution to approximately one-fourth of an inch above the asbestos fiber in the side arms of the cell.

The degassing was accomplished by bubbling nitrogen from a gas diffusion tube through the solution for at least thirty minutes. The nitrogen was treated by passing it through a train containing three oxygen scrubbers, a silica gel drier, and two presaturators containing 2-propanol.

Following the degassing of the solution, the reference electrodes were placed into their respective compartments, causing the displacement of the potassium chloride solution to fill the side arms of the cell. This procedure lessens the possibility of the saturated potassium chloride diffusing into the center compartment.

To check the polarographic purity of the solutions, polarograms were made prior to the onset of each series. If an amperometric titration was to be made, the proper potential was chosen by observing the polarogram, and the titration was carried out in the normal manner.

Following each run, the cell was scrubbed with "Tide," rinsed thoroughly with deionized water, then 2-propanol, and dried in an oven at 110°C. By the use of two cells, a series of runs could be completed within twenty-four hours.

In these experiments, two curious things involving electrode behavior were noted. First, maximums were seldom if ever noted in polarograms after the procedure of using "Tide" was started. It would appear that traces left in the cell acted as a maximum suppressor.

Secondly, on occasions the D. M. E. would stream. Various procedures were used in an attempt to prevent the streaming of the D. M. E. For unknown reasons, the following procedures were only periodically successful. These procedures were (1) surging the potential by turning on the additive voltage, (2) soaking the end of the D. M. E. in aqua regia or nitric acid, and (3) finally, wiping the surface of the electrode with a Kem-wipe. More favorable results were obtained by allowing the mercury to continue to flow between the runs in a series.

All runs were in the 10^{-3}M range and, unless otherwise indicated, using 0.1M tetramethylammonium chloride carrier. Stirring was accomplished by lowering the gas dispersion tube into the solution, thus allowing the nitrogen to bubble through it. At the start of each new series, a polarogram was made of the carrier.

Due to the solubility of the tetramethylammonium chloride in 2-propanol and its favorable decomposition potential, it was preferred above lithium nitrate as the carrier in this research. Lithium nitrate has a decomposition potential not too far above the half wave potential of the strong acid, making it less suitable as a carrier in this technique.

In order to become familiar with the acid wave described by Moran (41), several polarograms were made of 2,5-dimethylbenzenesulfonic acid and of hydrochloric acid. Other runs of potassium hydroxide versus acid, as amperometric titrations, were made. It was noted that it required less acid for the amperometric titration than for titrations employing colorimetric indicators, which was in agreement with results obtained by Jones. During the runs, precipitates were formed which plugged the asbestos fiber salt bridges. After several runs, it was necessary to treat the fiber with aqua regia before additional experiments could be performed.

Jones found that more desirable results were achieved in 2-naphthalenesulfonic acid versus potassium hydroxide nonaqueous amperometric titrations when phenolphthalein was replaced by bromcresol purple as an indicator in the colorometric standardization of the potassium hydroxide.

By following the standardization with a pH meter, it was observed that the 2-propanol, which is known to decrease the ionization of acids, particularly weak acids, decreases the amplitude of the pH curve and makes it less sharply rising. (Figure 5). The observed end point of the titration is dependent upon the indicator used and this in turn would influence the normality calculated for the reagent being standardized.

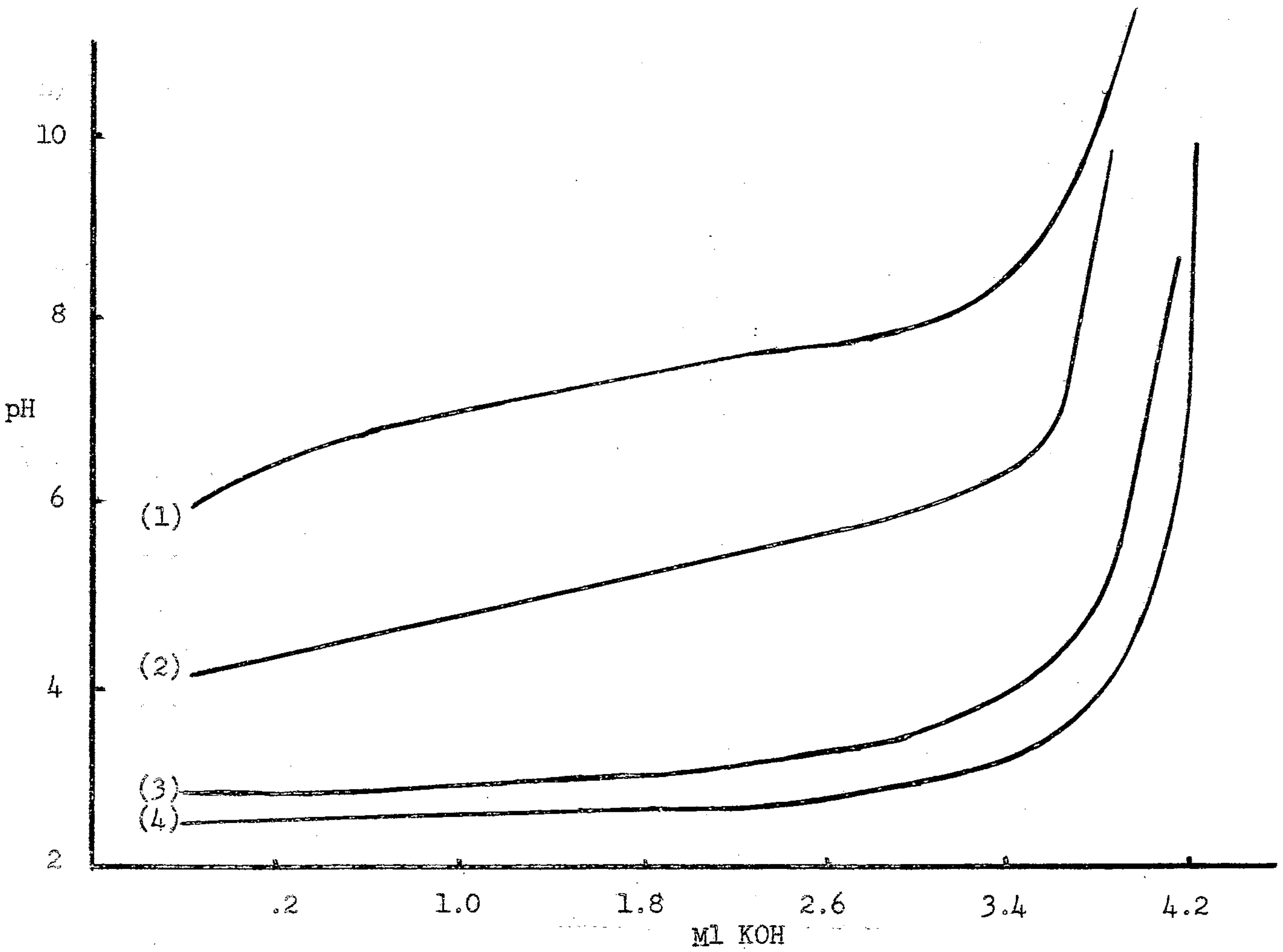


Figure 5. pH curves of:

(1) Potassium Hydrogen Phthalate vs. KOH 100% 2-Propanol
(2) Potassium Hydrogen Phthalate vs. KOH 50% water-2-Propanol
(3) Sulfamic Acid vs. KOH 100% 2-Propanol
(4) Sulfamic Acid vs. KOH 50% water-2-Propanol

Therefore, the selection of the proper indicator is most critical. From these results, it is suggested that a satisfactory technique be devised in order to standardize the reagents in a manner comparable to their specific uses in the media of the titration.

1,3-Diphenylguanidine and 2-amino 2(hydroxymethyl) 1,3-propanediol, being bases which were readily available in pure form and sufficiently soluble in 2-propanol, were thus tried. Titrations were made of these bases in order to determine their suitability as standards. Both the 2-amino 2(hydroxymethyl) 1,3-propanediol and the 1,3-diphenylguanidine were titrated with 2,5-dimethylbenzenesulfonic acid in 2-propanol. These titration produced characteristic curves similar to those of a satisfactory amperometric titration. After critical examination of the part of the curve before the end point, it showed the diffusion current increasing before the end point, indicating that a titratable species was formed or added during the titration. Following the titration of 2-amino 2(hydroxymethyl) 1,3-propanediol and 1,4-diphenylguanidine, a polarogram was run in which two waves were observed, one at 1.2 volts, which is the normal position of the strong acid wave, and the other at 1.8 volts. However, neither 2-amino 2(hydroxymethyl) 1,3-propanediol or 1,3-diphenylguanidine gave a polarographic wave preceding the titration. The end point was reproducible to within ± 2%.

Since the polarographic characteristics of the sulfonate ion were not known, the titrations were repeated, using, as the acid, anhydrous hydrogen chloride dissolved in 2-propanol. However, similar results were obtained indicating that the difficulty was not due to any reducibility of the sulfonate ion.

In preliminary amperometric titrations of potassium hydroxide versus sulfonic acid, very satisfactory curves were obtained. In an effort to devise a numerical basis for comparing the curves obtained in these titrations, ratios were obtained by calculating the slope of the curve after the end point to the slope of the curve before the end point. In potassium hydroxide versus sulfonic acid,titrations with a sensitivity setting of 0.003 microamps per millimeter produced a ratio of 60,000:1 (Figure 6a). In the titrations of 2-amino 2(hydroxymethyl) 1,3-propanediol versus sulfonic acid, utilizing the same sensitivity, the ratio produced was 3:1, (Figure 6c).

From Figures 6a and 6c, it is most apparent that 2-amino 2(hydroxymethyl) 1,3-propanediol does not exhibit the suitable characteristics for titrations of this type.

Salts of Weak Acids

The anion of a weak acid is a base; therefore, salts of weak acids lend themselves to titrations with strong acids. If the weak acid does not produce a polarographic wave, the salt should be suitable for amperometric titration.

Earlier reports indicated that acetic acid did not produce a polarographic wave, but that its presence in solution produced a positive shift in the decomposition potential of the carrier (23). This work provided evidence indicating that this might be the acetic acid wave observed just prior to the decomposition potential of the carrier.

Polarograms of various acids were run with results shown in Table I. It seemed reasonable to assume that acetic acid would not give interference in amperometric titrations since the titration would be run at a potential well below that of the observed wave.Thus, and on the basis of

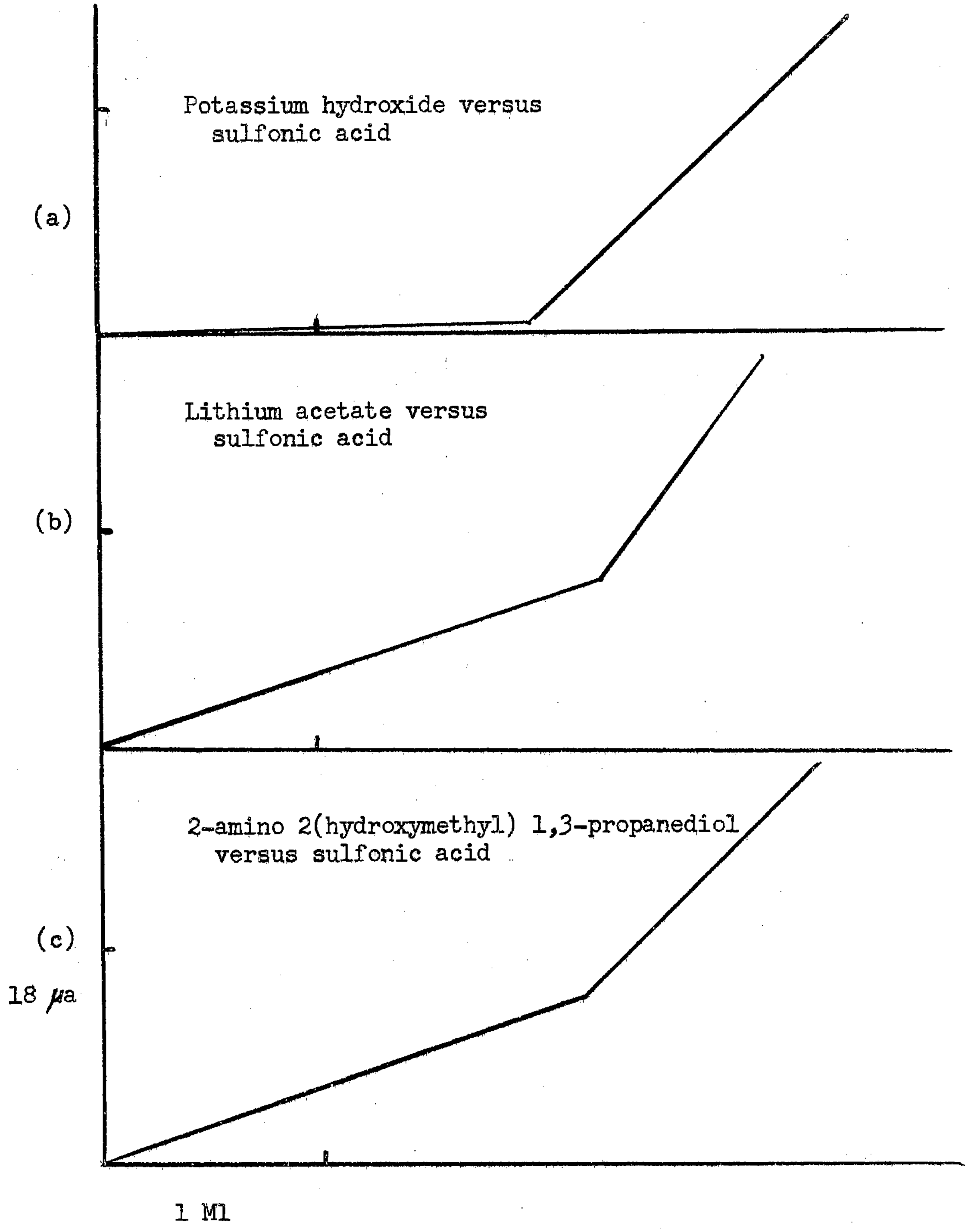


Figure 6. Titration Curves and Slopes

the solubility of the salts of the acids available, lithium acetate was chosen for a series of amperometric titrations using solutions of 2,5-dimethylbenzenesulfonic acid and of anhydrous hydrogen chloride in 2-propanol.

The results were similar to the ones obtained from the titrations of 1,3-diphenylguanidine and 2-amino 2(hydroxymethyl) 1,3-propanediol with the results being reproducible to within two percent. In Figure 6b, from titrations of lithium acetate versus sulfonic acid, it was observed that the ratio of the curves, before and after the end point, was greater than for those titrations seen in Figure 6c, 2-amino 2(hydroxymethyl) 1,3-propanediol versus sulfonic acid.

In determining the order of magnitude of the solubility of lithium acetate, a titration was attempted in which a large concentration of lithium acetate was present. In this titration, the lithium acetate was prepared by adding 15 milliliters of 2-propanol, saturated with lithium acetate to 40 milliliters of 2-propanol. Athough the concentration of the lithium acetate was too large to permit the completion of the titration, it was observed that upon the addition of the acid as the titrant, the diffusion current did not increase as it had in the 10^{-3}M lithium acetate titrations until 12 milliliters of the titrant had been added. This increase was reduced by prolonged stirring, indicating that whatever was being reduced was disappearing slowly from the solution.

An additional titration of lithium acetate, 0.002M, was performed by adding a weighed amount of lithium acetate directly to the cell, this being dissolved during the degassing procedure. This titration exhibited a much larger ratio of slope (24:1) than was the case for the 0.001M lithium acetate titrations.

The small slope of the curve before the end point in the more concentrated lithium acetate solution seemed to indicate either a more complete or a more rapid reaction between the reducible species and some other component of the solution.

TABLE I

STUDIES OF VARIOUS ACIDS IN 2-PROPANOL

	K_a*	E_d Volts	$E_{\frac{1}{2}}$ Volts
Oxalic acid	3.8×10^{-2} 4.9×10^{-5}	-1.20 -1.89	-1.66 -2.00
Benzoic acid	6.6×10^{-5}	-1.77	-1.95
Acetic acid	1.8×10^{-5}	-1.74	-1.98
Boric acid	5.5×10^{-10}	-2.28**	
Tetramethylammonium chloride		-2.28**	
2,5-Dimethylbenzenesulfonic acid			-1.18
Anhydrous hydrogen chloride			-1.18

*Values in aqueous solutions.

**Limiting value of carrier

Characteristics of the Strong Acid Wave in 2-Propanol-Water Solutions

It was felt that a series of runs should be made to see if the presence of water changed the characteristic of the acid wave. To accomplish this, two solutions were made in the following manner. The proper amount of carrier was placed in two volumetric flasks so that the resulting solutions would be 0.1M with respect to the carrier electrolyte. A sufficient amount of 2-propanol and water was added to their respective flasks to dissolve the carrier. A measured amount of the alcoholic acid was added to each flask. After mixing the solutions, they were diluted to volume. The resulting solutions were 100% 2-propanol and 10% 2-propanol containing the same amount of carrier electrolyte and acid in each.

A measured amount of the 100% alcoholic solution was placed in the polarographic cell and a polarogram was made in the usual manner. A measured amount of the water-alcohol solution was added to the cell, the mixture was stirred, than another polarogram was made. The bridge of the polarograph was stopped before and after the acid wave was reached, and in each case the applied bridge voltage was measured by a Sargent millivolt potentiometer. A polarogram was made 100%, 99%, 98%, 97%, 96%, 95%, 90%, 80%, 70%, 60%, 50%, and 40% 2-propanol. Two more solutions were made in the manner described above, with the exception that one was 100% water and the other 10% water. Polarograms were made for 0%, 10%, 20%, 30%, 40%, 50%, and 60% 2-propanol. It was observed that the half wave potential started from -1.18 volts in 100% 2-propanol, rose to a maximum at 70% 2-propanol and dropped slightly, -1.53 in 100% water (Figure 7). A slight maximum was observed when the composition of the solvent was

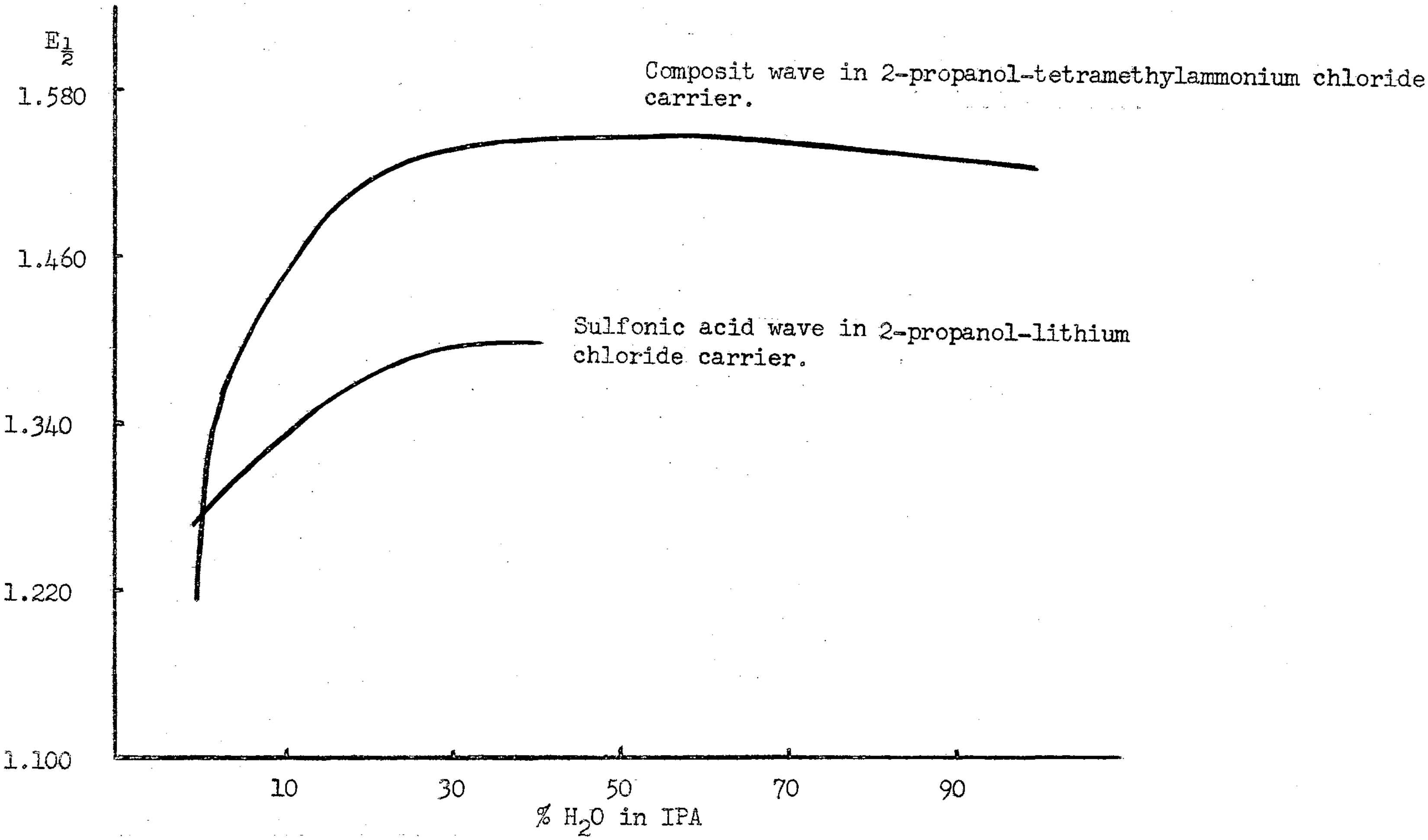


Figure 7. Half-wave Potentials of Hydrogen ion in 2-Propanol-Water Mixtures

70% 2-propanol. This was also accompanied by an increase in the diffusion current. Further, while in 100% 2-propanol, anodic waves have been observed at potentials up to -.03 volts, with the addition of water to the solution, these anodic waves decreased. If as much as 80% water were added, the anodic waves ceased to be observed. Polarograms were similar using 2,5-dimethylbenzenesulfonic acid and anhydrous hydrogen chloride. In order to prevent the possibility of the presence of a reducible bacterial species in the deionized water, a series of dilutions were repeated using distilled water. Both 2,5-dimethylbenzenesulfonic acid and anhydrous hydrogen chloride showed the same results with tetramethylammonium chloride as a carrier. A series of polarograms were made in the above manner using lithium nitrate as the carrier in place of tetramethylammonium chloride with 2,5-dimethylbenzenesulfonic acid. The results produced a change in the half-wave voltage from -1.18 in 100% alcohol to 1.39 in 60% 2-propanol, at which point the wave had increased to the decomposition voltage of the carrier electrolyte.

It was decided that it would be desirable to know the viscosity of these solutions and to correct for the changes of droptime, in order to help explain the increase of the diffusion current. In this new series, the manner of preparation of the solutions was also changed to prevent changes of concentration of the hydrogen ion, which were caused by the changes of volume due to mixing of alcohol and water solution. Four solutions were prepared: (1) 2-propanol-tetramethylammonium chloride, (2) water-tetramethylammonium chloride, (3) anhydrous hydrogen chloride-2-propanol, and (4) an aqueous hydrogen chloride solution prepared by passing the anhydrous hydrogen chloride gas into water. Both acid solutions were titrated colorimetrically and the proper dilutions made in order that the acid concentrations would be identical. A series of solutions were made, in the manner shown in Table II. In this manner, the acid concentration for each solution was presumed to be identical.

A separate run was made for each solution. Each run was made in the following manner. Several polarograms were made, usually five, until it was certain that a good representative polarogram was obtained for each particular solution. During each run, the bridge was stopped before and after the acid wave was reached, and the applied bridge voltage checked with the millivolt potentiometer. After the applied voltage had been checked for the last time and without changing the potential, a small glass cup was placed under the D. M. E. and the drop time for fifty drops was determined with a stop watch. This mercury was removed from the cell and weighed. A measured amount of the solution was pipetted into an Ostwald viscometer, which was in the constant temperature bath beside the polarographic cell, and the viscosity was determined. The specific gravity was determined for the solution by a Westphal Balance, before the cell was removed from the bath. It was noted that the drop time decreased slightly with the increase of potential in each run, while the droptime increased slightly with an increased percentage of water in solution. The diffusion current of these runs was corrected to a run which was made of 100% 2-propanol (Figures 8 and 9) (Table II).

Suggestions and Conclusions

If, as is generally believed, the ionization constants of a series of acids in a given nonaqueous solvent have the same relative position as they do in aqueous solutions, the Ka values of these acids for aqueous solutions could be used as a guide for amperometric titrations in nonaqueous systems.

TABLE II

HCl-2-PROPANOL- WATER SOLUTIONS

% 2-Propanol	HCl 2-Propanol ml	2-Propanol Carrier ml	Aqueous Carrier ml	Viscosity Centipoises	$E_{\frac{1}{2}}$ Volts	i_d μa	sec/drop	mg/sec	$m^{2/3}t^{1/6}$
100	5.00	95.00	0.00	2.238	1.17	1.34	4.83	0.892	1.205
95	5.00	90.00	6.00	2.289	1.41	1.61	5.05	0.910	1.230
90	5.00	85.00	11.52	2.476	1.48	1.88	4.69	0.921	1.225
80	5.00	75.00	22.08	2.818	1.53	2.47	4.43	0.905	1.199
70	5.00	65.00	32.43	3.046	1.54	3.16	4.81	0.908	1.219
60	5.00	55.00	42.52	3.091	1.51	3.72	4.70	0.896	1.203
50	5.00	45.00	52.57	2.986	1.52	4.57	5.17	0.895	1.222
40	5.00	35.00	62.51	2.704	1.50	4.96	5.19	0.881	1.209
30	5.00	25.00	72.15	2.308	1.51	5.74	4.87	0.901	1.214
20	5.00	15.00	81.48	1.795	1.50	6.76	4.88	0.935	1.245
10	5.00	5.00	90.25	1.308	1.50	7.85	5.14	0.893	1.218
00	5.00[a]	0.00	95.00	0.899	1.48	9.02[b]	4.47		

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[a] Aqueous acid.

[b] Uncorrected.

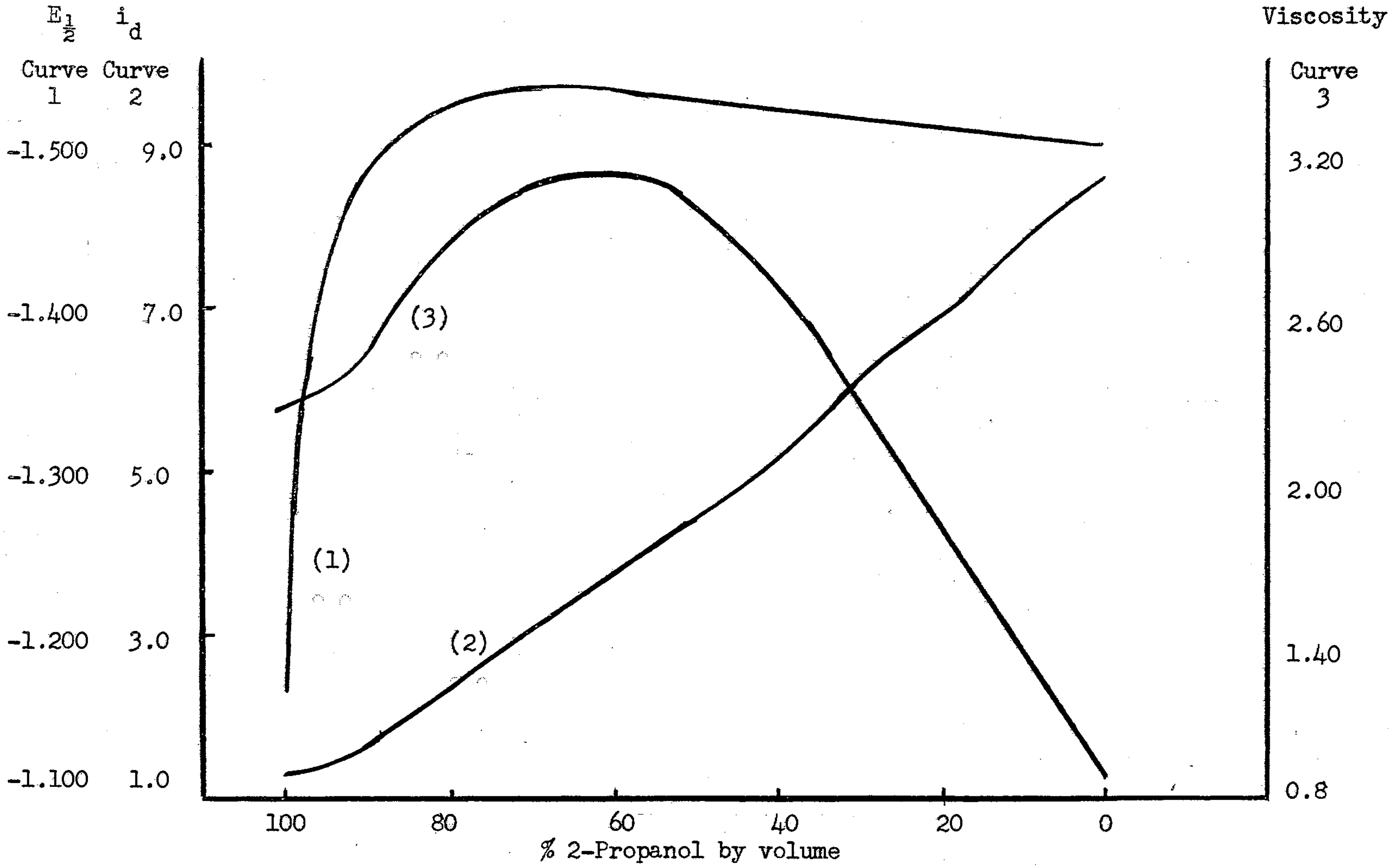

Figure 8. Hydrogen Chloride in 2-Propanol-Water Mixtures

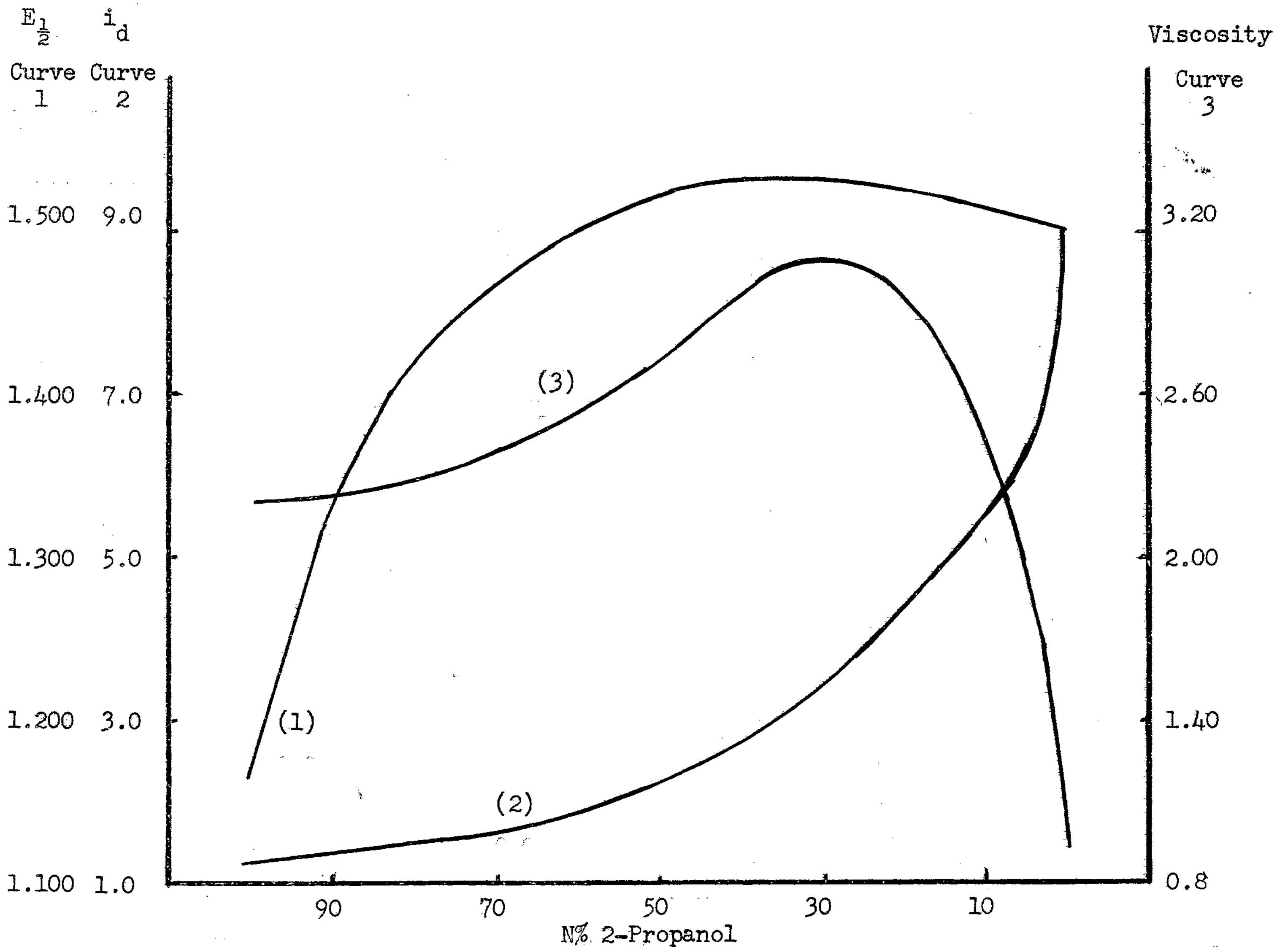

Figure 9. Anhydrous Hydrogen Chloride in 2-Propanol-Water Mixtures

It was observed that acids possessing values greater than 2 x 10^{-5} produced a wave near the wave of the titrant being used. Also, it was noted in the titrations of the acetate ion, 1,3-diphenylguanidine and 2-amino 2(hydroxymethyl) 1, 3-propanediol with anhydrous hydrogen chloride or 2,5-dimethylbenzenesulfonic acid, that polarographic species were present in the solution before the end point was reached.

This caused the curve prior to the end point to exhibit a slope very similar to the slope of the curve after the end point was reached. This decreased the sharpness of the intersection of the two curves, whereas potassium hydroxide versus anhydrous hydrogen chloride amperometric titrations demonstrated curves of greater definability.

Although the amperometric titrations of the acetate ion were reproducible to within two percent, it may be assumed that the accuracy of the titration is dependent upon the relative strengths of the particular acids and bases used in amperometric titrations. By considering potassium hydroxide a salt of a weak acid or by comparing the strength of the bases, acetate and hydroxide ions, it is possible that bases of comparable, or greater strength than the hydroxide ion, would give better results for amperometric titrations.

It is suggested that in future research along these lines reagents exhibiting greater basic characteristics be used in these titrations. It is also felt that other solvents which would tend to increase the basic qualities of the present reagents, be tested. From these suggestions, it is feasible that substances, not exhibiting acid-base characteristics in water, could lend themselves to amperometric titrations, provided a suitable solvent could be found. Also, substances that are soluble only in nonaqueous media could be titrated much more conveniently than is possible by methods presently employed.

The presence of polarographic species, at potentials less than the decomposition potentials of expected products of the titration, and the change in potential due to the change in solvent stresses the fact that simple ions are not present. Thus, high-resistance polarographic techniques may lend themselves to studies of solvation complexes, not only of the hydrogen ion but of other ions as well. It is further suggested that a series be run with different alcohols, ranging from low to high molecular weight, normal to highly substituted isomers and other solvents with more or less acidic characteristics. Also, by employing higher sensitivities, it may be possible to demonstrate a proton wave for a weak acid.

It is reasonable to assume that the diffusion current would increase with decreasing viscosity. However, results obtained and illustrated in Figures 7 and 8, indicate that the diffusion current increased with an increasing viscosity. Therefore, these results indicate that the hydrated and partially hydrated proton is more mobile than a completely alcoholated hydrogen ion.

By assigning values to the following equation

$$\frac{i_{d\text{water}}}{i_{d\text{alcohol}}} = \frac{M_{\text{alcohol}}\,\eta_{\text{alcohol}}}{M_{\text{water}}\,\eta_{\text{water}}}$$

the M (molecular weights) of the reducible species in both aqueous and nonaqueous solutions may be compared. Assuming the molecular weight of the reducible species in aqueous solution to be 19, it is found that the molecular weight of the reducible species in 2-propanol should be 342. This seems to indicate that in the complex there are five molecules of 2-propanol attached to one molecule of hydrogen chloride.

Such a conclusion should be treated with caution, however, for other factors such as the postulated skipping behavior of the hydrogen ion when it migrates through water solutions must certainly influence these results.

According to Kolthoff, the half wave potential of a complex is related to that of the simple ion by the equation

$$(E_{\frac{1}{2}})_c - (E_{\frac{1}{2}})_s = \frac{0.0591}{n} \log K_i - p\,\frac{0.0591}{n} \log C_x$$

where subscripts c and s refer to the complex ion and simple ion respectively, K_i is the instability constant for the complex ion, p is the coordination number, and C_x is the concentration of the ligand. Although values to substitute into this equation are not known for the situation, one could reason from it that the observed changes in half-wave potential are logical. It is generally agreed that the overall instability constant for the hydrated proton in water must be *much* smaller than that for the proton in alcohol. If other things are even of the same order of magnitude for the two cases, the equation would show that $E_{\frac{1}{2}}$ for the aqueous proton *must* be more negative than would the $E_{\frac{1}{2}}$ for the alcoholic proton, regardless of the state of the latter.

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