AMPEROMETRIC ACID-BASE TITRATIONS IN A

2-PROPANOL-2,2,4-TRIMETHYLPENTANE

MIXTURE

By

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PREFACE

Acid-base titrations are ordinarily carried out in an aqueous medium or in mixtures of water with other solvents of reasonably high dielectric constant. However, a sample to be analyzed may be present in a nonaqueous medium, the nature of which can render ordinary analytical techniques ineffective. This often requires that the component undergoing analysis be extracted, often tediously and incompletely, from the nonaqueous medium into an aqueous phase so that the analysis can be accomplished.

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

The purpose of this research was to establish conditions necessary for the quantitative amperometric determination of strong acids in a nonaqueous medium.

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CHAPTER I

INTRODUCTION

The Nature of Polarography

If two inert electrodes are placed in a solution with
a continuously increasing voltage impressed across them
eventually a potential will be reached which will give rise
to decomposition of the solution and to an increase in cur-
rent due to electrolysis. After the decomposition potential
has been reached, a further increase in voltage will cause
the current to rise rapidly to large values. If, however,
one of the electrodes is a very small, easily polarized
electrode, other interesting current-voltage relationships
are obtained.

The polarograph is an instrument with which a constant-
ly varying voltage can be impressed across two electrodes,
one of which does not polarize easily because of its large
size and the relatively small currents encountered in po-
larography, and the other of which is of small surface area
and is easily polarized. Usually the current is continuously
measured by a strip chart recorder which is synchronized
with the advancement of a motor-driven voltage divider with-
in the polarograph.

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The polarizable electrode is commonly a dropping mercury electrode (D.M.E.). This consists of a glass capillary tube about 8-10 centimeters long whose internal bore is of a size such that a head of mercury of about 30-40 centimeters, when connected to the upper end of the capillary, will cause a droplet of mercury to form and fall every three to six seconds. The most widely used non-polarizable or reference electrode is the saturated calomel electrode.

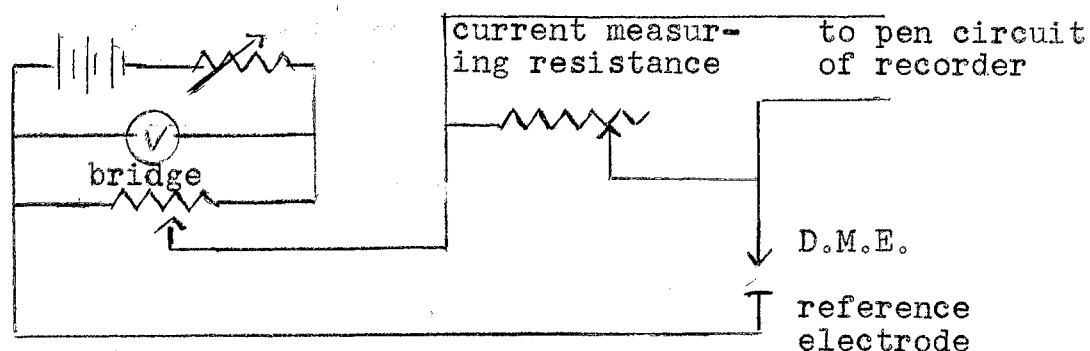A common polarographic circuit is illustrated in Figure 1.

Figure 1. Circuit of Common Polarograph

In order to understand the current-voltage relationships obtained in polarography, it is advantageous to consider the various parts of a typical wave or polarogram, such as the one in Figure 2.
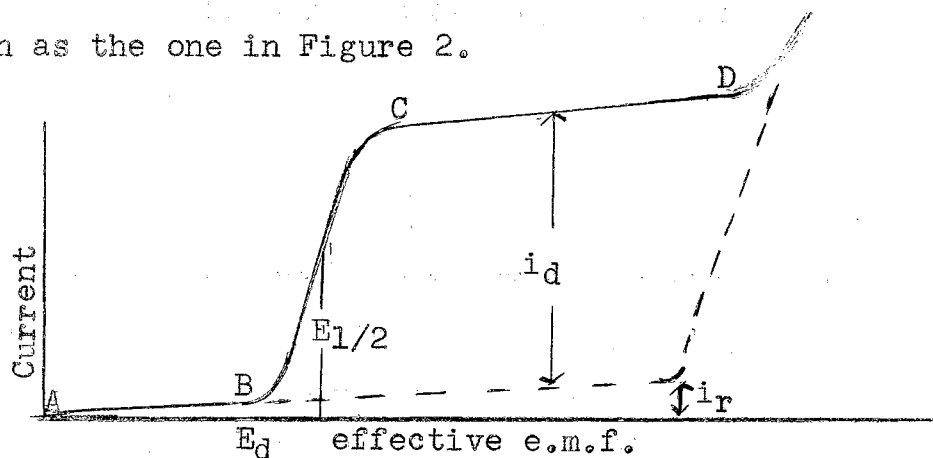
Figure 2. Normal Polarogram

As the applied voltage begins to increase at $\underline{A}$, a small residual current begins to flow. This current is composed of a condenser current which is attributed to the absorption of negative or positive ions on the surface of the mercury droplet, and to the electrolysis current which is due to decomposition of trace quantities of impurities such as oxygen and mercury ions in the solution. At $\underline{B}$, decomposition of the oxidizable or reducible species begins and the current rapidly increases with a small increase in voltage. Since electro-active material can reach the electrode by electrostatic attraction and by diffusion, both of these phenomena operate during the initial rapid rise in current from $\underline{B}$ to $\underline{C}$.

All of the ions in a solution contribute to the current flow through the cell. The fraction of the total current carried by each type of ion depends largely upon its concentration. Consider the case of a solution containing a large excess of A^+ ions and a small amount of B^+ ions. Then, if A^+ ions constitute 99 percent of the total cation concentration and B^+ ions constitute the other one percent, at point $\underline{B}$ on the polarogram, the voltage below which B^+ ions cannot be discharged, the small D.M.E. will be surrounded by a cloud of A^+ ions while B^+ ions will contribute practically nothing to the migration current, which is due to electrostatic attraction. This represents a condition of extreme polarization of the D.M.E. and, since only B^+ ions can be discharged at voltages less than $\underline{D}$, the only current from

$\underline{B}$ to $\underline{D}$ will be due to discharge of B^+ ions. At $\underline{C}$, the concentration of B^+ ions at the electrode becomes zero. The limiting current, $\underline{CD}$, will then depend upon the rate at which B^+ ions can diffuse in to the electrode. Since the diffusion rate of B^+ ions will be proportional to the concentration gradient of B^+ ions between the surface of the D.M.E. and the bulk of the solution, the current along line $\underline{CD}$ will be proportional to the concentration of B^+ ions in the bulk of the solution. The diffusion current thus assumes quantitative significance. The current increases very little with an increase in voltage until point $\underline{D}$ is reached at which voltage ions of A^+, contributed by what is called the carrier electrolyte, begin to discharge. The current between points $\underline{C}$ and $\underline{D}$ is called the limiting, or total current and is actually made up of the true diffusion current, $\underline{i}_d$, and the residual current, $\underline{i}_r$.

$\underline{E}_d$ is the lowest potential at which decomposition of B^+ ions can occur in the solution.

The half-wave potential, $E_{\frac{1}{2}}$, is the potential at the point of inflection of the current-voltage curve, half way between the residual current and the limiting current plateau. This potential is a characteristic of a given reducible or oxidizable species under a fixed set of conditions and can be used for identification purposes.

From diffusion current theory, and on a purely theoretical basis, Ilkovic derived the equation which bears his name and which describes the dependency of the diffusion current on several different quantities (19, 20).

The original Ilkovic equation is

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

where i_d is the average current in microamperes during the life of the drop, n is the number of faradays of electricity required per mole of reducible or oxidizable species, D is the diffusion coefficient of the reducible or oxidizable ion or molecule in cm.^{2} sec.$^{-1}$, C is 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 in seconds. From the equation it is seen that for a given electroactive species, when using a given capillary,

$$i_d = KC.$$

That is, the diffusion current is proportional to the concentration of the electroactive substance. This result has been found to be in essential agreement with experimentally determined results (33).

One form of the Ilkovic equation obtained by rearrangement is

$$I_d = 607 \, nD^{1/2} = \frac{id}{Cm^{2/3}t^{1/6}}$$

where I_d is called the _diffusion current constant_. This quantity should be independent of the electrode characteristics, m and t.

Amperometric Titrations

The principles of polarography can be utilized as the basis for an electrometric titration method. In this method, the voltage impressed across the two electrodes is held

constant and the changes in current due to changes in con-
centration brought about by the addition of a suitable rea-
gent is plotted against the volume of titrant added. Hence
the name amperometric titration.

That the method is polarographic in principle can best
be illustrated by considering what happens if substance A,
which yields a polarographic wave, is titrated with aliquots
of substance B, a reagent which removes A from the solution
and which itself gives no polarographic wave. A may be
removed from the solution by precipitation, complexation,
reduction or oxidation. The assumption is made for this
illustration that no products are formed which are them-
selves electroactive at the voltage used.

If a polarogram is run after the addition of each ali-
quot of B, a series of waves like the ones in Figure 3 will
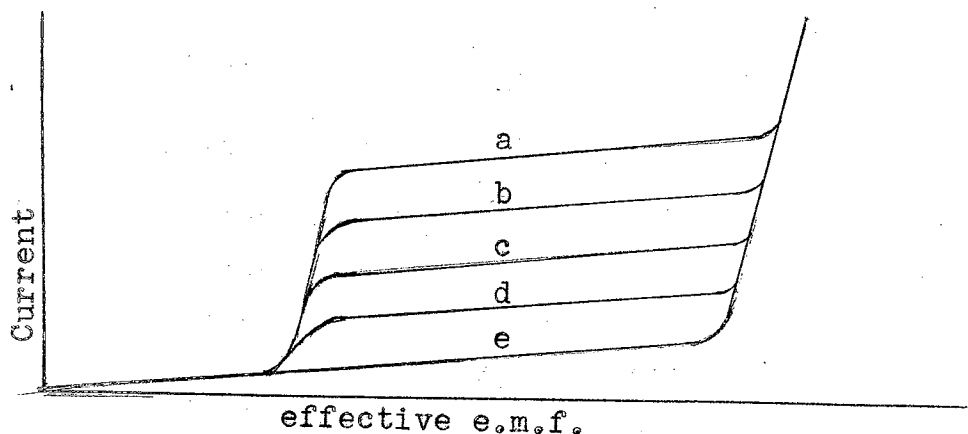be obtained. Wave a will be obtained before the titration

Figure 3. Current-voltage Curves Relating Amperometric
Titrations to Polarography.

starts. Wave b will be formed after the addition of the
first aliquot of B has been added. Waves c and d will be

obtained after the third and fourth aliquots, respectively, of $\underline{B}$ have been added. Wave $\underline{e}$ will be formed after stoichiometric reaction of $\underline{B}$ with $\underline{A}$ and the same wave, due to residual current only, will be produced essentially unchanged with further additions of $\underline{B}$. Now, if the diffusion currents corresponding to points $\underline{a}$, $\underline{b}$, $\underline{c}$, $\underline{d}$, and $\underline{e}$ are plotted against the volume of titrant added, a straight line with a descending slope will be obtained. The intersection of this line with the horizontal line obtained from points measured after the endpoint is passed corresponds to the endpoint itself. A curve similar to (a) in Figure 4 will be the result.

Figure 4. Three Common Amperometric Titration Curves
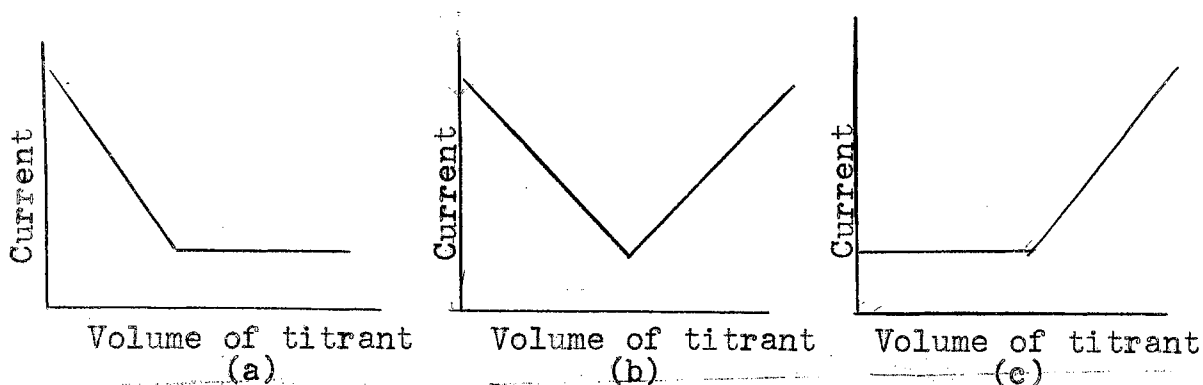
In practice, a fixed voltage is chosen which is on the limiting current plateau, and brief current measurements are made after each aliquot of titrant has been added. Thereby the necessary points are obtained for plotting with a minimum of effort and time.

If, in the titration described above, the titrant $\underline{B}$ served the same purpose, but itself was electroactive at

the voltage employed, additions of titrant past the end
point would lead to an increase in current due to the ex-
cess B present. In this case, a curve of type (b) in
Figure 4 would result.

Materials which give no polarographic wave can be ana-
lyzed amperometrically provided a titrant can be found which
reacts stoichiometrically with the material and which it-
self will give a polarographic wave. In this case, almost
no current will flow before the end point is reached and
past the end point the current will increase with the addi-
tion of each aliquot of excess titrant. Such a titration
curve is illustrated in (c) of Figure 4.

Volume changes during a titration can be neglected if
the ratio of the concentrations of titrant to titrated
species is ten or greater. Dilutions due to large volume
changes during the titration tend to result in curvature
of the titration lines and a corrective factor must be used.
In such cases

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

where V is the original volume of the solution and v is the
total volume of titrant added in order to obtain the meas-
ured current.

An excellent summary of the advantages and disadvantages
of the amperometric titration method has been presented by
Kolthoff and Lingane (28).

CHAPTER II

HISTORY

Theoretical Developments and Amperometric Applications

While studying the electrocapillary curve of mercury
in 1903, Kucera (32) observed that deflections in the
curve were obtained when reducible substances were pres-
ent. Upon Kucera's recommendation, Heyrovksy (13, 14)
investigated these curves further. After determining proper
diffusion conditions, he obtained reproducible currents.
From this work polarography was developed.

Although Salomon, as early as 1897, mentioned the
underlying principles of amperometric titrations, his method
utilized chemical rather than concentration polarization
(45, 46). He did show, however, that the currents obtained
were proportional to the concentration of the reducible
species. Salomon used the term "galvanometric titration"
to describe his procedure. Nernst and Merriam (41) also
pointed out the possible use of amperometric titrations and
Fresenius (10) later used their method in an attempt to de-
termine small hydrogen ion concentrations. In 1925, Heyrovsky
and Shikata (17) invented an automatic recording instrument
for their new method and introduced the terms "polarography"

and "polarogram". The "dead stop end point method" of Foulk and Bawden (9) resembled that of Salomon. With one type of application of this method, current flows at two depolarized electrodes until after the end point, when one electrode becomes polarized and the current drops to zero or close to zero.

Heyrovsky and Berezicky (15) used a depolarized anode and the dropping mercury electrode as an indicator electrode in the titration of barium ion with sulfate ion and probably were the first to perform an amperometric titration. They suggested the name "polarographic titration" for their method. Nejedly studied the diffusion currents of some metal ions and showed that an increase in current of about two percent per degree rise in temperature could be expected at the dropping mercury electrode (40).

Polarography took on particular theoretical significance in 1934, when Ilkovic presented his original derivation of the equation which bears his name (19, 20). His derivation was done on a purely theoretical basis, but he performed two short experiments which verified the validity of his postulates. Shortly afterwards, Heyrovsky and Ilkovic removed a large part of the empirical nature of polarography when they demonstrated the theoretical significance of the polarographic wave (16). In discussing the general principles of amperometric titrations Majer used the term "polarometric titrations" (38).

In 1937, Antweiler showed that a stirring effect in the solution near the dropping electrode accompanies the maxima

so often encountered with polarographic waves (2). At about this same time, Peracchio and Meloche studied the diffusion currents of the various alkali ions in alcohol-water, dioxane-water, ethylene glycol-water, and glycerol-water mixtures. They observed that the diffusion currents were smaller in these solvent systems than in pure water (44).

Perhaps the first exhaustive study of the underlying principles and theories of polarography was the one undertaken by Lingane and Kolthoff. One of their first studies was that of the Ilkovic equation for polarographic diffusion currents (33). Ilkovic theoretically derived his equation and checked its validity with only two simple polarographic systems. Lingane and Kolthoff subjected the equation to extensive testing and found that the equation and the postulates on which it was based were correct. Other studies were devoted to the characteristics of the limiting current (34). These authors were perhaps the first to prepare a comprehensive review of studies at the dropping mercury electrode (27).

In 1950, Strehlow and von Stackelberg explained the experimentally observed variations of the diffusion current constant with changing characteristics of the dropping mercury electrode. They demonstrated that the failure of the original Ilkovic equation to explain these variations was due to a neglect of the curvature of the electrode surface. The new equation became

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

where $\underline{A}$ was evaluated as 17 at 25°C. (48).

Independently about this same time Lingane and Loveridge (35) arrived at essentially the same conclusions as did Strehlow and von Stackelberg. Their modified equation is the same as the one above with the exception that $\underline{A}$ was evaluated as 39 at 25°C.

Macero and Rulfs, using the average of results obtained with six different ions, have very recently indicated that the correct value for $\underline{A}$ should be 31.3 ± 1.6 (37).

The term "amperometric titration" was first proposed by Kolthoff and Pan in view of the fact that in these titrations a current is measured as a function of concentration (30).

Many of the analyses which first lent themselves to this new technique were precipitation titrations. A typical one of this class, the titration of sulfate ion with lead ion, was studied at some length by Kolthoff and Pan (31). They suggested alcohol-water mixtures for such titrations in order to suppress the solubility of precipitates formed.

A method for the determination of mercaptans in alcoholic ammoniacal media by means of amperometric titrations was introduced in 1946 (26). Styrene was titrated with potassium bromate by Kolthoff and Bovey (25). They used a solvent of 75 percent methanol and obtained low, but satisfactory results. Olefins were titrated by Braae using a bromine titrant and the dead stop end point method (6).

An amperometric procedure for analyzing soluble mercapto group materials such as those present in blood was introduced

in 1950 (5). This utilized a rotating platinum electrode in a solvent composed of at least 80 percent ethyl alcohol. Employing the same type of electrode, Kolthoff and Medalia (29) obtained satisfactory titration curves while studying ferrous ion in 70 to 80 percent acetone.

Amperometric end points have been used to determine iodine values for fatty acids and oils (8), and titrations of fluoride with ferric chloride in 50 percent alcohol have been accomplished (24).

In 1955, mercaptan sulfur in hydrocarbons yielded to amperometric titration techniques utilizing silver ion (11). Lead ion has proven suitable as a reagent for the analysis of tungstate ion in 50 percent ethyl alcohol while acetone-water mixtures have proven suitable as solvent systems in the analysis of thallium with iodide and with dichromate (22).

Hinsvark and Stone (18) described the titration of oxalic acid with ammonium hexanitratocerate in glacial acetic acid. Acetone-water mixtures containing at least 90 percent acetone have been used to decrease the solubility of silver chloride such that solutions of chloride ion as dilute as 10^{-5} molar can be titrated (7).

High Resistance Polarography

Several approaches have been made to the problems encountered with solutions of high resistance. A conventional polarograph modified so that the recorder pen drives an

auxiliary bridge whose output, connected in series with the
polarograph, gives iR compensation has been described by
Nicholson (42). Jackson and Elving (21) have developed an
iR-compensator for use with a conventional polarograph. In
their compensator the iR-drop of a small resistor in series
with the electrolysis cell is made equal to the iR-drop of
the cell by amplification. This amplified voltage, put in
series with the polarograph, automatically augments the
bridge voltage thereby compensating for the iR-drop within
the cell. Employing principles similar to those used in
the Arthur polarograph (3, 4, 36), Sawyer, Pecsok, and Jensen
(47) have described an automatic recording polarograph using
two reference electrodes. More recently Oka (43) and Kelly,
et al. (23) have described iR-compensators which also uti-
lize two reference electrodes.

It is known that the **applied voltage** obtainable from
the bridge of a conventional polarograph is used in two
ways. A portion of the voltage is the **effective voltage**
which brings about electrolysis within the polarographic
cell while the remainder of the voltage is used to overcome
the iR-drop within the cell. Thus

$$E_{applied} = E_{effective} + E_{iR}.$$

In aqueous solutions whose resistances are only a few hun-
dred ohms the E_{iR} term is very small and, for most pur-
poses, may be neglected. For this reason, conventional
polarographs plot the current as a function of the applied
voltage. In solutions whose internal resistances are quite

large, however, the applied voltage may be almost entirely
utilized to overcome iR-drop and with conventional polaro-
graphs an unintelligible polarogram will result.

One means by which this problem can be overcome is
that described by Arthur and Lloyd (3, 36). The schematic
for this device is given in Figure 5.
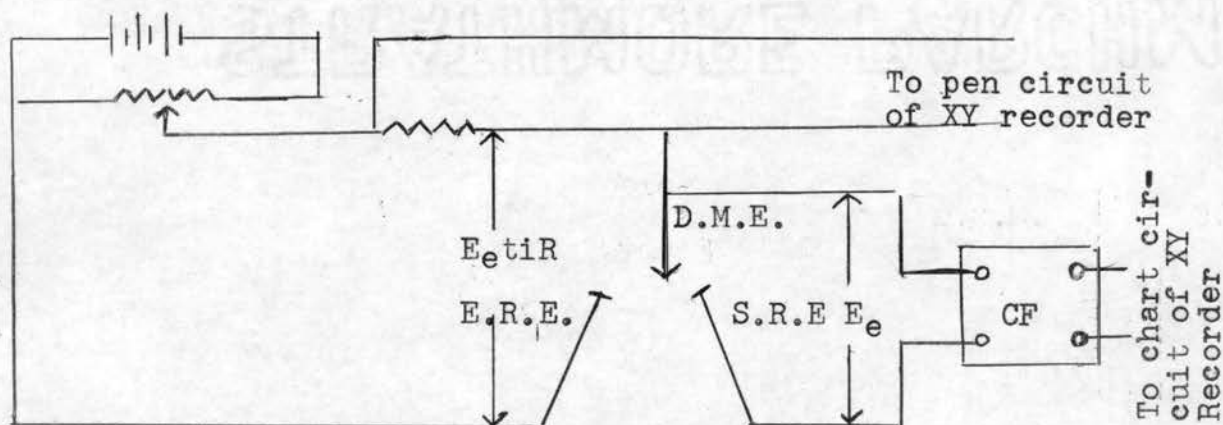
Figure 5. Schematic of One Type of High
Resistance Polarograph

This instrument uses a strip-chart function plotter
(XY recorder) the pen of which moves as a function of one
potential (which is proportional to the current) while the
chart moves as a function of the effective potential. This
apparatus employs the usual electrolysis reference electrode
(E.R.E.) and the dropping mercury electrode (D.M.E.), but
in addition requires a second stable reference electrode
(S.R.E.). It is this second reference electrode against
which the effective voltage of the microelectrode is mea-
sured. The input impedence of the cathode follower (CF)
is quite large; consequently, the current flow in this part
of the circuit is negligibly low and the chart moves as a

function of the true potential difference between the D.M.E. and the S.R.E.

Consideration of the circuit above shows that the potential difference between the S.R.E. and the E.R.E. should be numerically equal to the iR-drop within the electrolysis branch of the cell. This difference of potential has been utilized by Arthur (4) as the basis for an improved type of iR-compensator.

This apparatus (see Figures 6 and 7) employs the same type of polarographic cell as did the earlier model but
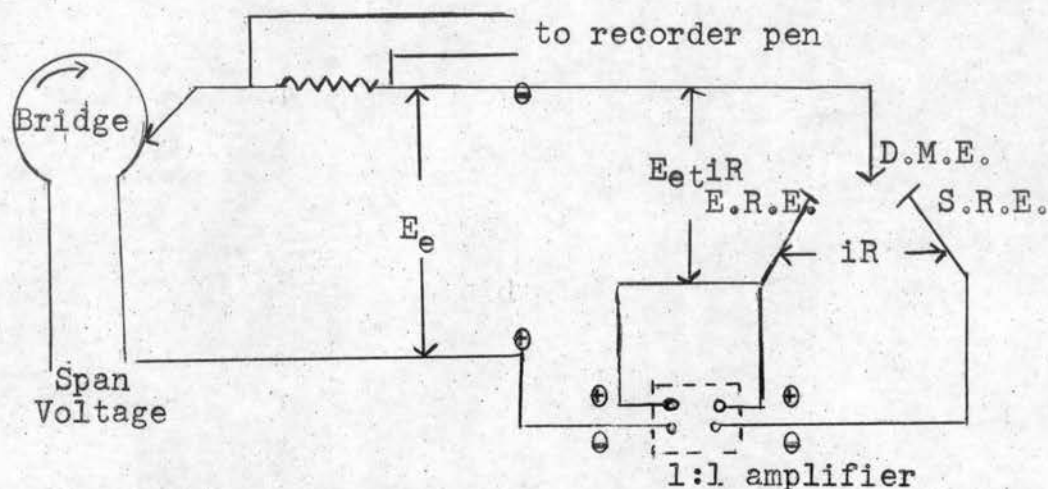
Figure 6. Schematic of Improved High Resistance Polarograph

differs from it in that a conventional polarograph may be used. The bridge of the polarograph supplies the effective voltage but this voltage, before being impressed across the electrolysis branch of the circuit is augmented by the output potential of the 1:1 amplifier, the latter being connected in series with the polarograph. Thus the polarogram obtained is conventional in form and may be easily evaluated

using well-known standard techniques. The 1:1 amplifier
is again essentially a cathode follower of high input
impedance which can measure the potential difference (iR-
drop) between the E.R.E. and the S.R.E. without drawing
appreciable current. The amplifier, which was developed
by Arthur (4) in collaboration with E. H. Sargent and
Company, is shown in detail in Figure 7. This apparatus
possesses, in addition to its more obvious advantages, that
of being contained in a small unit which can be used as an
attachment to almost any conventional polarograph.
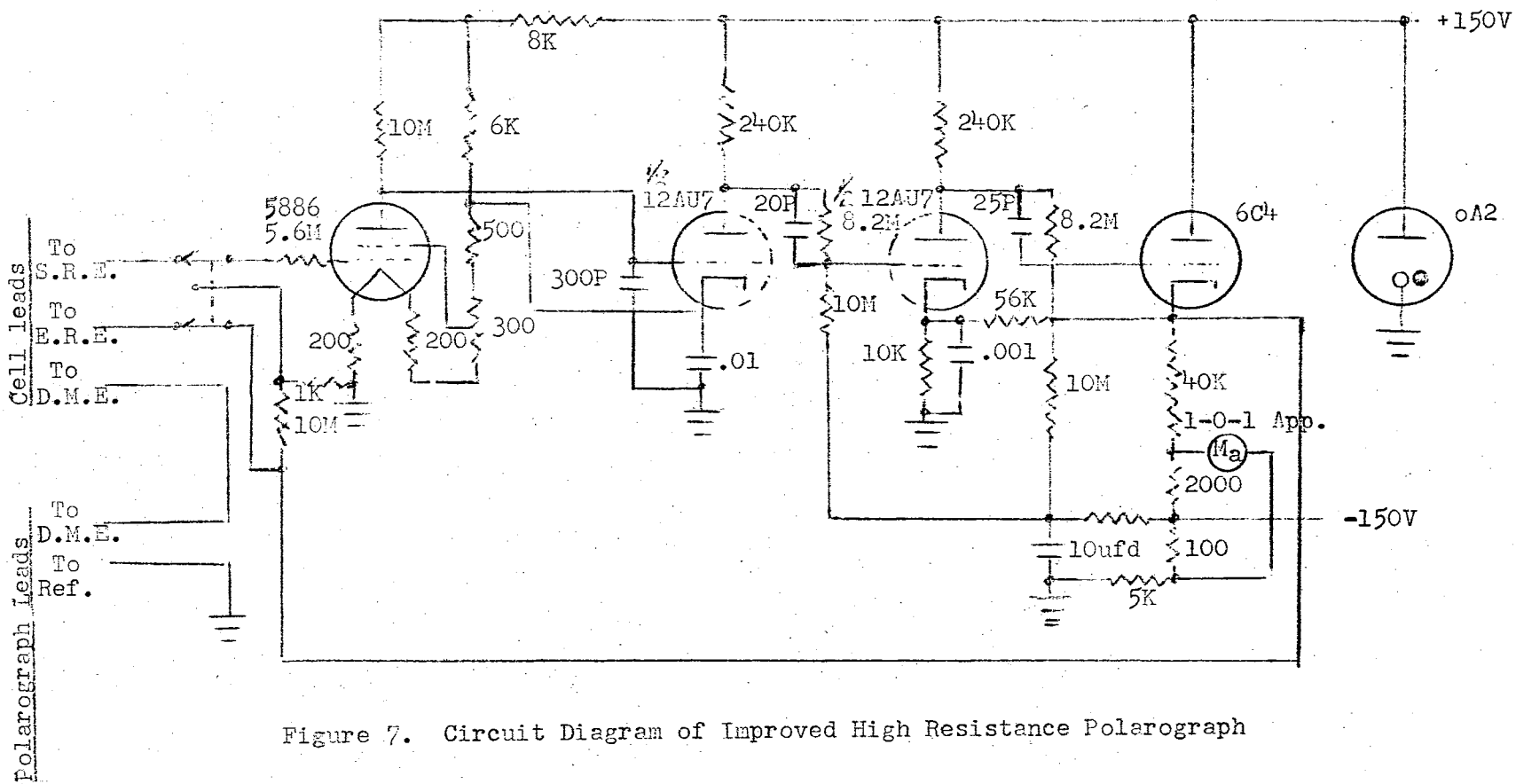
Figure 7. Circuit Diagram of Improved High Resistance Polarograph

CHAPTER III

SCOPE OF INVESTIGATION

The primary purposes of this investigation were to study the polarographic behavior of solutions of strong acids and to attempt the development of a method which would allow this class of compounds to be quantitatively determined in solutions of high resistance. The ideas for this research evolved, to a great extent, from the work done in this laboratory by Mr. Paul Moran who investigated the polarographic behavior of certain oil additives which contained the sulfonic acid or sulfonate group.

The basic apparatus employed was that already proven reliable in high resistance polarographic studies in this laboratory.

CHAPTER IV

APPARATUS

Preliminary experiments were performed with the high resistance polarograph developed by Arthur and Lloyd (3, 36) in which had been substituted the cathode follower described by Gucker and Peterson (12). Plate voltage for the cathode follower was provided by a ninety-volt dry battery and the filament supply was a six-volt storage battery.

The last portions of this work were performed using the improved iR-compensator developed by Arthur (4) and described in detail in Chapter II.

The electrolysis cell, which was one developed by the author and his advisor, is shown with a reference electrode vessel in Figure 8. The enlarged portions of the side arms of the electrolysis cell were filled with approximately one milliliter of three percent agar in 0.10M lithium chloride. The side arms of the reference electrode vessels were packed with absorbant cotton which had been moistened thoroughly with a saturated solution of potassium chloride. This arrangement allowed little or no contamination by foreign ions of solutions either in the reference electrodes or in the electrolysis cell. This arrangement also facilitated
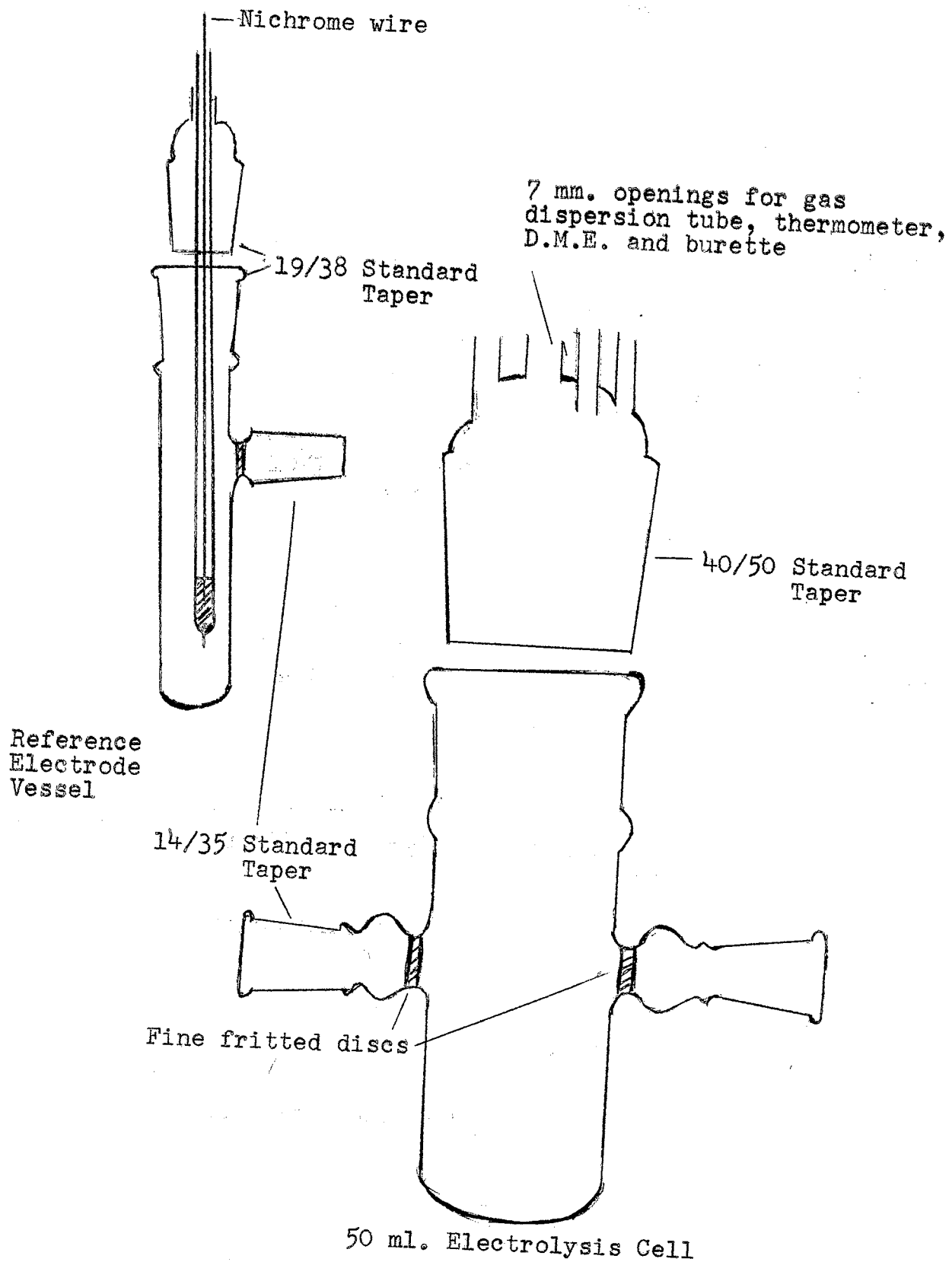
Figure 8. Electrolysis Cell Assembly

cleaning of the assembly and changing of the side arm pack-ings. New cotton packings and new agar were used for each experiment.

Both reference electrodes were aqueous saturated calomel electrodes.

Mercury purification was accomplished with a type "G" Mercury Oxifier from Bethlehem Apparatus Company and a vacuum still from Gaertner Scientific Company.

The dropping mercury electrode assembly was that de-scribed by Lloyd (36).

All pH measurements were made with a Beckman pH Meter, Model H2.

All experimental measurements utilizing the electrolysis cell were made at a temperature of $25.0 \pm 0.1^{\circ}C$. which was maintained by a mineral oil constant temperature bath.

Microburettes with capacities of five milliliters were used for all titrations. These had graduations of 0.01 ml. but the nearest 0.001 ml. could be estimated with the aid of a magnifier. The burettes were actually Exax white line pipettes which had attached to them a short piece of surgi-cal rubber tubing and a tip made from a short section of capillary tubing. Within the section of surgical rubber tubing was contained a solid glass bead which prevented the flow of titrant until the tubing immediately surrounding the bead was squeezed with a gentle pressure. Very good regulation of the flow could be had using this improvised stopcock. The usual type of glass stopcock proved useless

since the titrant used was an alcoholic solution of potassium hydroxide. This solution quickly dissolved the usual stopcock lubricants, which led to contamination of the titrant and freezing of the stopcock.

The burette was filled by forcing titrant up through the bottom tip by means of nitrogen pressure within the polyethylene bottle which was used to store the titrant. The top of the burette was protected from atmospheric carbon dioxide by an ordinary drying tube filled with ascarite.

CHAPTER V

REAGENTS

Acetic acid - Dupont 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
O.S.U. chemistry storeroom was used without further purifi-
cation.

Cetyldimethylethylammonium bromide - Matheson, Coleman,
and Bell technical grade was used without further purifi-
cation.

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

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

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

Lithium chloride - Mallinckrodt analytical reagent
grade was used after being dried for several days at 110°-
115° C.

Mercuric chloride - Merck reagent grade was used with-
out further purification.

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

Mercury - Goldsmith Brothers reagent grade was used after filtration with a gold filter.

Methyl Orange - Baker and Adamson reagent grade was used without further purification.

Methyl Red - Baker and Adamson reagent grade was used without further purification.

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

Nitrogen - Water-pumped Airco was used after passing successively through three towers of chromous sulfate-sulfuric acid-amalgamated zinc, a column of Pyrex brand wool filtering fibre, a column of Fisher Scientific indicating silica gel (6-16 mesh), and two presaturator towers filled with the solvent system.

The chromous scrubbers were prepared in a manner similar to the one described by Altieri (1) and modified by Moran (39). Zinc amalgam was prepared by the addition of three pounds of reagent grade zinc shot to a solution of 21 g. of mercuric chloride dissolved in 500 ml. of water. This was shaken occasionally for about fifteen minutes, separated by decantation and washed with water. The zinc was divided equally among three 250-ml. towers. To each tower were added 75 ml. of 0.6M sulfuric acid solution and 75 ml. of chromic sulfate solution, the latter consisting of 100 g. of chromic sulfate in 225 ml. of solution. The

towers were closed immediately. After a few hours the characteristic blue color of the chromous ion was evident. The third tower was not needed, but it was included in case the first two became expended during a long series of experiments.

Originally, the gas scrubbers were prepared with twenty-mesh zinc granules, but the recovery rate of the solution, i.e., the rate of formation of chromous ion, was not sufficiently rapid. This was due to the small surface area of the zinc presented to the bulk of the solution. The very small size and the tightly packed nature of the zinc particles prevented the flow of solution over their surfaces. In addition, a thin film of basic zinc salts appeared as a scum over the top of the zinc layer, further diminishing the reducing action of the metal on the chromic ion. The use of zinc shot allowed larger interstices through which the solution could pass. Stirring was accomplished by inserting the end of the gas inlet tube well below the surface of the zinc layer.

The use of 0.6M sulfuric acid greatly lengthened the useful life of the scrubbers over that obtained when 0.10M sulfuric acid was used as suggested by Moran (39). Although 0.6M sulfuric acid was used, it is probable that more concentrated acid would reduce the formation of basic salts. However, a much higher acid concentration could cause excessive hydrogen evolution by reaction with the zinc.

The glass wool served to prevent the spraying of scrubber solution onto the indicating silica gel which was used as the

drying agent. The presaturators prevented evaporation from the titration cell.

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

Potassium hydroxide - Fisher Scientific reagent grade was used without further purification.

2-Propanol - Fisher Scientific reagent grade was purified by distillation through a six-ball Snyder column to remove traces of polarographically reducible substances which were present.

Sodium carbonate - Anhydrous Fisher Scientific reagent grade was used after heating for two hours at 285° C.

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

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

2,2,4-Trimethylpentane - Conoco reference grade was used after simple distillation and Eastman Kodak spectro grade was used without further purification.

Zinc - Fisher Scientific reagent grade shot was used without further purification.

CHAPTER VI

EXPERIMENTATION AND DISCUSSION

Since considerable work done previously in this lab-
oratory had shown that 1:1 by volume mixtures of 2-propanol
and 2,2,4-trimethylpentane are easily prepared and relative-
ly stable, this solvent mixture was chosen for subsequent
work (39). Although the two components have reasonably low
boiling points, adequate presaturation prevented any large
changes in solvent composition during an experiment. Solu-
tions of 0.10-0.20M lithium chloride in 2-propanol were
readily prepared and the 1:1 by volume mixture was prepared
from these, resulting in solutions which were 0.05-0.10M
in lithium chloride. On a few occasions the solvent mix-
ture seemed unable to accommodate the 0.10M concentration
but the reason for this is not known.

It was discovered very early in the course of this re-
search that the 2-propanol provided by the manufacturer
was polarographically impure. A wave which could not be
topped except at very insensitive current settings was
obtained at a potential of about -1.0 volt. Simple dis-
tillation was sufficient to remove the impurity and the
alcohol remained free of impurities for at least two months.
Distillation to dryness yielded small amounts of insoluble

material which was probably the contaminant since the alcohol collected in this manner was polarographically pure.

The titrant used throughout this work was a standardized solution of potassium hydroxide in 2-propanol. The solution was prepared by weighing approximately the desired amount of solid potassium hydroxide pellets and adding this to one liter of 2-propanol in a two-liter suction filter flask. The mixture was then carefully heated on an electric mantle. The heating aided the solution process and digested the large amount of potassium carbonate which was present. After solution was accomplished, the alcoholic potassium hydroxide was cooled under nitrogen and pumped with nitrogen pressure through a scintered glass frit into a polyethylene bottle which was used for storage. Cooling the solution under nitrogen prevented further carbon dioxide absorption as did the transfer with nitrogen pressure from the filter flask to the polyethylene bottle. The glass frit prevented passage of precipitated potassium carbonate from the digestion vessel to the storage vessel. The polyethylene bottle was arranged with inlet and outlet tubes of glass, one of which was below the surface of the solution, and a two way stopcock which permitted filling of the burette with nitrogen pressure. The top of the burette was protected from carbon dioxide with an ascarite tube. The titrant prepared in this manner suffered no change in titer for periods up to three weeks.

The alcoholic potassium hydroxide was standardized with either standard hydrochloric acid or potassium hydrogen

phthalate or both. The standardization was done with sufficient water present so that at the equivalence point the resulting mixture would be approximately 50 percent water and 50 percent alcohol. Visual indicators used were phenolphthalein and bromcresol purple. Some standardizations were performed utilizing a pH meter. Of the two visual indicators used, bromcresol purple proved to be the most useful since its color change interval lies within pH values outside those at which absorbed carbon dioxide error becomes appreciable. Repeated checks with the pH meter indicated that the phenolphthalein end point occurred at an apparent pH of about 9.2 pH units while the bromcresol purple end point occurred at an apparent pH of about 6.8 pH units.

In order to determine the appearance of the acid wave described by Moran (39), samples of sulfuric acid in solutions of 0.10M lithium chloride in 2-propanol were prepared. Sulfuric acid concentrations of 1×10^{-4}M, 2×10^{-4}M, and 4×10^{-4}M were subjected to polarographic analysis and the wave heights were determined to be proportional to the concentration of sulfuric acid. The waves obtained were normal polarograms whose decomposition potential and half-wave potential were -1.01 volts and -1.09 volts, respectively. A similar experiment with solutions of hydrochloric acid in 2-propanol yielded identical results.

In order to make a comparison of the behavior of the strong acids with that of weak acids, samples of acetic

acid and stearic acid whose concentrations ranged from 1.0×10^{-4}M to 1.0×10^{-3}M were prepared in 0.10M lithium chloride in 2-propanol. No waves were obtained in any of these attempts and the only observable effect was a shift in the positive direction of the decomposition potential of the carrier electrolyte with an increase in acid concentration.

So that behavior of the aforementioned strong acids and weak acids could be observed in a solution of higher resistance, samples of these acids were prepared in a solution of 0.10M lithium chloride in a 1:1 by volume mixture of 2-propanol and 2,2,4-trimethylpentane. The waves which resulted were like those described by Moran with the exception that a slight maximum was exhibited by waves of sulfuric acid and of hydrochloric acid. The weak acids gave no observable waves in this solvent system. Next, polarograms were obtained from solutions of two typical sulfonic acids, 2-naphthalenesulfonic acid and 2,5-dimethylbenzenesulfonic acid. These samples were prepared in the 1:1 solvent mixture also. Very similar waves were obtained in both cases. The decomposition potential of 2-naphthalenesulfonic acid was -1.03 volts and that of 2,5-dimethylbenzenesulfonic acid was -1.01 volts. The half wave potentials measured for the naphthalene derivative and the benzene derivative were -1.15 volts and -1.11 volts, respectively.

The next step undertaken was the amperometric titration of a typical sulfonic acid with a titrant of potassium

hydroxide in 2-propanol. The acid chosen was 2-naphthalene-
sulfonic acid. This acid was readily available and has
only a slight tendency to be hygroscopic. It is a pale tan,
finely powdered solid with a molecular weight of 226.25.
A sample of $4.00 \times 10^{-3}M$ acid in a solution of 0.20M lithium
chloride in 2-propanol was readily prepared. Since it was
assumed originally that the solution of the acid would be
relatively stable, one liter of the solution was prepared.
The preparation was made in 2-propanol alone so that aliquots
could be taken for aqueous standardization. Aliquots of 25
ml. could also be added to the titration cell, together with
an equal volume of 2,2,4-trimethylpentane, so that the re-
sultant solution would have the desired solvent composition,
acid concentration, and carrier electrolyte concentration,
i. e., 0.10M in lithium chloride.

The concentrations of alcoholic titrant and sulfonic
acid were chosen such that the ratio of the concentration
of base to the concentration of acid would be about 35 for
the titration. This would make very small the error intro-
duced by dilution of the sample during the titration.

The initial aqueous standardizations of the alcoholic
sulfonic acid solutions were carried out using phenol-
phthalein. Samples were prepared for standardization by
taking 25 ml. of the alcoholic solution of the sulfonic acid
and adding to this an equal volume of distilled water. This
alcohol-water ratio made the titration essentially aqueous.
However, this later proved to be poor procedure in that the

end point read with the phenolphthalein included an amount of titrant consumed by (presumably) absorbed carbon dioxide, this amount being of considerable magnitude.

As a means of determining the effect of the alcohol-water ratio upon the end point of the aqueous standardizations, titrations were made of samples of 4.00×10^{-3}M 2-naphthalenesulfonic acid which had been prepared in a solution of 0.20M lithium chloride in 2-propanol. Three groups of 25 ml. aliquots of the acid were titrated after addition to 10, 25, and 40 ml. of water, respectively. Phenolphthalein was used as an indicator and the titrant was 0.0541N potassium hydroxide in 2-propanol. Results obtained with the 25 ml. alcohol-10 ml. water mixture differed by 1.3 percent from the results obtained with the 25 ml. alcohol-40 ml. water mixture. The differences were explainable on the basis of the relative amounts of carbon dioxide absorbed by the various amounts of water. All subsequent titrations were carried out in an approximately 1:1 mixture by volume of 2-propanol and water.

The first few attempts to titrate solutions of the 2-naphthalenesulfonic acid, although unsuccessful, proved valuable in that familiarity with a microanalytical method was obtained. The burette tip was not capable of proper drainage and in order to duplicate conditions it was necessary to leave a small drop of titrant on the burette tip and to touch the side of the degassing tube frit to the drop. This technique left on the burette tip the same

amount of titrant after the addition of every aliquot.
Then the gas frit was lowered into the titration cell so
that reaction could be quantitative. Stirring was accom-
plished with the nitrogen bubbles from the gas tube frit.
A small amount of insoluble white precipitate was formed
after the addition of each aliquot of titrant. Temperature
was constantly monitored with a thermometer with 0.05° C.
graduations.

Early results showed indications of erratic capillary
behavior. This behavior was traced to the storage of the
capillary in a solvent mixture which contained lithium
chloride. This practice is not advisable since small amounts
of the salt may be deposited within the bore of the capillary
which renders the capillary almost useless for regular and
duplicable drop times. Correction of the situation was
simple and subsequently the capillary was stored in a 1:1
mixture of alcohol and hydrocarbon with no carrier electro-
lyte present. In addition, a given capillary was used in
only one solvent system in order to get satisfactory per-
formance.

As was stated previously, the first several titrations
were unsuccessful. The titration curves obtained by plotting
the diffusion current against the volume of titrant added
exhibited extreme curvatures. The graphical end points were
from two to five times as great as those obtained with aque-
ous standardizations. Analysis of the titrant proved that
no reducible species was being added during the course of

a titration. Finally it was shown that solutions of 2-naphthalenesulfonic acid in 2-propanol age rather rapidly to form products of an undetermined nature which gave rise to the deviations from linearity among the amperometric titration curves. Shortly before every subsequent experiment a new solution of 250 ml. of the sulfonic acid was prepared. Solutions under fifteen hours old gave rise to no observable curvature of the titration curve.

The use of fresh acid solutions resulted in linear plots of diffusion current versus volume of titrant added, but difficulties were encountered in attempts to obtain quantitative agreement between the results of the aqueous standardizations and those of the amperometric determinations. More specifically, the analysis of the solutions amperometrically gave results which were almost 16 percent below those obtained when the same acid sample was analyzed by the visual indicator method (see Table I). Since Moran had utilized the aqueous standardization of the sulfonic acid with phenolphthalein as indicator, first attentions toward the solution of the problem were directed toward the amperometric behavior of sulfonic acid solutions. Such solutions were found to be well behaved, however, since the addition of aliquots of 0.035M 2-naphthalenesulfonic acid in 2-propanol to a titration cell containing only the solvent-carrier system gave a straight line passing through the origin when a conventional amperometric titration plot was made. This result was evidence that the currents obtained

TABLE I

TITRATION WITH POTASSIUM HYDROXIDE IN 2-PROPANOL OF 2-NAPHTHALENESULFONIC
ACID IN 0.10M LITHIUM CHLORIDE IN 1:1 2-PROPANOL-2,2,4-
TRIMETHYLPENTANE

4.00×10^{-3}M Acid; 0.0446N Potassium Hydroxide

Sample	Recovery*	Deviation	E_d (-volt)	$E_{1/2}$ (-volt)
1	0.834	0.008	0.99	1.11
2	0.834	0.008	1.00	1.10
3	0.848	0.006	1.00	1.10
4	0.848	0.006	1.00	1.10
5	0.848	0.006	0.99	1.10
6	0.838	0.004	0.99	1.09
Mean:	0.842	0.006	1.00	1.10

*Recovery is: <u>milliliters of base consumed in amperometric titration</u>
milliliters of base consumed in aqueous standardization with phenelphtalein

were directly and linearly proportional to the concentration
of 2-naphthalenesulfonic acid within the titration cell. It
should be noted that in this "blank" titration no precipitate
was formed.

It was shown previously that only strong acids could be
titrated amperometrically. This information, together with
a knowledge of the aqueous behavior of phenolphthalein, led
to the belief that the aqueous standardization could include
the titration of weak acids, since the phenolphthalein color
change interval lies considerably above seven pH units.
This suspicion was born out when titration of a sample of
2-naphthalenesulfonic acid in a 1:1 alcohol-water mixture
with a pH meter showed two distinct breaks, one whose equiv-
alence point occurred at a pH of 7, and one whose equiva-
lence point occurred at a pH of 8.5. Simultaneous use of
the pH meter and phenolphthalein showed that the phenolphthalein
end point occurred at a pH of about 9.0 so that the fifteen
percent discrepancy between amperometric and aqueous end
points was shown to be due, at least in part, to error intro-
duced by the visual indicator method. The excess consumption
of base seemed most probably the result of carbon dioxide
absorption during the aqueous standardization. In order to
decide how much of the discrepancy between end point volumes
was attributable to this absorption, several samples of
4.00×10^{-3}M 2-naphthalenesulfonic acid in a solution of
0.20M lithium chloride in 2-propanol were diluted 1:1 by
volume with distilled water. Titrations were performed

using a pH meter so that both equivalence points could be
detected, one of which corresponded to the titration of
the total strong acids, and one of which corresponded to
the titration of carbonic acid and other weak acids. These
checks were made on various days at various hours of the
day and it was observed that the potassium hydroxide con-
sumed by weak acids varied from one time to the next which
indicated that varying amounts of absorbed carbon dioxide
were responsible. This consumption due to weak acids
ranged from six to eight percent of the total volume con-
sumed by all acids present. Equivalence points obtained
with the pH meter could be duplicated exactly with brom-
cresol purple, a visual indicator which gave a very sharp
color change from yellow to green at a pH value of about
6.9 as measured by the pH meter. These observations led
to the conclusion that with the techniques employed, the
discrepancy between end points obtained by amperometric and
volumetric techniques would be, on the average, no less than
about seven percent.

All amperometric measurements up to this point in the
research had been made on the high resistance apparatus
described by Lloyd (36). However, the presence in the lab-
oratory of a new iR-compensator, one recently developed by
Dr. Paul Arthur in collaboration with the E. H. Sargent
Company, made it worthwhile to investigate the behavior of
the system under study utilizing this new and different kind
of apparatus. In order to check first the functioning of

the new apparatus, aliquots of 0.025M cadmium chloride in 2-propanol were added to a solution of 0.10M lithium chloride in a 1:1 2-propanol-2,2,4-trimethylpentane mixture. The observed currents were plotted against the volume of cadmium chloride added. The result was the expected straight line passing through the origin, indicating that the instrument was functioning properly and that the cadmium chloride system was well behaved.

Polarograms obtained with the new instrument from samples of 2-naphthalenesulfonic acid in the solvent-carrier system already described resembled those traced by the earlier model with the exception that the wave fronts were characterized by an apparent maximum at about -1.25 volts. These observations led to a search for a means of removing this maximum. Values of the decomposition potential and the half-wave potential obtained on the two different instruments were essentially identical as long as the concentration of lithium chloride was not greatly varied.

It was found that small amounts of methyl red would eliminate the maximum observed. However, a polarogram was run using a saturated solution of methyl red in 2-propanol and the observed wave exhibited two plateaus. The half-wave potentials for the two waves were about 0.0 volts and -1.10 volts. This concentration of methyl red gave a current reading of 0.60 microamperes as compared to currents of the order of 3.0 microamperes normally obtained with 2×10^{-3}M 2-naphthalenesulfonic acid. The presence of the

methyl red wave led to the search for a more desirable max-
imum suppressor.

The next substance studied as a potential maximum sup-
pressor was cetyldimethylethylammonium bromide. It is known
that the tetraalkylammonium halides are, in general, surface
active agents and should lend themselves to maximum suppres-
sion rather well. They also possess the distinct advantage
of not giving a polarographic wave at the voltages commonly
used for amperometric titrations.

A one percent solution of the cetyldimethylethylammonium
bromide was prepared in 2-propanol. An aliquot of 0.50 ml.
of the solution was added to 50 ml. of the sulfonic acid
solution which was ready for titration and contained within
the thermostated electrolysis cell. The wave obtained show-
ed no maximum, and the wave was very well formed. However,
the drop time alternated in a very regular fashion between
six seconds and two seconds. The addition of another one
milliliter of the suppressor solution, added in 0.50 ml.
aliquots, caused no change.

Since the capillary misbehaved in the manner described,
it was thought that the one percent solution of cetyldi-
methylethylammonium bromide was too concentrated. This be-
havior could be attributed to an excess of the surface
active agent near the capillary tip which would change the
surface tension of the mercury at the glass tip of the
capillary, thus changing the drop time.

An attempt to use a more dilute solution of the suppressor was made. However, it was very quickly learned that the suppressor had not been a good choice. Despite very careful cleaning, rinsing and drying of all glassware before each run, the tetraalkylammonium bromide could not be thoroughly cleaned from the electrolysis cell as evidenced by the formation of polarograms during the next few runs which possessed no maxima although no attempt at suppression was made. Apparently contamination of the titration cell had resulted from absorption of the cetyldimethylethylammonium bromide into the side-arm frits of the cell. A new capillary functioned for a short time without exhibiting erratic behavior but this lasted only about five minutes after insertion of the new capillary into the solution contained in the titration cell. There was little hope held for the successful use of more dilute solutions of the tetraalkylammonium halide; subsequent attempts to suppress the maximum, using a 0.10 percent solution of the surface active agent, were accompanied by the same erratic capillary behavior. Repeated washings and rinsings eliminated the quaternary ammonium salt whereupon normal polarograms, on which maxima were evident, were obtained.

The next substance chosen for study was the acid form of methyl red. A very slight wave was obtained from samples of 0.05 percent by weight of the substance in 0.10M lithium chloride in a 1:1 mixture of 2-propanol and 2,2,4-trimethylpentane. This form of methyl red proved to have

no effect on the maximum of the 2-naphthalenesulfonic acid wave.

It should be mentioned that it was observed that when currents were erratic at a fixed value of the applied potential -- as during a single current measurement -- the erratic behavior could be eliminated by running the entire polarogram from 0.00 volt to the potential at which the carrier began to undergo decomposition, or by manually either increasing or decreasing the applied potential momentarily, and then returning the bridge to the pre-selected voltage value chosen for the titration.

An examination of the capillary with a magnifying glass revealed that wetting of the capillary always accompanied erratic behavior of the drop time. This wetting was evidenced along a length of two to five centimeters within the capillary bore. The wetting was manifested as a random scattering of fine droplets of clear solution which separated the mercury column from the walls of the bore. It is believed that this effect was surface tension dependent since the advancing voltage technique tended to prevent the wetting. It is well known that the surface tension of mercury varies with the applied voltage. It is possible that the fixed voltages chosen for the amperometric titrations, coupled with the fact that the anion of the 2-naphthalenesulfonic acid is rather large and capable of acting as a surface active agent, led to capillary-solution interfacial tensions which were conducive to the creeping of solvent and dissolved salts into the tip of the capillary thereby wetting

the inner surface of the bore in an irregular manner. The
wetting proved not to be of such a nature that a state of
equilibrium could be established by preliminary soakings.
This is understandable since the continual change of 2-
naphthalenesulfonate anion concentration was a natural
consequence of the titration. It was noted that capillary
drop times became shorter as a titration progressed. The
change of drop time varied almost linearly with the volume
of titrant added, and, therefore, with a change in concen-
trations of the 2-naphthalenesulfonate anion. This reduc-
tion in drop time was regular until about 0.50 to 0.60
milliequivalents of alcoholic potassium hydroxide had been
added. At this time, the drop time would suddenly become
extremely short. Sometimes the drop time became quite
irregular when the average drop time underwent this sudden
decrease, while at other times the sudden decrease in drop
time would not introduce any irregularity into the wave form
because the individual drop times, though very short, were
duplicable.

In order to try to isolate the cause for the extremely
erratic and almost uncontrollable changes in drop time, a
new capillary was installed and placed into a 1:1 by volume
mixture of 2-propanol and 2,2,4-trimethylpentane. The drop
time changed from 9.8 seconds to 1.0 seconds during the
course of one hour. The drop time in pure 2-propanol be-
came erratic after about 10 minutes, varying in length from
6.0 to 10.0 seconds and similar behavior was observed in

pure 2,2,4-trimethylpentane. There was reason to believe
that this change might be caused, in part at least, by
oily plasticizers leaking onto the mercury from the tygon
tubing connecting the D.M.E. assembly to the leveling bulb.
This tubing was replaced with ordinary machined rubber
tubing which had been soaked overnight in 1N potassium
hydroxide and thoroughly rinsed and dried. Subsequently,
drop times in the pure solvents and in a 1:1 solvent mix-
ture were quite regular for several hours.

This treatment did not eliminate entirely the tendency
for the drop time to become shorter and shorter during the
course of a normal titration. One attempt to restore nor-
mal drop time near the end of a titration utilized the
sodium salt of methyl orange. The drop time changed from
one second to twenty seconds when two milliliters of a
saturated solution of the salt in 2-propanol was added
directly to the titration cell. Two other attempts to use
the sodium salt of methyl orange as a maximum suppressor
awakened the experimenter to a very important fact. The
maximum suppression, which was complete whenever the methyl
orange salt was used, seemed to be entirely independent of
the drop time behavior as the titration progressed. This
directed attention away from the maximum towards the real
difficulty, namely, that the capillary behavior was normal
at the beginning of a titration but grew progressively worse
as more and more alcoholic potassium hydroxide was added.

For the next run, the concentration of the sulfonic acid was reduced to 1.00×10^{-3}M. This resulted in a normal wave with a decomposition potential of -1.06 volts and a half-wave potential of -1.17 volts. After each aliquot of titrant was added, the drop time was carefully measured and it was noted that the drop time still decreased almost linearly as the consecutive aliquots were added. The drop time was constant during a given current measurement and drop time measurements were made only while the fixed potential was impressed across the D.M.E. This decrease in drop time resulted in a decrease in the average electrode area and, consequently, in a decrease in the average diffusion current. Ilkovic's equation predicts this dependence of the diffusion current on the drop time. Thus the diffusion current decreases not only due to the decrease in concentration of reducible species, as desired, but also due to the decrease in drop time. This explains, in part, why the amperometric end points could be short of the stoichiometric end points.

The capillary used in the previous titration was cleaned and placed into a 1:1 solvent mixture. The drop time in this mixture changed in twenty-four hours from 5.6 seconds to 10.0 seconds. This indicated that there was occurring a slow cleaning of the capillary due to the removal of some material from inside the bore or off of the tip of the capillary. Inspection of the capillary before this twenty-four hour cleaning period revealed that the inside bore of the

capillary had been wetted along a length of two centimeters of the bore. After the cleaning, the amount of solution which was wetting the bore appeared unchanged. It is believed now that the removal of the lithium and potassium salts of the 2-naphthalenesulfonic acid was being accomplished by the slow soaking process, by a diffusion mechanism, or (in the case of the purging with a decrease or increase in voltage, as previously noted) by radical changes in the surface tension. A further possibility was checked by placing the cleaned capillary in a new sample of the 1:1 solvent mixture. The drop time was steady at 10.0 seconds. The addition of two milliliters of 2-propanol or two milliliters of 2,2,4-trimethylpentane in excess caused no noticeable change in drop time. Thus the solvent changes encountered during a titration, through evaporation or through the addition of titrant prepared in 2-propanol only, should not be too influential upon the drop time.

In order to isolate the species which brought about this change in drop time, some careful measurements of drop time were made, using a new capillary, in a 1:1 solvent mixture, a 1:1 solvent mixture made 0.05M with lithium chloride, and a 1:1 solvent mixture made 2×10^{-3}M with 2-naphthalenesulfonic acid, in that order. The times recorded, in all cases, were the times required for five drops of mercury to fall. The time recorded when the capillary was placed in 1:1 solvent mixture was 44.4 seconds and was regular over a period of two hours. The time recorded when

the capillary was placed into the 1:1 solvent mixture made 0.05M with lithium chloride was 42.8 seconds and was regular over a period of three hours. Forty-five minutes after the capillary had been placed in the 1:1 solvent mixture which had been made 2×10^{-3}M with the sulfonic acid, the recorded time changed, over a five minute interval, from 41.6 seconds to 12.7 seconds and was very irregular thereafter for seven hours, varying from 12.7 seconds to 16.8 seconds. Any attempt to pre-soak the capillary so that it might be brought to some sort of equilibrium state previous to its use in a titration proved futile. Capillary behavior was at first satisfactory after such soakings (which lasted for a period of about twenty-four hours), but behavior was normal only until two or three aliquots of alcoholic titrant had been added, whereupon the drop time became extremely short.

This study indicates that the 2-naphthalenesulfonic acid exerts a rather strong influence on the mercury-solution interface. It is not impossible that the phenomenon is localized entirely at the outer interface of the capillary tip and the solution, and that the wetting of the capillary is incidental to a direct result of this phenomenon, rather than the cause, as was previously suggested. These difficulties led to a study of the behavior of a simpler system, in terms of potentially surface active species, that of the behavior of anhydrous hydrogen chloride solutions in 1:1 2-propanol and 2,2,4-trimethylpentane.

The solutions of hydrogen chloride were prepared by very slowly bubbling the anhydrous gas through a quantity of 2-propanol. A small amount of heat was evolved but it was probably no more than would be expected from the normal solvation process. Care was taken to avoid a rapid rate of bubbling since there is some possibility of forming, at higher temperatures, undesired organic products.

Titrations were performed on several samples of 2.00×10^{-3}M hydrogen chloride solutions which had been prepared exactly as described for the sulfonic acid solutions. For three of the titrations a sample of 25 ml. of the hydrogen chloride in 2-propanol was used. This was made 0.20M with lithium chloride and then added to 25 ml. of 2,2,4-trimethylpentane in the titration cell. The nitrogen degassing tube was inserted into the sample and bubbling was continued for at least thirty minutes. The titrations were accompanied by the formation of white, finely divided, granular precipitate which settled out only after a few hours standing. The results of the titrations are shown in Table II.

Three more samples of 4.00×10^{-3}M hydrogen chloride were prepared in 2-propanol and 25 ml. aliquots of these were added to 25 ml. of a solution of 0.20M lithium chloride in 2-propanol. These were titrated amperometrically and the same formation of a precipitate was noted. The results of these three titrations are shown in Table III.

TABLE II

TITRATION WITH POTASSIUM HYDROXIDE IN 2-PROPANOL OF
ANHYDROUS HYDROGEN CHLORIDE IN 0.10M LITHIUM
CHLORIDE IN A 1:1 MIXTURE BY VOLUME OF
2-PROPANOL AND 2,2,4-TRIMETHYLPENTANE*

4.00×10^{-3}M Acid; 0.0829N Potassium Hydroxide

Sample	End Point (ml.)	Deviation	E_d (-volt)	E (-volt)
1	1.16	0.01	1.07	1.17
2	1.17	0.00	1.08	1.18
3	1.17	0.00	1.07	1.17
Mean	1.17	0.003	1.07	1.17

Mean of End Points = 96.6% of Acid Present

*Data obtained with the improved high resistance polarograph.

TABLE III

TITRATION WITH POTASSIUM HYDROXIDE IN 2-PROPANOL OF
ANHYDROUS HYDROGEN CHLORIDE IN 0.10M LITHIUM
CHLORIDE IN 2-PROPANOL*

4.00×10^{-3}M Acid; 0.0829N Potassium Hydroxide

Sample	End Point (ml.)	Deviation	E_d (-volt)	E (-volt)
1	1.17	0.00	1.10	1.18
2	1.18	0.01	1.09	1.18
3	1.17	0.00	1.10	1.18
Mean	1.17	0.003	1.10	1.18

Mean of End Points = 96.6% of Acid Present

*Data obtained with the improved high resistance polarograph.

From the results shown in Table II and Table III it can be seen that titrations of anyhdrous hydrogen chloride in 2-propanol and in 1:1 mixtures of 2-propanol and 2,2,4-trimethylpentane are not strictly quantitative if the aqueous standardizations are assumed to be correct. However, the results are gratifying in view of the simplicity with which they were performed. No erratic capillary behavior was observed which further substantiates the hypothesis that the large anion of 2-napthalenesulfonic acid caused the extremely erratic behavior encountered in the study of that system. Observations of drop times during these last series of titrations showed that very good regularity and duplicability among drop times recorded after consecutive additions of titrant could be expected.

Bromcresol purple was used for the aqueous standardizations of the hydrogen chloride samples.

The deviation from ideal results could possibly be explained as a result of absorption as previously suggested. This explanation is feasible in view of the relatively profuse formation of the white precipitate whose fine, granular state would expose a very large surface area to the solution.

It is very gratifying to observe that there is no significant difference in the results obtained when using pure alcohol and those obtained when using the alcohol-hydrocarbon mixture. This is indicative that the apparatus employed for these titrations should within the near future lead to the acceleration of work performed in the general area of nonaqueous polarography.

CHAPTER VII

SUMMARY AND CONCLUSIONS

At the outset of this research it was hoped that a method could be developed for quantitatively converting salts of sulfonic acids to the parent acids by conversion in nonaqueous solvents with anhydrous hydrogen chloride. Analysis of such salts could then be carried out by means of amperometric titrations.

This idea soon gave way to the more intimate problem of the behavior of the dropping mercury electrode in non-aqueous solutions whose surface tensions are considerably less than that of water. Attempts to quantitatively titrate the sulfonic acids themselves by an amperometric method resulted in end points which were short of the expected end points. It is believed that the discrepancy is not due in any way to instrumentation difficulties, but rather to capillary misbehavior which has its origin in surface tension effects. However, if the alcoholic potassium hydroxide had been standardized with an amperometric technique, it appears, from the foregoing results, that the accuracy of the titrations would have approached the excellent precision obtained.

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The hydrogen chloride system was found to be well be-
haved and quantitative titrations of the acid could be
carried out which were reasonably satisfactory. This is
because no species which could exert a large influence as
a surface active agent was present in the system. Such a
species can lower the duplicability of the drop time of the
D.M.E. as was elucidated by the studies of the systems of
which the large ions of a quaternary salt and a sulfonic
acid were a part.

It is possible that studies of these same systems at
solid electrodes would lead to the discovery of conditions
under which undesirable surface tension effects could be
minimized or eliminated.

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