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COULOMETRIC TITRATION OF ACIDS IN NONAQUEOUS SOLVENTS

by

Frank Edward Gainer

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Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1967

TABLE OF CONTENTS

	Page
INTRODUCTION	1
NONAQUEOUS TITRATION OF ACIDS	4
General Principles	4
Titrants	6
Solvents	8
Methods of End Point Detection	10
COULOMETRIC TITRATIONS	12
Historical Background	12
General Considerations	16
Requirements for Ideal Conditions	17
Supporting electrolyte and solvent	17
Titration cell	19
Generating and measuring electrode systems	21
Variety of acids titrated	24
TITRATIONS IN TERTIARY BUTYL ALCOHOL	25
Experimental	25
Apparatus	25
Reagents	29
Procedures	30
Quality of the Basic Titrant	32a
Primary electrode reactions	32a
Solvent purification and solvent blanks	32b
Results of Titrations	38
Indicator end point detection	38
Potentiometric end point detection	44
TITRATIONS IN ACETONE	51
Experimental	51
Apparatus	51
Reagents	51
Procedure	53
Results of Titrations	53
DISCUSSION OF RESULTS	60
General Considerations	60
Variations in Titration Assemblies	64
Possible Secondary Electrode Reactions	68

	page
Role of Ion Exchange Membranes in Coulometry	70
General considerations	70
Cation exchange membrane separator	73
Anion exchange membrane separator	77
Combination anex and catex membrane separator	70
Effect of Water on Titrations in Acetone	79
Suggestions for Future Work	81
SUMMARY	86
LITERATURE CITED	88
ACKNOWLEDGEMENTS	91

INTRODUCTION

The two primary objectives of this investigation were: (1) to extend the practical and theoretical knowledge of coulometric analyses in nonaqueous systems and (2) to devise improved methods for the determination of micro concentrations of acidic compounds in organic solvents. The investigation entailed the titration of acidic compounds in acetone and tertiary butyl alcohol solvents with an electrolytically generated basic titrant. In this research an effort was made to eliminate many of the weaknesses, limitations, and disadvantages of previously published ideas on coulometric titrations in nonaqueous systems.

Several important advantages of coulometric titrimetry are listed in a textbook by Vogel (46, p. 676). Coulometry eliminates or minimizes problems associated with the preparation of standard solutions, sample dilution, indicator corrections, and impurities in the generating solution. The method, which is largely electrical in nature, is readily adapted to remote control and is ideally suited for use on a micro or semimicro scale. It may be adapted to automatic control because of the relative ease of the automatic control of current. The fact that only very small amounts of titrant need be prepared by the coulometric method was most significant in this study. This obviates the difficulties involved in the storage and standardization of dilute solutions.

Strong inorganic bases are particularly difficult to store and quaternary ammonium hydroxides are no exception. Dilute solutions of strong bases are subject to continuous changes in titer by sorption of carbon dioxide and etching of glass containers. Quaternary ammonium hydroxides decompose on long standing and are relatively unstable in most organic solvents. The basic titrant prepared in this investigation was generated in small amounts and used immediately.

This research entailed an investigation into the development of a rapid but accurate coulometric titration procedure for a wide variety of acidic organic and inorganic compounds in essentially nonaqueous systems. It was not a major attempt to devise a scheme of titration for all acid concentration ranges. Instead, it proposed a concise method of titration of many acids within a limited concentration range of the microequivalent region for which the coulometric method is ideally suited, although attempts were made to titrate milliequivalent amounts.

Mineral acids, carboxylic acids, dicarboxylic acids, enols, imides, phenols, and sulfonic acids were titrated coulometrically within a 10 to 60 microequivalent range in tertiary butyl alcohol and acetone solvents. Both visual indicator and potentiometric end points were utilized in the tertiary butyl alcohol solvent but only potentiometric end point determinations were made in the acetone solvent.

Representative acids were chosen from each group and used in this investigation.

The most difficult problems encountered in the investigation were cell designs and materials used in the cells. The schemes proposed in this investigation employed organic solvents and quaternary ammonium salts as electrolytes in both compartments. Ion exchange membranes were used to separate the anode and cathode compartments of the cells used for titrations in tertiary butyl alcohol. Many of the limitations of previous nonaqueous coulometric methods are overcome by this investigation. The improvements are significant to the enrichment of the area of nonaqueous titrimetry.

NONAQUEOUS TITRATION OF ACIDS

General Principles

Acid-base titrations represent a valuable method of determining organic compounds having pronounced acidic or basic properties. Nonaqueous acid titrations, however, permit the titration of many acidic compounds that cannot be titrated readily in aqueous solution. The titration of such compounds in aqueous solution is limited in scope because of the insolubility of a large number of organic compounds in water and the failure of many organic compounds to give a sharp end point when titrated in aqueous solution. Acids weaker than about $pK_a = 7$ cannot be titrated in water but they can be determined accurately by titration with a strong base in the proper nonaqueous solvent.

Much of the literature on nonaqueous acid-base titrations deals with macro or semimicro methods. However, these procedures can be made applicable to micro determinations by: (1) scaling down the sample size and quantities of solvent and titrant used (2) using more dilute titrant or (3) a combination of these two.

Although most organic reactions proceed with measurable velocity, acid-base reactions occur almost instantaneously. Lewis and Seaborg (28) observed that acids such as boron trichloride and hydrogen chloride react instantly with certain indicator bases at temperatures as low as -70°C .

The large majority of compounds that are recognized as acids behave in this manner.

Ionization in nonaqueous solvents is not completely understood. However, some solvent-solute interaction (or solvation) must occur or the solute would not dissolve in the solvent. Nonionized compounds certainly must react with the solvent in some way in order for ionization to take place. An acid requires a solvent with basic properties and if everything else is equal, the degree to which an acid ionizes will be determined by the basic properties of the solvent. The relative resonance ability of the ionized and nonionized forms of an acid in a given solvent must also play an important role. The dielectric constant of a solvent also affects ionization of a solute in that solvent. If the dielectric constant of a solvent is low, positive and negative ions have greater attraction for each other and ion pair formation is promoted. Ion-pairs as well as free ions are likely to be present in solvents having a high dielectric constant. Ions exist exclusively as ion-pairs in solvents of very low dielectric constant. It should be emphasized, however, that extensive ionization in solution is not a prerequisite to successful acid-base titrations. As early as 1912 Folin and Flanders (13) used conductivity data to show that solutions of carboxylic acids in benzene were essentially nonionized, but could be titrated accurately and quantitatively with sodium

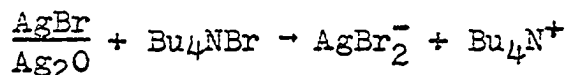
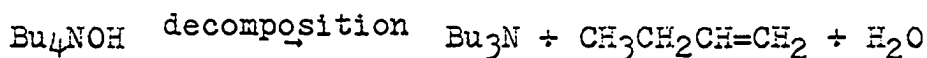
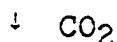
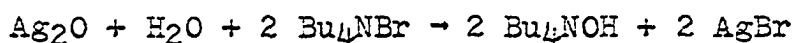
ethoxide.

Titrimants

The titrant for use in nonaqueous solvents should be a strong base dissolved in a nonacidic solvent and should be stable on standing (14, p. 24). Alcoholic sodium and potassium hydroxide are satisfactory titrimants for moderately weak acids. Solutions of potassium and sodium methoxide (17) in benzene-methanol are better titrimants for weak acids and are generally useful for the titration of all acidic compounds. In the titration of most weak acids, results are improved considerably by titrating with methoxide in benzene-methanol instead of methoxide in methanol alone.

Quaternary ammonium hydroxides, notably tetrabutylammonium hydroxide, have at least two distinct advantages over other titrimants for use in nonaqueous solvents. One is the fact that the tetraalkylammonium salts formed are generally soluble in the nonaqueous solvent, in contrast to the salts of alkali hydroxides or alkoxides. The other advantage is that excellent potentiometric curves are obtained in a variety of solvents with ordinary glass and calomel electrodes. The "alkali error" (16, p. 46) limits the use of the glass electrode in conjunction with alkali metal alkoxides in basic solvents but the very large tetraalkylammonium ion is apparently free from this difficulty.

Tetraalkylammonium hydroxides like tetramethylammonium (36), triethyl-n-butylammonium (19), and tri-n-butylmethylammonium (30,45) have been used as titrants, but tetra-n-butylammonium hydroxide (5,12,23) has been used most frequently as titrant in nonaqueous media. It is difficult to prepare tetrabutylammonium hydroxide and other quaternary titrants that do not contain some weaker base as an impurity. The tetrabutyl titrant is usually prepared by the silver oxide method. Three impurities are likely to be present in any titrant prepared by the silver oxide process - tetrabutylammonium carbonate, tri-n-butylamine, and silver in anionic complex form. The origins of these impurities are shown below.



Tri-n-butyl amine may also be introduced by the quaternary salt. The tertiary amine is a weaker base than the tetraalkylammonium hydroxide and, in the titration of an acid, may cause an error similar to that in an aqueous acid-base titration with sodium hydroxide that is not carbonate-free.

The removal of these three impurities from the hydroxide is time-consuming and was undertaken by Marple and Fritz (31).

Solvents

The organic solvent for titration of acids should readily dissolve acidic compounds to be titrated but should have no acidic properties itself (14, p. 24). For the successful titration of mixtures, the solvent should not be a strong enough base to level the acids in the mixture. Solvents such as acetone (19) acetonitrile (4,45), and pyridine (5) have been used extensively for the titration of weak acid with tetraalkylammonium hydroxides. When titrated potentiometrically in these solvents most carboxylic acids and phenols give titration curves with an unusually long potential range between 0 and 95% titration. Harlow and Bruss (22) and Van der Heijde (44) attributed this steepness in slope to association between a molecule of the acid and a molecule of the acid anion. This behavior makes it more difficult to carry out differentiation titrations of mixtures.

Amphiprotic solvents such as alcohols do not exhibit appreciable intermolecular association and the titration curves are flat. In general the lower alcohols are too acidic to give good results in the potentiometric titration of weak acids but there is one notable exception, tertiary butanol. Pritchett (36) and Fritz and Marple (18) have

shown that tertiary butyl alcohol is an excellent solvent for the titration of weak and very weak acids. Tertiary butyl alcohol is less acidic than ethanol, methanol, and isopropanol (25) and gives very good potential breaks for the titration of weak acids. Titration curves of carboxylic acids and phenols in tertiary butanol are very flat so this solvent is well suited for differentiating titration of acids and for the titration of weakly acidic compounds.

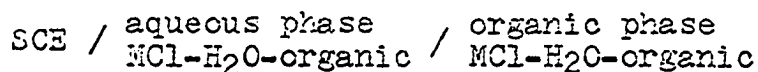
There are several other features which make tertiary butanol particularly applicable to the general determination of acids (18). It does not show an appreciable leveling effect for strong acids, and strong mineral acids, with the exception of anhydrous sulfuric and hydrochloric acids, are stable in tertiary butanol. Perchloric acid, the strongest acid found, is stable indefinitely in tertiary butanol. An important advantage of tertiary butanol is that solutions of tetrabutylammonium hydroxide are stable for short periods of time in this solvent. Thus potentials are steady in the presence of excess base when a potentiometric titration is performed. This is in contrast to the behavior in pyridine or acetone where potentials in the presence of excess base are very unsteady. A further advantage of tertiary butanol is that it can be obtained commercially in a highly purified form with very low acid blanks.

Methods of End Point Detection

Titration of acids in nonaqueous solvents usually are followed potentiometrically or the end points are detected by means of visual indicators. Throughout the history of nonaqueous titrations potentiometric end point detection probably has played a larger role in the determination of acids than has visual detection of end points using indicators. For routine analysis, however, an indicator end point is preferred to a potentiometric end point. Until recently, routine visual titrations in organic solvents were restricted to only a few indicators owing to the lack of other reliable indicators. Generally thymol blue was recommended for the titration of medium strength acids, azo violet for weak acids, and p-nitro-p'-aminoazobenzene for very weak acids. Malmstadt and Vassallo (30) have given the approximate transition ranges of some indicators in acetone. Marple and Fritz (32) determined the visual transition ranges of thirteen indicators in tertiary butyl alcohol relatively accurately. Fritz and Gainer (15) established both the visual transition ranges and the more accurate photometric transition ranges of thirteen common acid-base indicators in pyridine.

The accurate determination of transition ranges of indicators in tertiary butanol and pyridine was made possible by the development of a suitable electrode system by Marple and Fritz (31). Previously a simple glass-calomel electrode

system was commonly used for potentiometric titrations with tetraalkylammonium hydroxides. The aqueous electrolyte in the calomel electrode was replaced by a saturated solution of potassium chloride in methanol. Although excellent titration curves were obtained in several solvents, potentials were not reproducible and were often unstable with the glass-modified calomel system. These discrepancies were believed to be the result of a difference in junction potential between the solution and the modified calomel electrode. The electrode system developed by Marple and Fritz gave relatively stable potentials and reproducible titration curves in very weakly acidic solvents. The system was a glass-two phase salt bridge - SCE electrode system, and similar systems were devised for acetone, isopropanol, pyridine, and tertiary butanol. The salt bridge systems were of the type



and they were developed to avoid the problem of crystallization of salts at the junction of the consecutive salt solutions in the salt bridge.

COULOMETRIC TITRATIONS

Historical Background

The coulometric technique has been used extensively only for the past 15 years but interest in the subject dates as far back as 30 years. The Treatise on Analytical Chemistry (10) offers a list of 254 references to theory and applications of the method. Bard (1) compiled a combined review of electroanalysis and coulometric analysis with 306 references.

The coulometric titration of bases in nonaqueous systems has been studied fairly extensively (20,33,34,39) and a similar study of acid titrations has been initiated. Most previous research in the area of coulometric titrations of acids has involved titrations in aqueous solutions and has made use of the platinum cathode-silver anode generating electrode system. One of the earliest papers on the titration of acids by electrolytically generated hydroxyl ions was that of Szebelledy and Somogyi (41). They used a platinum cathode and a silver anode for the electrolysis in an aqueous solution of potassium sulfate and/or potassium chloride as electrolyte to determine hydrochloric acid and sulfuric acid. A bromocresol green indicator end point was used and results were considered to be excellent when compared with results from titrations of the acids against potassium hydrogen carbonate. The quantity of electricity and thus the quantity of acid was determined from the

deposition of silver in a silver weight coulometer which had been connected in series with the electrolysis cell.

Epstein and co-workers (11) generated hydroxyl ions in a sodium bromide electrolyte solution that was saturated with hydroquinone. Microgram quantities of hydrochloric acid were titrated, and the end points were determined potentiometrically by the use of a Pinkof system (27, p. 148), thus eliminating the need of indicators. They indicated that their method was adaptable to automatic and continuous analysis of gases, in air, which were acids or pyrolyzable to acids. In 1957 Liberti (29) actually titrated volatile acids and carbon dioxide as acid by collecting the titrable materials in an absorbing solution and generating hydroxyl ions at a platinum cathode that was separated from a cylindrical carbon anode by a collodion membrane. White (48) has titrated carbon dioxide as an acid on the microscale by using acetone as the absorbing and titrating medium. He used thymol blue as visual indicator and experienced a generation efficiency of 99-100%. It was necessary to have methanol in the system as well as a minimum concentration of water (0.010-0.015%) in the absorbent for best results.

Carson and Ko (2) were probably the first to publish their work on the coulometric determination of acids in a partially nonaqueous medium. They determined micro amounts of organic acid in the presence of large amounts of mineral

acid in a 70% isopropyl alcohol-30% water medium and employed a platinum cathode-platinum anode generating electrode system. Crisler and Conlon (4) used lithium chloride as the electrolyte for the coulometric titration of organic acids in a 1:1 benzene-methanol solvent system. The end points were detected potentiometrically by an antimony-glass electrode pair after generation of base by a platinum cathode-silver anode electrode system. Their system was completely anhydrous and in effect the methoxide ion was generated at the cathode and silver ion at the anode. According to the Lewis theory the methanol, an amphiprotic solvent, assumed a role similar to water in the neutralization reaction in the nonaqueous medium.

Rossett and Trémillon (38) conducted coulometric titrations of perchloric-acetic acid mixtures in 85% acetone-15% water solution. Sodium chloride was used to generate sodium hydroxide and the chloride ion was taken up at a silver electrode. Streuli and coworkers (40) generated tetrabutylammonium hydroxide in acetone containing either 0.2 or 0.5 percent water for the titration of benzoic acid, p-toluenesulfonic acid, and 2,4-dinitrophenol. It is noteworthy that unlike previous researchers they used a quaternary ammonium salt as a supporting electrolyte. Their predecessors had all used inorganic salts as supporting electrolytes.

Johansson (26) reported results for the titration of

acids as weak as barbitol in isopropyl alcohol and isopropyl alcohol-methyl ethyl ketone solvents with sodium perchlorate as electrolyte. Thymol blue was used for most end point determinations but the indicator end point was checked by potentiometric titration. A platinum cathode-silver anode generating electrode system was employed. Two cell arrangements were described, one in which the anode and cathode were separated, and one in which they were in the same vessel. Cotman and others (3) reported the coulometric titration of dibasic acids and dinitrophenol in a single vessel containing silver, platinum, and glass electrodes, and a quaternary ammonium halide. Either a benzene-methanol or a tertiary butyl alcohol-methanol solvent was used. They noted erratic current throughout the titration at high concentrations of tertiary butanol so they used a 60:40 (V/V)% tertiary butanol-methanol solvent mixture. The cathode reaction yielded tetrabutylammonium methoxide but they were unable to prepare the titrant when sodium perchlorate was eliminated completely from the system.

Ho and Marsh (24) applied anion and cation exchange membranes to the separation of the anode and cathode compartments in automatic coulometric acid-base titrations. They titrated strong acids in aqueous medium and used indicators for spectrophotometric end points. Feldberg and Bricker (12) and Hanselman and Rogers (21) studied some theoretical and

practical aspects of ion exchange membranes in coulometry.

General Considerations

The coulometric method may be classified according to the electrode process or according to the type of current control. Classification according to electrode process results in primary and secondary coulometric analyses and classification according to current control results in constant current and constant potential coulometry. The titration of acids in nonaqueous solvents may be categorized as secondary constant current coulometry.

The fundamental requirement of a coulometric analysis is that the electrode reaction used for the determination proceed with 100 percent efficiency. The end point or the completion of the desired reaction may be determined by a variety of conventional methods such as visual indicator, amperometry, potentiometry, spectrophotometry, or a thermometric technique. The essential equipment for constant current coulometry consists of a reliable constant current source, a current measuring device, and a time measuring device. The efficiency of the current supply is only as good as the timer and current measuring device. A current supply wherein the current and timer are turned on simultaneously is recommended.

Although the coulometric method has several advantages over conventional methods of titration there are some sources

of error which should be considered when doing a coulometric titration (42). It is of prime importance that the stoichiometry of the electrode process and any of its indirect reactions be completely defined. Side reactions can alter results. A further source of error may arise from ionic migration from the electrolysis chamber. Errors, both accidental and systematic, can arise in the determination of the end point as in conventional titrations. Errors can arise also from faulty calibration of the apparatus used for the measurement of the current and the time.

Requirements for Ideal Conditions

Supporting electrolyte and solvent

The most suitable supporting electrolyte should be readily soluble in the solvent and it should possess a cation which forms a strong base with the species generated at the cathode. The cation of the electrolyte also should be such that it forms soluble salts with the acids titrated. The supporting electrolyte should not interfere with the response of the glass electrode or other potential indicating or measuring electrodes. The quaternary ammonium halides meet the basic requirements for good supporting electrolytes. Fritz and Hammond (16, p. 46) suggested that the glass electrode was subject to a considerable "alkali error" in basic solutions containing the sodium ion. This error is less with the potassium ion and probably greater with the lithium ion than

with the sodium ion. The "alkali error" has the net effect of decreasing the sharpness of end points when acids are titrated. Several workers (2,4,26) have used supporting electrolytes containing alkali metal ions and one group (3) used a quaternary ammonium halide as electrolyte but found it impossible to titrate acids, with any degree of precision, without adding an alkali metal salt to the system.

The ideal solvent for conventional nonaqueous titrations of acids should dissolve readily a large variety of acids and should have no acidic properties itself and the titrant should be a strong base dissolved in a non-acidic solvent (14, p. 24). The same criteria apply to a solvent for nonaqueous coulometric titrations. Further, the solvent should dissolve the supporting electrolyte readily in large quantities and if the solvent is reduced at the cathode it should yield a strong titrant for weak acids. Alkali alkoxides have been used considerably for both conventional and coulometric (2,4,26) titrations. Methanolic solvents have been used by some researchers (3) but the methanol imparts more of an acidic nature to the nonaqueous system owing to its acidic properties. Crisler and Conlon (4) even used lithium chloride as electrolyte for coulometric titrations in a methanolic system but Ting and others (43) have concluded, since that time, that lithium methoxide behaves as a weak base in some nonaqueous titrations. Tertiary butyl alcohol satisfies the

demands for a good nonaqueous solvent for titration of acids. Although other researchers have used alcohols other than methanol in their solvent systems, they have made no attempts to eliminate the "alkali error" by using supporting electrolytes other than the inorganic alkali salts. It may be concluded that a quaternary ammonium halide and tertiary butyl alcohol form an excellent supporting electrolyte-solvent combination for coulometric nonaqueous titrations.

Titration cell

Principally, the titration cell should be designed so as to prevent entirely or impede the mixing of anode and cathode reaction products. If used frequently, the cell should not be difficult to construct, it should be convenient and simple to use, and it should be small and compact. A small compact cell would allow the use of small volumes of electrolyte solution. This means that the overall concentration of all samples titrated will be greater than if large volumes were used. Often small volumes and increased concentration will sharpen potential breaks and enhance chances of titration of very weak and weak acids. Small volumes also can sharpen indicator color changes.

The large volume of 50 ml. or more employed by others (3,26,40) can be reduced by more than a factor of one-half by using the cells described in this work. The cell recommended by Streuli and others (40) probably will not be favor-

able for the titration of very weak acids because the seepage of water into the cathode compartment will alter the potential breaks at the end points. Furthermore, the potassium ions supplied by the potassium nitrate from the salt bridge will increase the "alkali error". Carson and Ko (2) also maintained that the use of a salt bridge in electrolysis is a distinct drawback, especially for microtitrations. The cell used by Johansson (26) is bulky and inconvenient because two separate titrations have to be performed or a transfer of about 10 ml. of solution has to be made in order to account for acid that migrated from the cathode compartment to a connecting compartment.

Another important feature of an ideal titration cell is that it have low electrical resistance. The electrical resistance of a cell is influenced partially by the solvent system and by the material which separates the anode and cathode compartments. Sintered glass frits and simple salt bridges have been used frequently to separate electrode compartments, but when used without further modifications these dividers possess certain undesirable qualities. These undesirable qualities can be overcome by the use of ion exchange membranes which are readily usable without modifications. The problems of hydrostatic flow or pressure and non-permeability are eliminated when ion exchange membranes are used instead of sintered glass frits and salt bridges for separating electrode compartments. Furthermore, these

membranes are inert and possess low electrical resistivity. This low resistance should simplify maintaining constant current during a titration with less sophisticated current supplies.

Johansson (26) tried a titration cell for external generation of reagent similar to that described by DeFord and others (9), but he found that the electrode surfaces employed were too small for use in nonaqueous solvents. Not only is the high resistance of such a cell undesirable but the set-up enhances the error in titrations resulting from dilution of test solutions. The use of a one compartment titration cell would simplify its construction but the silver anode which is used most frequently in a one compartment cell tends to become coated with finely divided silver chloride as electrolysis proceeds. This continuous build-up of silver chloride constantly increases the electrical resistance of the cell, requiring that the electrode be cleaned frequently. It is easy to see how a constantly changing resistance, although low, could complicate the maintenance of a constant generating current. Although these hindrances may not be too difficult to overcome, there are other factors which preclude the use of a one compartment titration cell with a silver anode.

Generating and measuring electrode systems

Although some researchers (3,4) employed the platinum cathode-silver anode generating electrode system there are

some serious drawbacks to the use of these electrodes in the same solution. Taylor and Smith (42) found that the small but finite solubility of silver chloride in the supporting electrolyte solution caused the reduction and subsequent deposition of silver on the cathode when a single compartment cell was used. Johansson (26) clearly showed this by his consistent low results when he used the platinum-silver generating system in the same solution. However, he used this generating electrode system in separate anode and cathode compartments and obtained good results if the anode compartment contained sodium tetraphenylboron to precipitate the silver formed in the anode reaction. A platinum anode and platinum cathode system for generation of the basic species probably is preferable to most other generating electrode systems because of its clean reactions.

The generating electrode system should allow quantitative and immediate usage of the desired material generated at the electrode of interest. Ideally, there should be no hold-up between the point of generation and the test solution. Large generating electrodes are desirable because they decrease the resistance of the system while increasing current efficiency. Generating electrodes must be of sufficient area to permit a low enough current density to keep electrode polarization within the limits necessary for 100 percent efficiency (49). The two prerequisites mentioned immediately

above reduce the usefulness of external generating electrodes in nonaqueous systems.

The ideal measuring electrode system should provide for rapid equilibrium and a relatively stable potential. For potentiometric end points the operation of the glass electrode is hindered by the flow of current and must be shielded carefully from the generator electrode system (2,33). Johansson (26) found that the interferences resulting from current flow were less if the glass electrode were placed in a region where the voltage drop was very small. However, he found it necessary to disconnect the coulometric apparatus completely when the potential measurements were made.

In one phase of this research an attempt was made to generate titrant while simultaneously recording the potential but considerable interference was encountered as a result of current flow. The current source employed in this work never had to be disconnected completely from the generating electrodes when measuring potentials after each incremental generation of titrant. Only the cell current was turned off and a few seconds allowed for equilibrium to be reached before reading the potential. Actually, only minor potential instability was experienced with the systems used.

One group of workers (40) used a saturated solution of tetramethylammonium chloride in the calomel reference electrode to replace the aqueous potassium chloride. Although

good results were obtained for the acids titrated the tetramethylammonium chloride has deleterious effects. According to Marple and Fritz (31) tetramethylammonium salts cause decomposition of the mercurous chloride in the calomel reference electrode.

Variety of acids titrated

For greater versatility the titration procedure should provide a means of determining a large variety of acids with relatively good accuracy. Most of the previous work has involved the determination of moderately weak acids but no report has been made of the determination of very weak acids. Cotman and coworkers (3) admitted that they could not titrate phenols successfully and the results of titrations of dibasic acids and dinitrophenol were successful only to 4% in benzene-methanol solvent. Johansson (26) did titrate an enol (5,5-dimethyldihydroresorcinol) but its strength is approximately equal to that of benzoic acid, a moderately strong acid. Barbital, with a pK_a of about 7.98 was the weakest acid that he titrated.

The method reported here has the advantage that both mineral and organic acids with pK_a (in water) values ranging from less than 1 to 9.9 can be titrated coulometrically with either an indicator or a potentiometric end point.

TITRATIONS IN TERTIARY BUTYL ALCOHOL

Experimental

Apparatus

Current supply and voltmeter Constant current for generation of basic titrant was supplied by a commercial Sargent Model IV Coulometric Current Source. The voltage across the generating electrodes was measured, if necessary, with a Kay Lab Microvoltmeter by connecting the voltmeter across the terminals of the coulometric current source.

Generating electrodes Two platinum electrodes served as generating electrodes (anode and cathode) for all titrations. For potentiometric end points the titrant was generated at a cathode made of 19.3 cm² sheet platinum and the anode was 16.6 cm². Both electrodes made contact with the current source by a piece of platinum wire that was spot-welded to the platinum sheet. When indicator end points were used both generating electrodes were about 4 cm² in size.

Measuring electrode system Solution potentials were measured with a Corning Model 12 pH Meter using the glass-modified calomel electrode system developed by Marple and Fritz (31).

Titration cells The titration cell for generation of base and employing potentiometric end point determinations is shown in Figure 1. The cell is just a small scale replica of the titration cell recommended by Marple and Fritz (31).

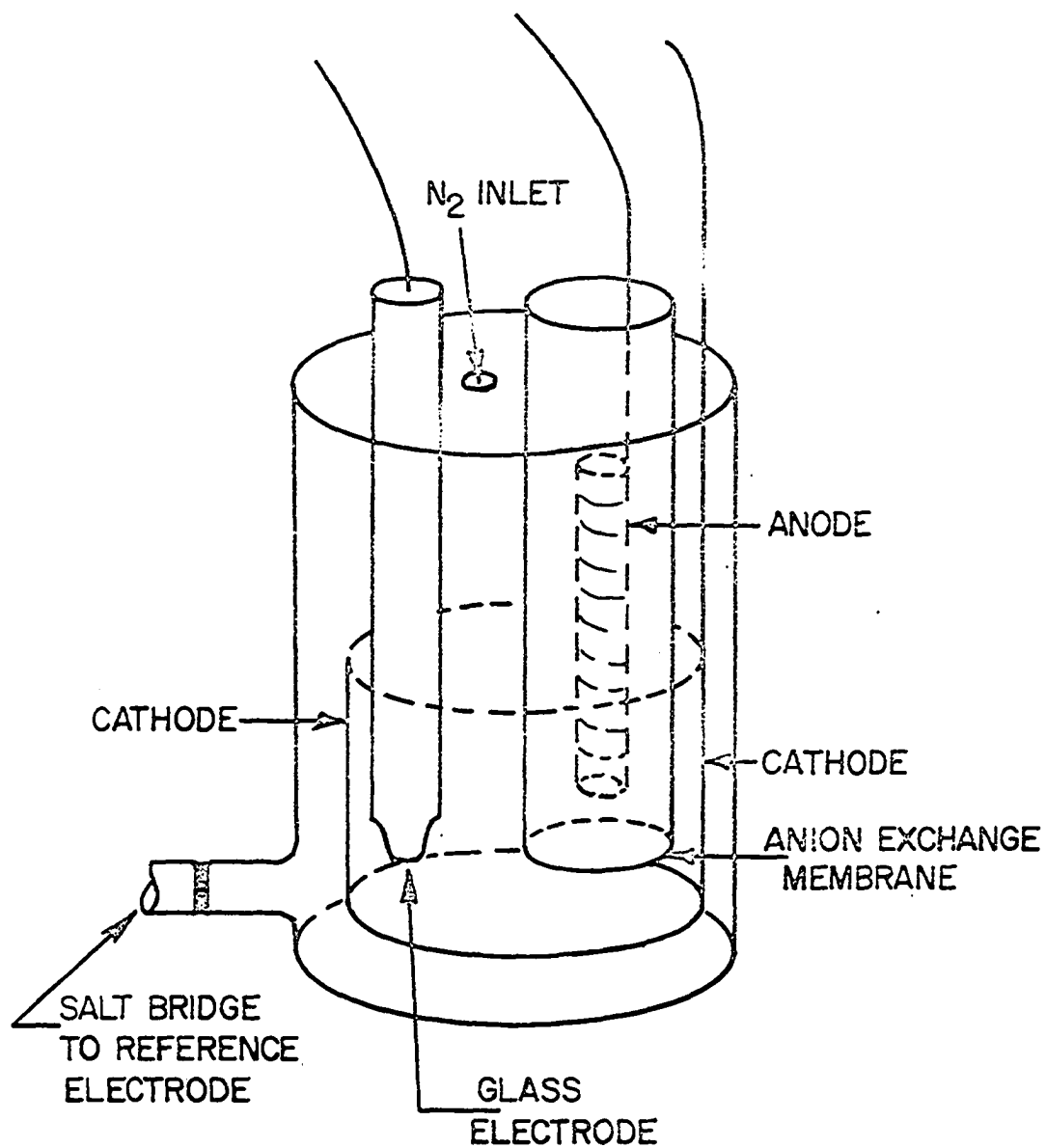


Figure 1. Coulometric titration assembly for potentiometric end points in tertiary butyl alcohol solvent

Only one-half of the assembly is shown in the figure. The cathode compartment was made of glass tubing 8 cm. high and 3 cm. internal diameter. The anode compartment was made of plexiglas tubing 10 cm. high and 9.5 mm. internal diameter with a disc of anion exchange membrane affixed to one end by epoxy glue or Eastman No. 910 adhesive. The Eastman adhesive had the advantage of being readily usable and quick drying.

Figure 2 shows the cell design that was used for coulometric titrations with indicator end points. The cell was made of 1/4 inch thick plexiglas having all sides cemented with ethylene dichloride. The cell consisted of two halves of a rectangular box which were clamped together by threaded rods and wing nuts. The membranes and plastic, if used, were placed in between these halves thus forming the anode and cathode compartments having internal dimensions $1 \times 1 \times 2$ ($1 \times w \times h$) inches and the complete cell with dimensions $2 \times 1 \times 2$ inches. The cell was made leak proof by placing rubber cement in the cracks between the two halves (sides and bottom) after clamping them together. A plexiglas cover was made and used on the box to reduce atmospheric effects on the test solutions.

Ion exchange membranes The cation exchange membrane, Nepton 61AZL065, and the anion exchange membrane, Nepton 111BZL065, were obtained from Ionics, Inc., Cambridge, Mass. The cation exchange membrane was cation-selective and com-

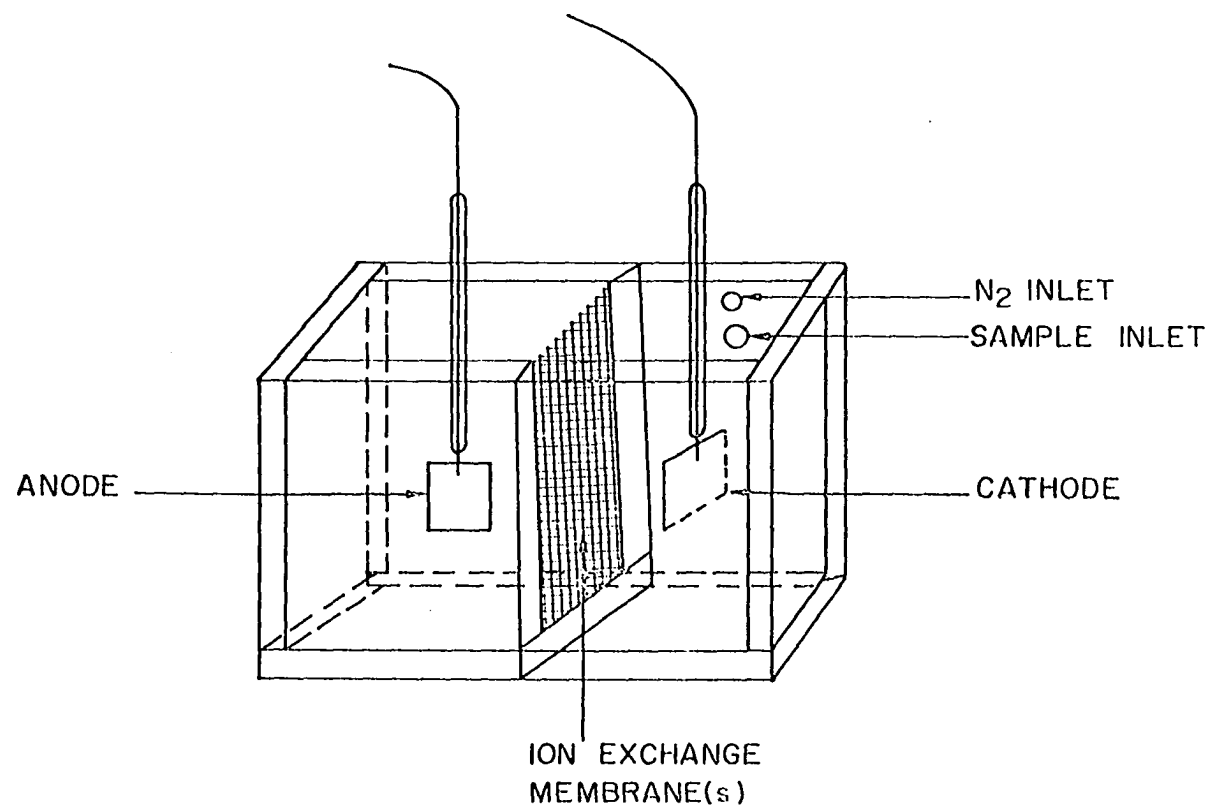


Figure 2. Coulometric titration assembly for indicator end points in tertiary butyl alcohol solvent.

prised sulfonated copolymers of vinyl compounds. The anion exchange membrane was anion selective and comprised copolymers of vinyl compounds containing quaternary ammonium groups and tertiary amine groups. Both types of membranes were homogeneous films cast in sheet form on a synthetic cloth backing.

Reagents

Tertiary butyl alcohol was obtained commercially and used without any purification other than boiling to expel dissolved carbon dioxide. The water content of the unpurified tertiary butyl alcohol was 0.15% as determined by the Karl Fischer method. Although most titration results were obtained by using the boiled solvent other data showed that the solvent blank was reduced considerably by fractional distillation of the commercial grade alcohol before use. These data will be discussed under the section dealing with the quality of the titrant since purification of the solvent was instrumental in the attainment of a good quality base. The enols and imides were supplied by Eastman Organic Chemicals. The indicators used are all available commercially. The tetramethylammonium bromide was purchased from Matheson, Coleman, and Bell and the polarographic grade tetrabutylammonium bromide was purchased from Southwestern Analytical Chemicals, Inc., Austin, Texas. A non-polarographic grade of the butyl salt was obtained from Eastman Organic Chemicals. A 0.1 M solution of the methyl salt in methanol was used as electrolyte in the anode com-

partment. The butyl salt was prepared as 0.1 M solutions in tertiary butyl alcohol and used as supporting electrolyte in the cathode compartment. All acid sample solutions were prepared such that a 2 ml. aliquot would approximate the desired number of microequivalents. The basic species was the hydroxide ion as borne out in another section.

Procedures

When using indicator end points approximately 10-15 ml. of the appropriate electrolyte solution was placed in the anode and cathode compartments and several drops of indicator solution were added to the cathode compartment. The cover and generating electrodes were set in place and nitrogen was then bubbled through the electrolyte solution in the cathode compartment to purge the system of dissolved carbon dioxide. Nitrogen was bubbled continuously over the test solution during titrations in order to expel any air which may have seeped into the compartment after the initial purge with nitrogen. Although nitrogen was generally used it was sometimes possible to eliminate its use depending on the type and quantity of acid titrated. A magnetic stirrer under the cathode compartment and the cell current were turned on. Titrant was generated until the indicator changed to the appropriate color. The number of microequivalents required was recorded as the solvent blank. The acid sample was added and base was generated again until the indicator changed to

the appropriate color. This number of microequivalents was recorded as the solvent blank plus sample. The difference between the two values was recorded as the number of microequivalents of acid in the sample and was compared with the theoretical value in order to find the percent recovery. The same applied current value was used for both blank and sample titrations.

When using potentiometric end points the salt-bridge system was prepared according to Marple and Fritz (31). Approximately 10-15 ml. of electrolyte solution was placed in the cathode compartment and purged with nitrogen. Only about 5 ml. of solution were required for the anode compartment. The platinum cathode and the rubber stopper with the anode and slender bodied glass electrode were set in place and titrant was generated in small increments. After each incremental generation of base the potential of the solution was measured and recorded. This process was continued to several increments beyond the end point in order to be assured of enough points to plot a complete titration curve. The acid sample was then added and base was generated in large increments until the end point was approached, then in smaller increments until the end point was exceeded. Two graphs of potential (mv.) vs. microequivalents of base were plotted, one corresponding to the blank titration, the other corresponding to the sample. The difference in values after corrections was the number of microequivalents of acid present in the

sample. The applied current setting corresponding to 4.825 milliamps was used for titration of the blanks. The current setting corresponding to 19.3 milliamps was used to titrate the samples.

Quality of the Basic Titrant

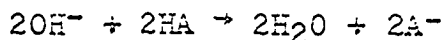
Primary electrode reactions

The primary generating electrode reactions depend predominately on the reducible or oxidizable materials in the cathode and anode compartments. It is essential that the cathode reaction be well-defined for the titration of acids in the cathode compartment. A well-defined cathode reaction is a key to the type, quality, and purity of the generated basic titrant.

The tertiary butyl alcohol solvent contained 0.15% water as determined experimentally. Water is reduced electrolytically before tertiary butyl alcohol and the solvent contained enough water to produce a sufficient amount of base to neutralize 10 to 60 microequivalents of any acid sample. On the basis of these facts it was concluded that the reduction of water was the primary reaction at the cathode. The reaction produces hydrogen gas and hydroxide ions according to the equation

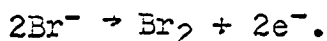


The hydroxide ions subsequently react with the acid sample in the cathode compartment.



Since tetrabutyl ammonium bromide was used as supporting electrolyte it was concluded further that tetrabutylammonium hydroxide was the principal basic titrant used in this investigation.

The principal reaction at the anode was the oxidation of the bromide ion according to the equation



The yellowish color imparted by bromine in dilute solution was apparent in the anode compartment immediately after turning on the current source.

Solvent purification and solvent blanks

It was important to ascertain the purity of the base that was generated at the platinum cathode. Extensive study was undertaken to determine this degree of purity in the tertiary butyl alcohol solvent. The platinum cathode produced clean reactions so the two main sources of impurities in the generated titrant were the quaternary salt and the tertiary butyl alcohol solvent. Another possible source of impurities was decomposition of the base owing to a high resistant electrolysis system. A high resistant system could cause heating at the cathode surface and it is an established fact that heat decomposes the quaternary ammonium hydroxide.

The tertiary butyl alcohol was purified by fractional distillation and the purification step was probably the most

significant contribution to the final purity of the basic titrant. The purification of the solvent made it possible to obtain satisfactory results from potentiometric titrations of dibasic acids and mixtures of acids. Without purifying the solvent it was impossible to obtain good equivalent results based on either the first or second end point for the titration of dibasic acids. Purification of the tertiary butanol was significant in reducing the solvent blank. In general, the size of the blank was dependent upon volume of electrolyte solution, the quality of the quaternary salt, and the amount of dissolved carbon dioxide. Conditions and experimental results leading to purification of the solvent will follow. An investigation of the solvent blanks was most important. Effects of solvent purification on final purity of the titrant are presented.

An obvious way to check on the purity of the basic titrant was to titrate a quantity of generated base with a strong mineral acid and to note any extra inflections in the potentiometric titration curve. A second method was to titrate a strong mineral acid to a potentiometric end point with coulometrically generated titrant. Both methods were employed in the test for purity of titrant. Both methods were valuable because impurities in the system appeared in the titration curves either as extra inflections or by reducing the sharpness or slope of the potential breaks.

The procedure for titrating a quantity of generated base with a strong mineral acid made use of the plexiglas box-like electrolysis cell, Figure 2. A quantity of base was generated at the desired current setting and subsequently titrated with perchloric acid without removing the base from the cell. The perchloric acid in tertiary butyl alcohol was added in increments from an ordinary buret. Potentials were followed with a combination glass-modified calomel electrode system.

Curve B of Figure 3 shows the titration of a quantity of generated base that was exposed to the atmosphere. When the curve was compared with results obtained by Marple and Fritz (31) one of the extra inflections was labeled as carbonate impurity. The two most logical sources of carbonate were the atmosphere and electrolyte solution because no Ag_2O was used to prepare the hydroxide. Curve A was obtained by titrating generated base under deaerated conditions. Both curves were obtained under conditions employing undistilled tertiary butyl alcohol and a non-polarographic grade quaternary salt. The disappearance of one of the inflections in going from the conditions of Curve B to Curve A verified that carbonate was an impurity in Curve B and that it could be eliminated by simply deaerating the catholyte and cathode compartment with purified nitrogen.

The inflection remaining in Curve A was labeled tri-n-butylamine initially. The use of a polarographic grade tetrabutylammonium bromide to prepare the catholyte reduced the

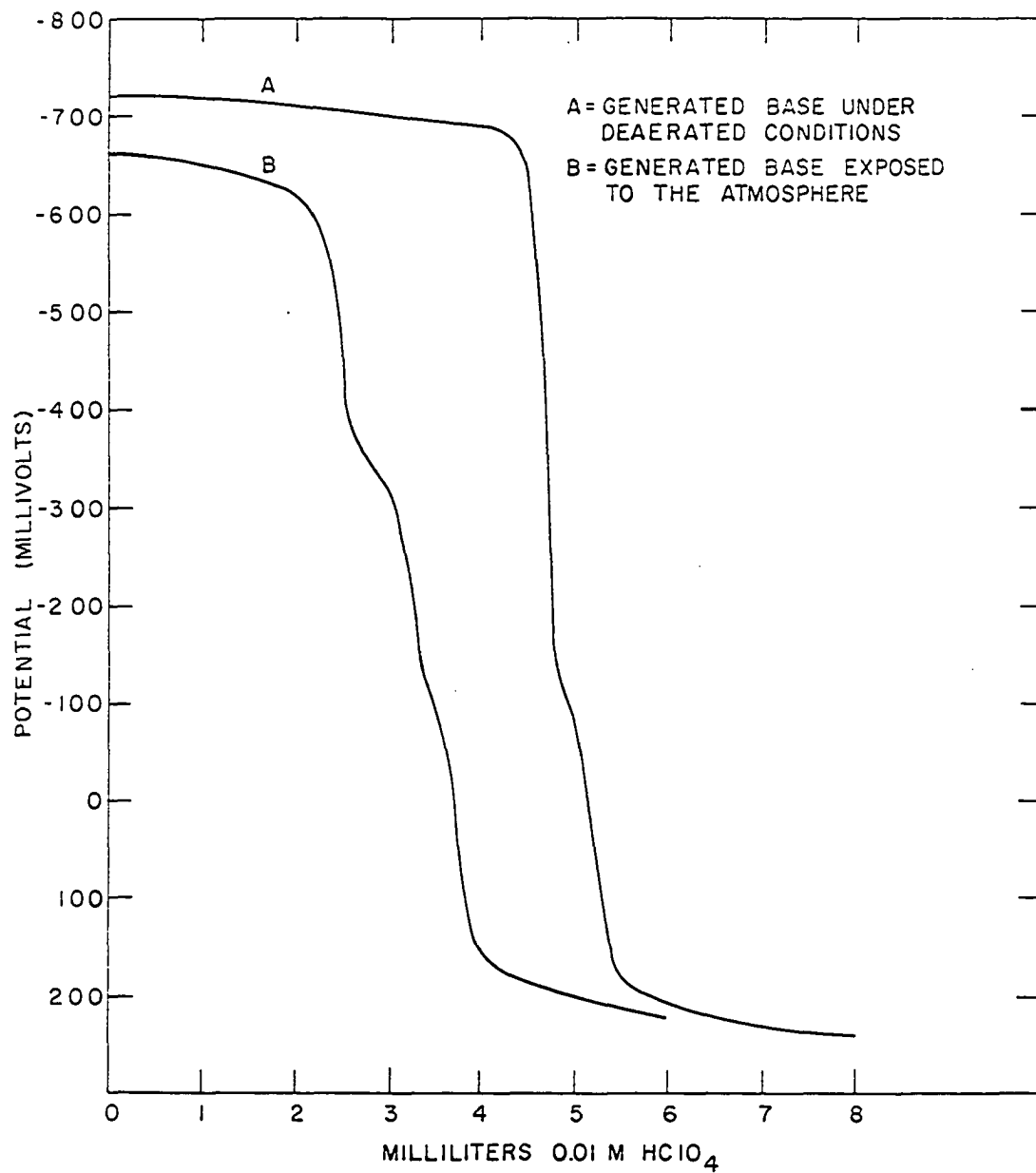


Figure 3. Carbonate as an impurity in the generated titrant

inflection as seen in Curve C, Figure 4 but did not eliminate it completely. The titration of a large sample of the quaternary bromide under conditions suitable for nonaqueous base titrations did not reveal conclusively any tri-n-butylamine in the polarographic grade salt. Purification of the solvent was proposed since the t-butanol used to obtain Curve C was not distilled. Furthermore a relatively large solvent blank was observed when acids were titrated with generated base.

The nature and scope of the solvent blank was investigated. Preliminary titrations showed that the blank of the undistilled solvent increased proportional to the volume of electrolyte solution but was not increased by a ten-fold increase in quaternary bromide concentration. This was an indication that the bulk of the solvent blank resulted from the solvent itself and not the salt. Figure 5, Curve F is a blank titration curve of undistilled tertiary butyl alcohol. The blank was reduced substantially after fractional distillation of the t-butanol as shown by Curve G. Further reduction in solvent blank resulted from a second distillation of the t-butanol. Curve H, Figure 5 shows the extent of the blank reduction. Each blank solution consisted of 15 ml. of 0.1 M polarographic grade Bu_4NBr in tertiary butyl alcohol.

Curve D, Figure 4 is a curve resulting from the generation and titration of hydroxide in single distilled tertiary butyl alcohol. The increase in slope of Curve D as compared

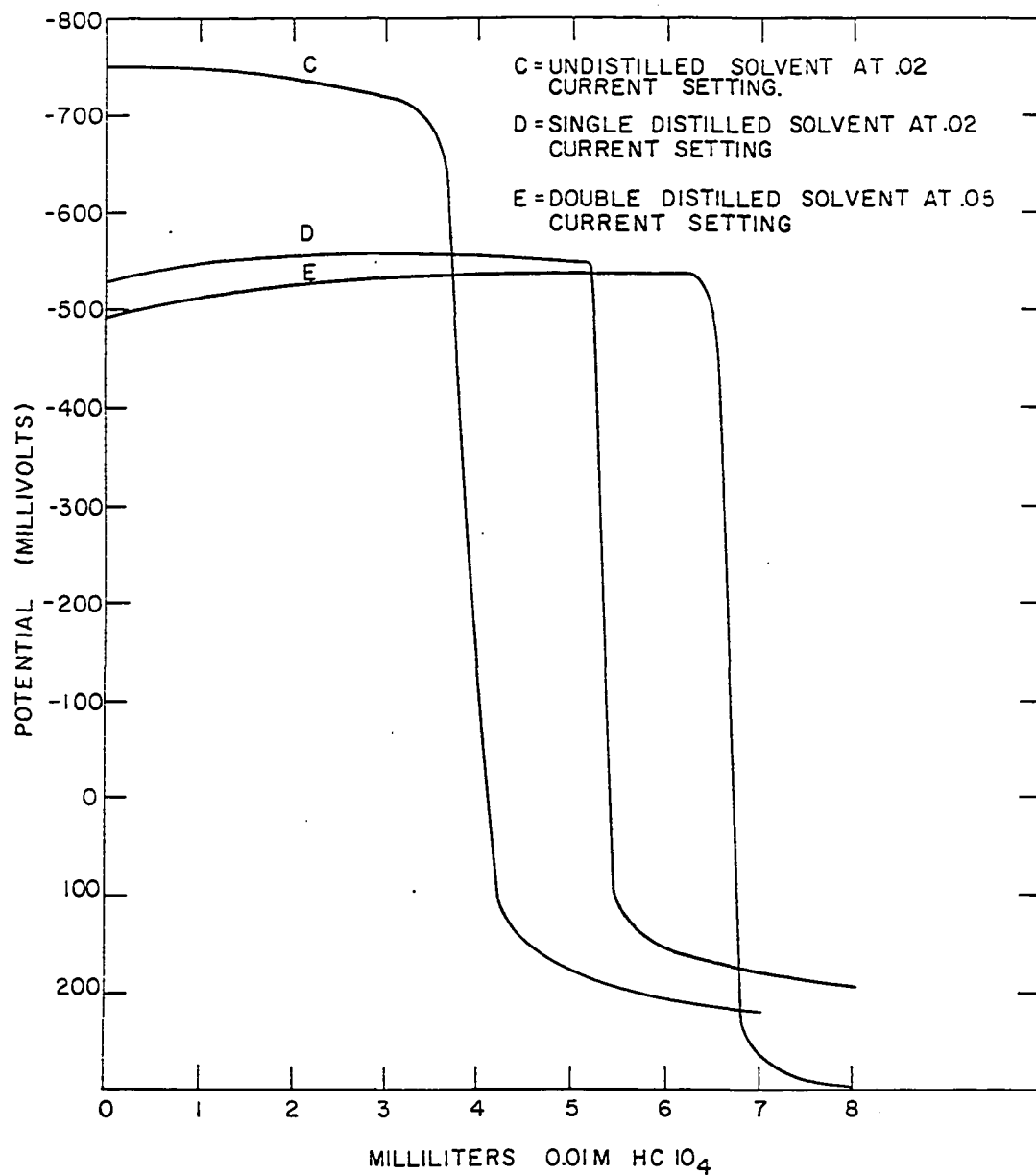


Figure 4. Effects of quaternary salt, solvent and generation rate on the quality of base

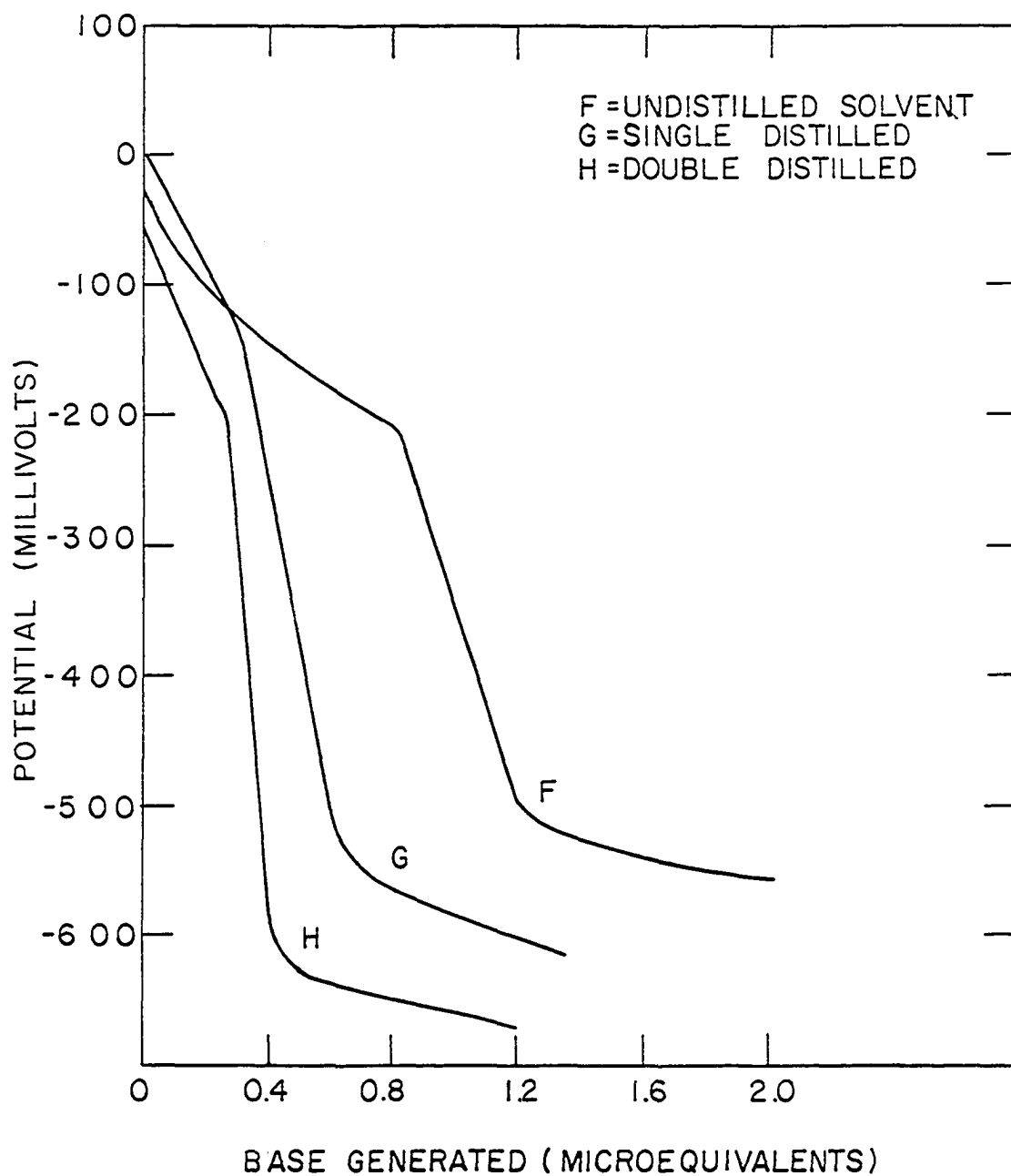


Figure 5. Titration of tertiary butyl alcohol solvent blanks with electrolytically generated titrant

to Curve C was definite evidence of improvement, in the quality of base generated in tertiary butyl alcohol, by the distillation process. The titration shown by Curve E removed doubts concerning the introduction of impurities, particularly tri-n-butylamine, into the system by decomposition of tetrabutylammonium hydroxide by heat produced at the cathode surface. The base prepared for Curve E was generated at a rate and current setting two and one-half times higher than the setting used to prepare base for Curve D.

Further evidence that a good quality titrant was generated is shown in Figure 6. Curve B represents the titration of perchloric acid in single distilled tertiary butyl alcohol with the base generated at .02 current setting. Base was generated at .05 current setting in double distilled t-butanol for the titration shown by Curve A. Both curves have excellent potential breaks with slopes which are essentially the same. The similarity of the curves in Figure 6 helped to substantiate the fact that the quality of generated base was not affected by the rate of generation.

Results of Titrations

Indicator end point detection

Table 1 shows the results of titrations of acids in tertiary butyl alcohol with indicator end points. The average percent recovery and standard deviations are given for convenience. The results in Table 1 were based on the assumption

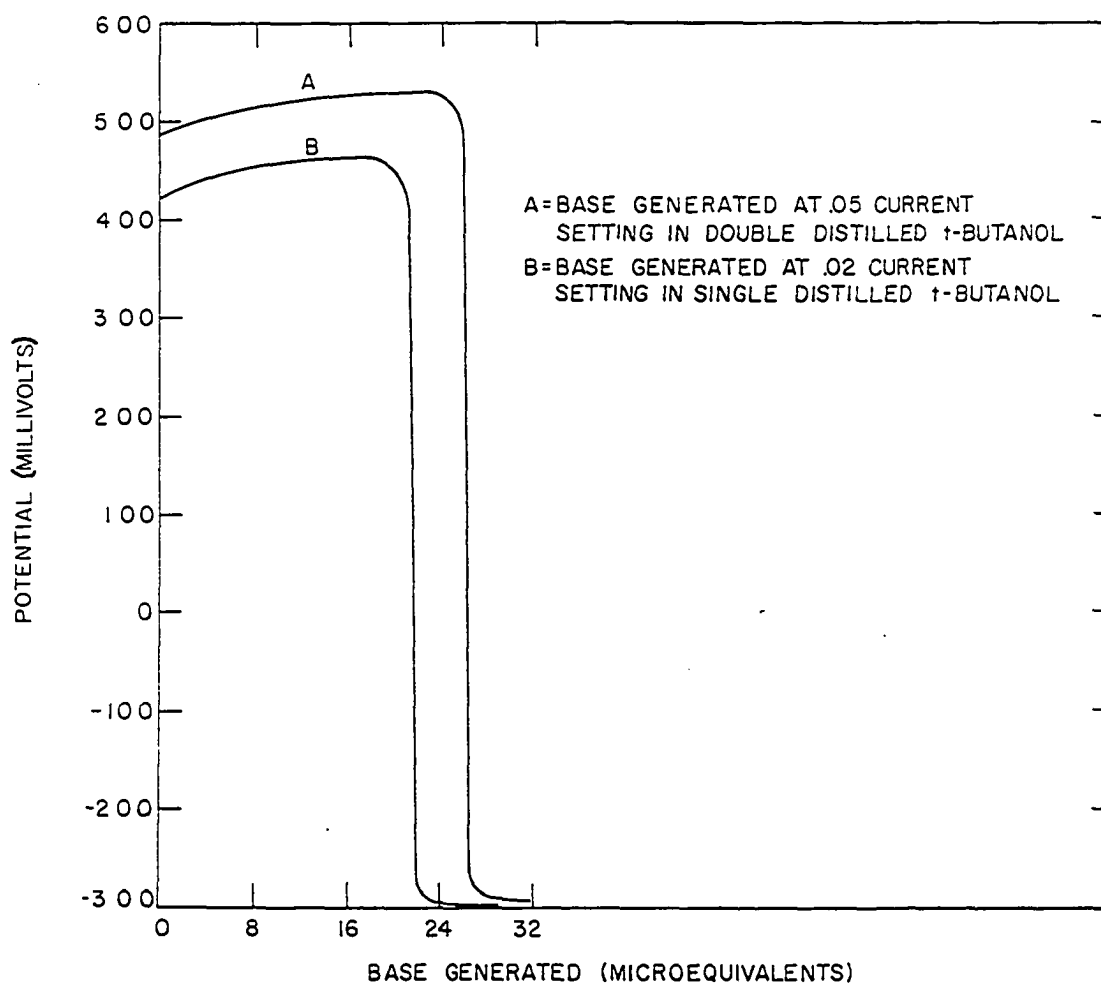


Figure 6. Titration of perchloric acid in tertiary butanol with electrolytically generated titrant

Table 1. Coulometric titration of acids with indicator end points
Electrolyte: 0.1 M tetrabutylammonium bromide in tertiary butyl alcohol

Compound titrated	Number of samples	Microequivalents Taken	Microequivalents Found	Recovery (%)	Std. dev.	Indicator
Benzoic acid	6	10.02	10.18	101.7	0.19	2,4-dinitrodi-phenylamine
"	8	15.16	15.21	100.3	0.07	"
"	5	20.00	20.00	100.0	0.04	"
"	13	30.08	30.02	99.8	0.19	"
"	9	40.08	40.05	99.9	0.14	"
"	12	50.04	50.02	99.9	0.27	"
"	7	60.08	60.15	100.1	0.20	"
Phenol	15	12.10	12.20	100.8	0.14	o-nitroaniline
"	17	15.56	15.52	99.7	0.20	"
"	10	20.30	20.51	101.0	0.16	"
"	13	31.60	31.63	100.1	0.24	"
"	14	40.47	40.40	99.8	0.23	"
"	16	46.78	46.67	99.8	0.19	"
"	11	61.34	61.18	99.3	0.37	"
2,4,6-tri-methylphenol	7	20.40	20.35	99.8	0.41	"
o-hydroxyphenol	6	20.20	20.32	100.6	0.19	azoviolet
anthranilic acid	12	9.78	9.82	100.4	0.07	2,4-dinitro-
"	10	20.02	20.07	100.3	0.13	aniline
"	11	40.08	39.92	99.6	0.12	"
"	8	60.15	60.22	100.1	0.23	"
Oxalic acid 1st H ⁺	2	20.18	19.95	98.9		bromthymol blue
2nd H ⁺	3	40.07	39.84	99.4		p-nitro-p'-amino-azobenzene
Succinic acid 1st H ⁺	12	10.14	10.12	99.8	0.08	bromthymol blue
" "	1	20.04	19.80	98.8		"
" 2nd H ⁺	13	20.28	20.21	99.7	0.13	azoviolet
" "	3	40.08	39.65	98.9		"
" "	1	60.10	59.10	98.3		"

Table 1. (Continued)

Compound titrated	Number of samples	Microequivalents Taken	Microequivalents Found	Recovery (%)	Std. dev.	Indicator
Acetoacetanilide	10	20.03	20.00	99.9	0.12	azoviolet
Dibenzoylmethane	12	20.02	20.04	100.1	0.12	"
"	10	47.46	47.33	99.7	0.09	"
Succinimide	10	10.29	10.27	99.8	0.09	"
"	6	20.58	20.59	100.1	0.05	"
"	9	61.52	61.46	99.9	0.29	"
Hydantoin	8	20.16	20.09	99.4	0.13	o-nitroaniline
"	8	20.16	20.03	99.7	0.09	azoviolet
2-Cyano- acetamide	12	20.88	20.81	99.7	0.15	p-nitro-p'-amino- azobenzene
Ethylcyanoacetate	10	20.12	19.94	99.1	0.07	azoviolet
2,4-Pentanedione	8	26.79	26.11	97.5	0.06	"
p-Toluene- sulfonic acid	8	20.11	20.10	100.0	0.08	bromthymol blue
"	4	60.05	59.99	99.9		"

that all acids were 100% pure and that the current source operated at the same efficiency irrespective of the applied current setting. The three applied current settings used were .005, .01, and .02 which corresponded to 4.825, 9.65, and 19.3 milliamps constant current respectively. The current output at each setting was checked against a standard resistor in series with a Leeds and Northrup potentiometer at the start of this investigation. Any deviations from the indicated constant current output values were negligible. Benzoic acid was used as the primary standard acid and results showed that the titration efficiency was better than 100.0 ± 0.5 percent for all benzoic acid concentrations except the 10 microequivalent samples. Indicators and their color changes to be used for each acid were selected from the paper by Marple and Fritz (32).

The phenols probably were the most difficult to titrate. As a result the following are some notes or helpful hints for successful titrations of phenol using o-nitroaniline as indicator.

- (1) It was necessary to bubble nitrogen over the test solution of acid and electrolyte in the cathode compartment throughout all titrations. It is highly recommended that nitrogen be passed through the electrolyte solution in the cathode compartment before titration of blank and addition of acid sample.

- (2) Sharper indicator color changes were observed when the higher current setting (19.3 ma.) was used.
- (3) Indicator color changes were sharper for small quantities of phenol than for large amounts (i.e. 10-30 microequivalents vs. 30-60 microequivalents).
- (4) The color change of the indicator (yellow to orange) was a bit sharper at the end of the blank titration than at the end of the titration of the acid sample.
- (5) The point at which the indicator first begins to change to the basic color (orange) should be taken as the end point. Owing to the dullness of the end point, to titrate beyond the first noticeable orange color would exceed the end point and result in high acid recovery. This will be very important when titrating the larger amounts of phenols, particularly, and even more so when titrating the larger amounts at the .01 applied current setting.

The titration of 2,4,6-trimethylphenol with o-nitrophenol as indicator was not very satisfactory although a good average recovery was obtained. The color change from yellow to orange was not very sharp and this decreased the precision of the titrations. 2,4,6-Trimethylphenol is such a weak acid that better results actually could not be expected. The extremely low results for the enol, 2,4-pentanedione, were explained by a gas chromatogram of the enol which showed the presence of

considerable impurities. The low solubility of some enols and imides in tertiary butyl alcohol is probably the limiting factor to the extent of titration of these types of compounds in this solvent.

Potentiometric end point detection

The results of titrations of monobasic acids in tertiary butyl alcohol with potentiometric end points are presented in Table 2.

Table 2. Coulometric titrations of acids with potentiometric end points
Electrolyte: 0.1 M tetrabutylammonium bromide in tertiary butyl alcohol

Compound titrated	Number of samples	Microequivalents		Recovery (%)
		Taken	Found	
Benzoic acid	5	20.21	20.24	100.1
Phenol	4	20.08	20.26	100.9
Acetoacetanilide	2	20.03	20.14	100.5
Dibenzoylmethane	3	20.02	20.34	101.6
p-Toluenesulfonic acid	6	20.11	20.07	99.8
Benzoic acid ^a	2	22.00	21.99	100.0
p-Toluenesulfonic acid ^a	2	20.11	20.24	100.6

^aResults obtained from differentiating titration of a mixture of benzoic and p-toluenesulfonic acids.

The titration curves were excellent and potentials were stable and reproducible. The reproducibility of potentials was shown by the superimposable nature of two curves of the same acid and sample size. Figure 7 shows typical titration curves of phenols, enols, and imides. The tertiary butyl alcohol

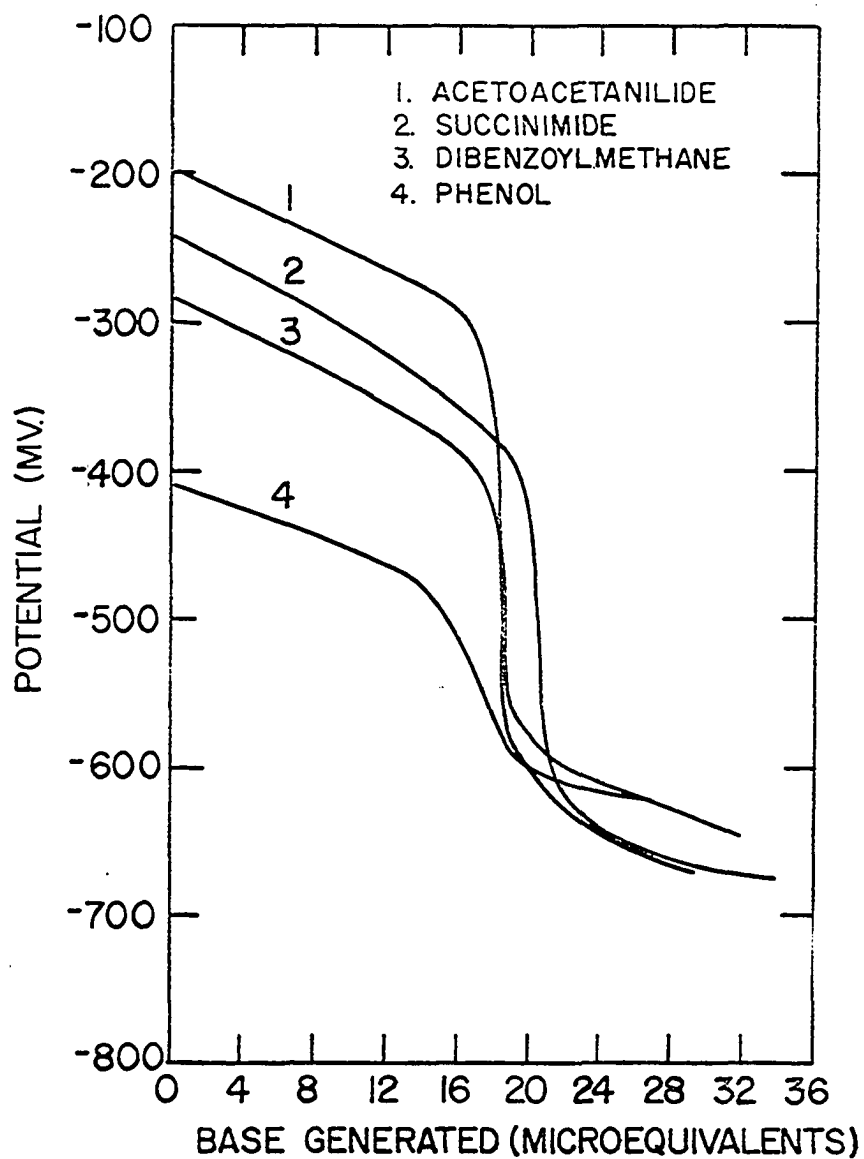


Figure 7. Titration of enols, imides, and phenols in tertiary butanol with electrolytically generated titrant

solvent was as suited for differentiating titrations via coulometry as by the conventional titrimetric procedure. A differentiating titration curve of benzoic acid and p-toluenesulfonic acid is shown in Figure 8 along with the titration curve of each of these acids when titrated in the absence of the other.

During work in measuring exactly the two equivalents of dibasic acids in unpurified solvent the two equivalents were always unequal. The total acidity values were acceptable but the second equivalent was consistently higher than the first. The acid mixture reported in Table 2 also yielded results which were not exactly in accord with the expected values when unpurified solvent was used. No discrepancies in results were observed in the determination of monobasic acids when titrated alone. Cundiff and Markunas (6,7,8) did a detailed investigation of solvent-solute reactions and the effects of impurities in the titrant when titrating dibasic acids, strong mineral acids, and mixtures of strong and weak acids in various solvents.

It was no longer difficult to titrate dibasic acids and mixtures after purification of the tertiary butanol. The curves for the titration of dibasic acids shown in Figure 9 are typical and the stoichiometry between the first and second end points was very good after supplying blank corrections.

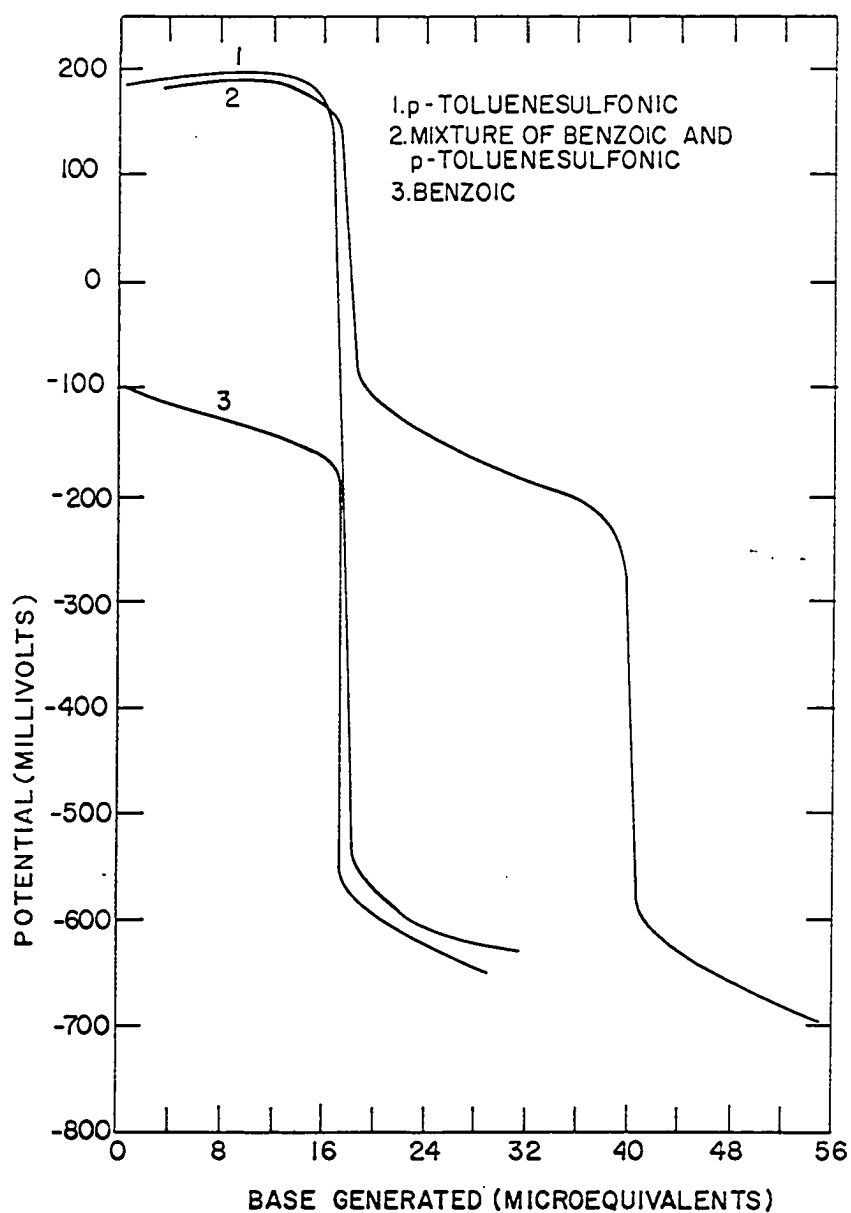


Figure 8. Differentiating titration of benzoic acid and p-toluenesulfonic acid in tertiary butanol with electrolytically generated titrant

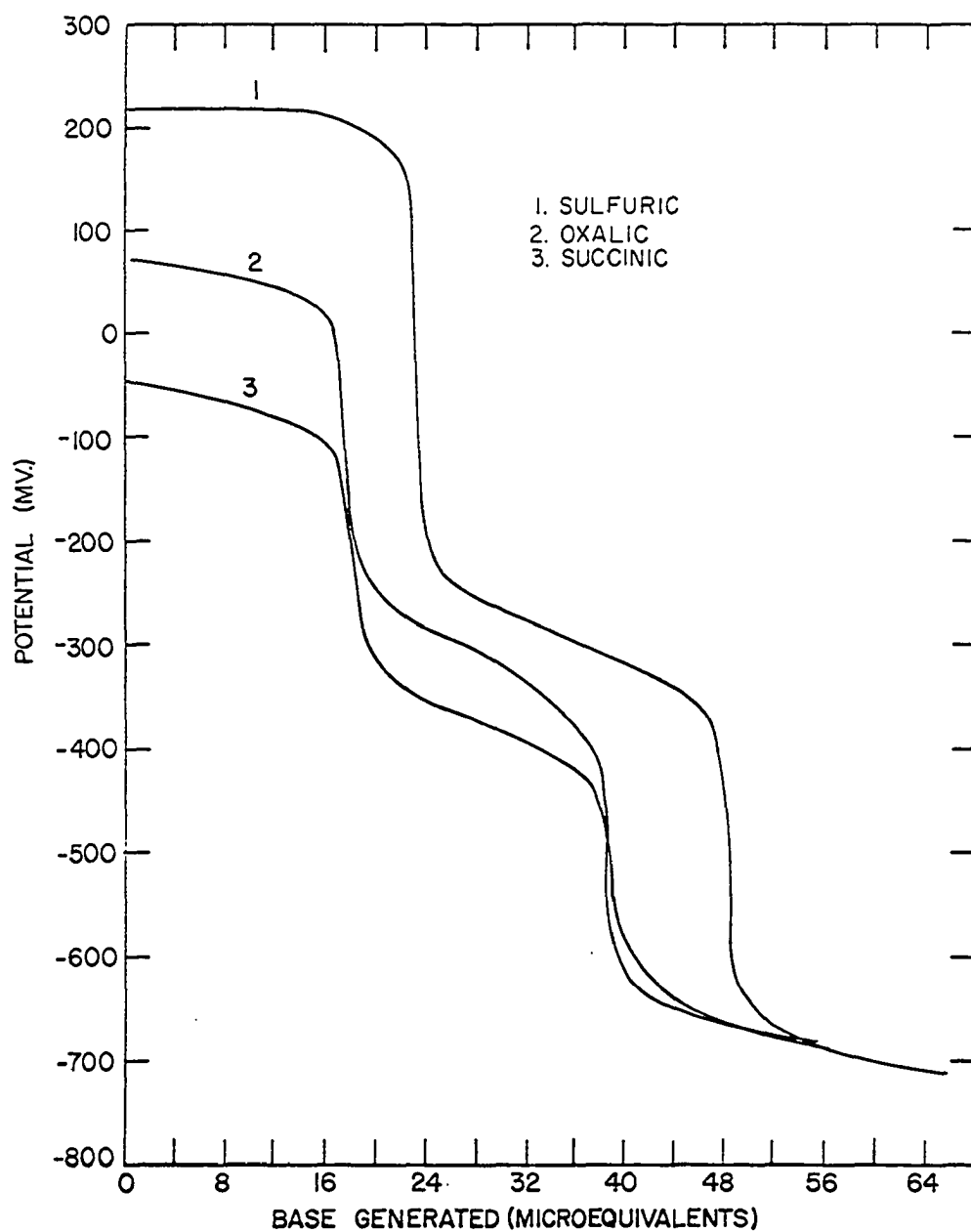


Figure 9. Titration of dibasic acids in tertiary butanol with electrolytically generated titrant

Table 3 shows the results of titrations of dibasic acids in tertiary butyl alcohol that was purified by double fractional distillation. The results are excellent for the micro amounts titrated and they exemplify the value of purification of the solvent. Fritz and Marple (18) experienced no problems with stoichiometric relationships when titrating dibasic acids in tertiary butyl alcohol. It is believed that the discrepancies encountered in this work were the results of a small acid to impurity ratio which was increased greatly after distillation of the alcohol solvent.

Table 3. Coulometric titrations of dibasic acids with potentiometric end points
Electrolyte: 0.1 M tetrabutylammonium bromide in tertiary butyl alcohol

Compound titrated	Number of samples	Amount taken (μ eq.)	Amount found (microequivalents)					
			A	Recovery (%)	B	Recovery (%)	C	Recovery (%)
Sulfuric acid	2	50.18	50.21	100.1				
	1		41.40		20.70	100.0	20.70	100.0
	1		40.40		20.20	100.0	20.20	100.0
	1		20.60		20.30	100.0	20.30	100.0
Oxalic acid	2	40.09	40.03	99.9				
	2		38.50		19.20	99.7	19.20	99.7
	2		19.44		19.40	99.8	19.44	100.0
Succinic acid	1	40.08	40.60	101.3				
	2		20.44		20.40	99.8	20.48	100.2

A - Based on total number of microequivalents.

B - Based on number of microequivalents to first end point.

C - Based on difference in microequivalents between final and first end point.

TITRATIONS IN ACETONE

Experimental

Apparatus

The titration cell for potentiometric end point determinations in acetone differed significantly from the cell used for similar titrations in tertiary butyl alcohol. The cathode compartment was a glass cylinder 8 cm. high and 3 cm. internal diameter. The anode compartment was a piece of glass tubing 10 cm. high and 10.5 mm. internal diameter with an ultrafine porosity glass fritted disc on one end. The measuring electrode system was a slender bodied combination glass-calomel electrode with the aqueous saturated potassium chloride replaced by saturated potassium chloride in methanol. The generating electrode system was the same as that used in tertiary butyl alcohol. Figure 10 shows the titration assembly used in acetone.

Reagents

A spectrographic grade of acetone was obtained from Eastman Organic Chemicals and used in this study without further drying or purification. The acetone contained 0.35% water (v/v). The electrolyte solution for the cathode compartment was 0.1 M polarographic grade tetrabutylammonium bromide in spectrographic grade acetone. Tetramethylammonium bromide in methanol served as electrolyte solution in the anode compartment. The basic species generated at the cathode

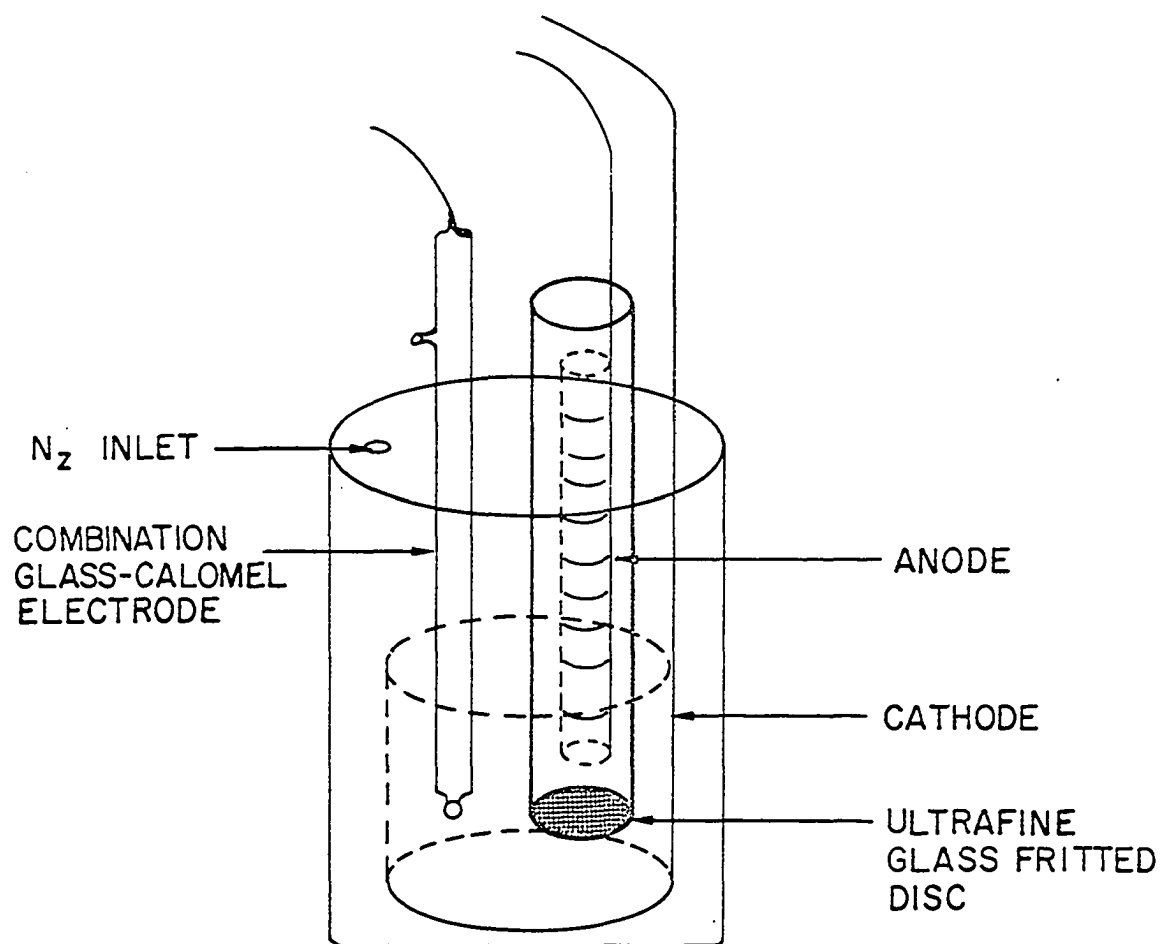


Figure 10. Coulometric titration assembly for potentiometric end points in acetone solvent

was the hydroxide ion owing to the water in the acetone. In effect, tetrabutylammonium hydroxide was the basic titrant.

Procedure

The procedure for base generation to potentiometric end points in acetone was identical to the procedure used in the tertiary butyl alcohol system.

Results of Titrations

The results of titrations in acetone are shown in Table 4. A relatively large blank correction had to be applied to the data obtained for the titrations but most results were excellent after making the proper correction. The large blank correction was made after each titration and was dependent on the length of time required for the titration. The ultrafine fritted disc separating the anode and cathode compartments was not impervious to passage of solution in the anode compartment. Seepage of the anolyte containing bromine into the cathode compartment resulted in high acid values owing to the use of some electrons to reduce bromine to bromide ion at the platinum cathode. The approximate number of microequivalents of bromine seeping into the cathode compartment during the period of the titration was the applicable blank correction. A standard rate of seepage of bromine into the cathode compartment was determined under conditions similar to an actual titration.

Table 4. Coulometric titrations of acids with potentiometric end points
Electrolyte: 0.1 M tetrabutylammonium bromide in acetone

Compound titrated	Number of samples	Microequivalents Taken	Microequivalents Found	Recovery (%)
Benzoic acid	3	10.06	10.16	101.0
"	3	20.11	20.08	99.9
"	3	30.17	30.94	102.6
"	4	60.89	60.81	99.9
Acetoacetanilide	3	10.11	10.08	99.7
"	3	20.21	20.32	100.5
"	4	30.32	30.36	100.1
"	5	40.42	40.28	99.7
"	3	60.16	59.81	99.4
5,5-dimethyl-1,3-cyclohexanedione	4	20.16	19.55	97.0
dibenzoylmethane	3	20.07	20.17	100.5
succinimide	2	20.26	20.53	101.3
phenol	1	21.13	21.15	100.1
2,4-dinitrophenol	2	20.20	20.20	100.0
s-diphenylthiourea	2	20.11	20.13	100.1
p-toluenesulfonic acid	3	10.37	10.34	99.7
"	3	20.73	20.76	100.1
"	3	31.10	31.39	100.9
"	3	60.66	60.59	99.9

The titration curves for individual acids in acetone solvent were not exactly reproducible but the potential breaks were sharp and well defined. Thus, the detection of end points could be achieved with little difficulty. The titration curves of benzoic and sulfonic acids are shown in Figure 11. Most of the curves are well suited for differentiating titrations provided there is a sufficient difference in the acid strength of the compounds involved. Figure 12 contains titration curves of phenols.

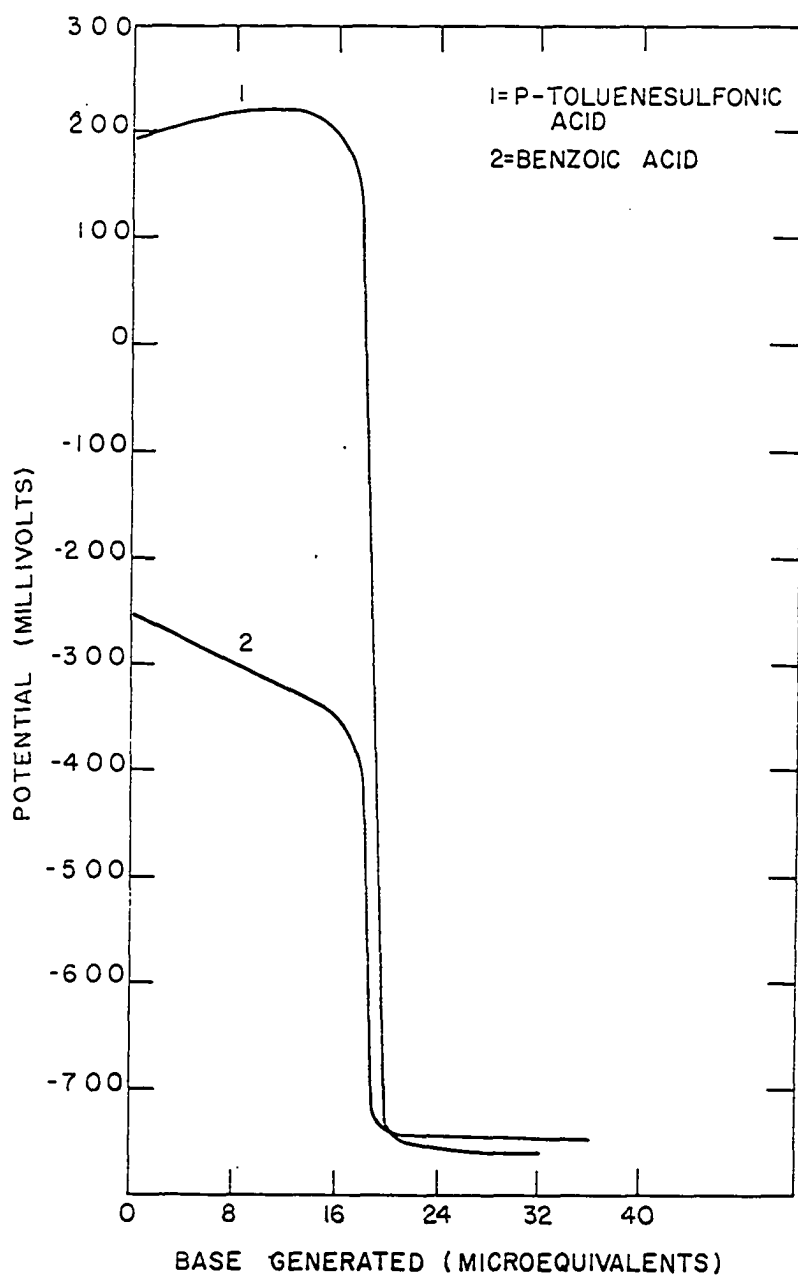


Figure 11. Titration of benzoic acid and p-toluenesulfonic acid in acetone with electrolytically generated titrant

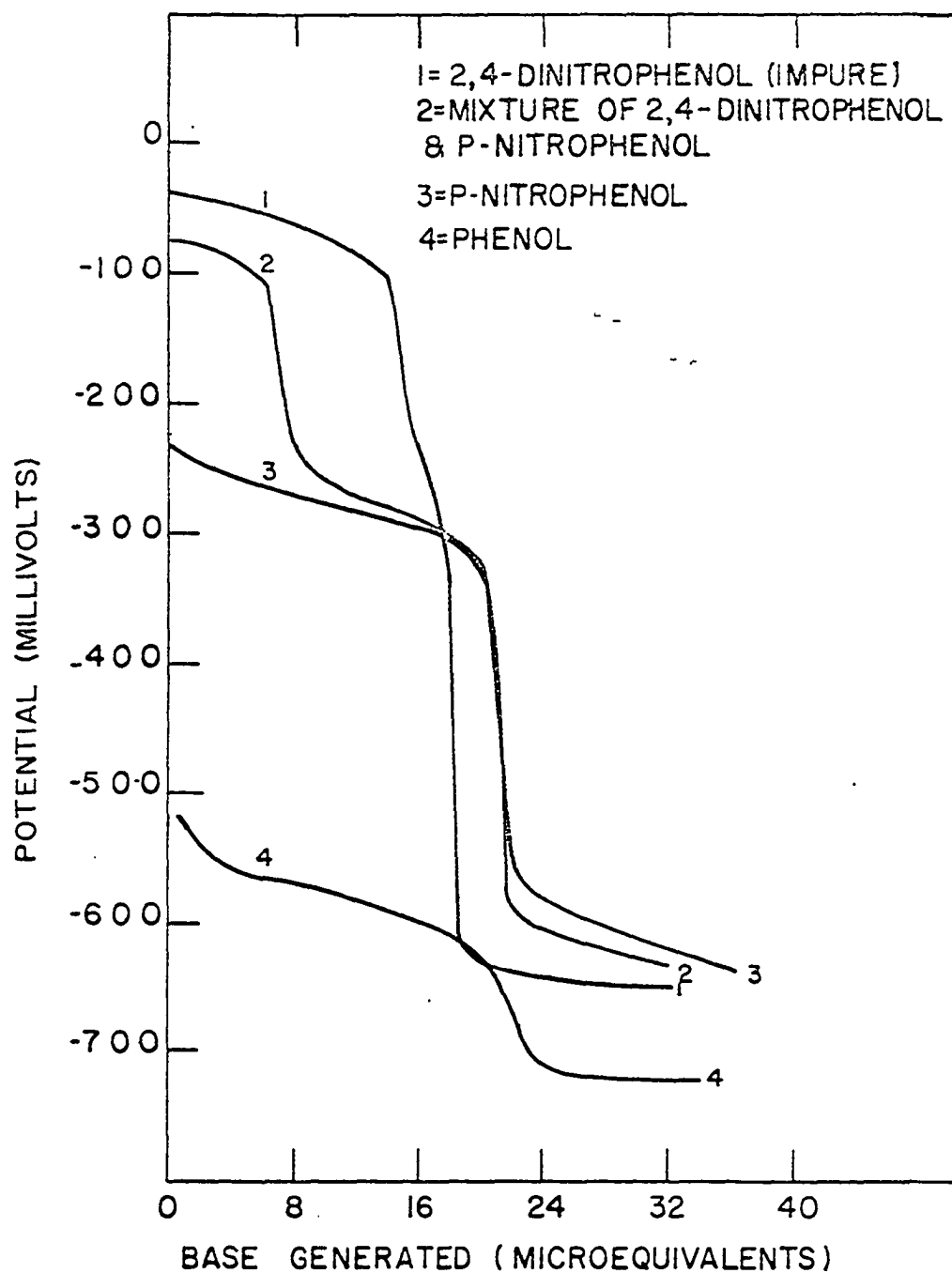


Figure 12. Titration of phenols in acetone with electrolytically generated titrant

The graphs in Figure 12 show the differentiating character of acetone as a solvent for coulometric titrations. The extra inflection in the curve for 2,4-dinitrophenol is due to the titration of an impurity. This impurity was p-nitrophenol as was borne out by the titration curves for pure p-nitrophenol and the prepared mixture of p-nitrophenol and impure 2,4-dinitrophenol. The second plateau in the curve for 2,4-dinitrophenol is not very distinct because the impurity was present only as a trace quantity. However, the differentiating titration curve for the mixture shows two well defined plateaus.

The titration of strong mineral acids in acetone was not attempted because experiences of past researchers (6,19) showed that there was a definite loss of stoichiometry when titrating such compounds. This loss in stoichiometry was apparently a result of reaction of the acetone solvent with the strong acids. Figures 13 and 14 show curves for the titration of enols and imides in acetone respectively.

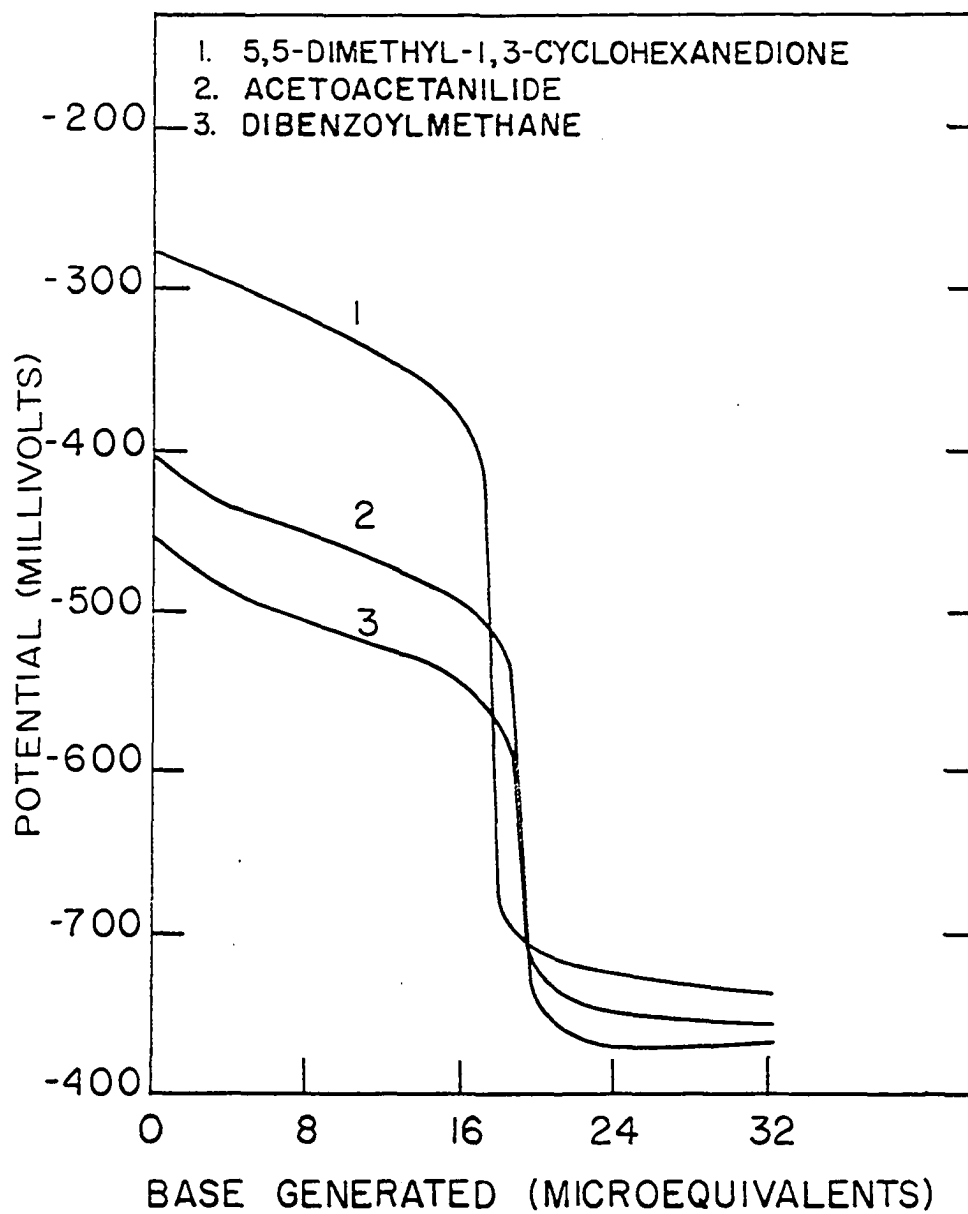


Figure 13. Titration of enols in acetone with electrolytically generated titrant

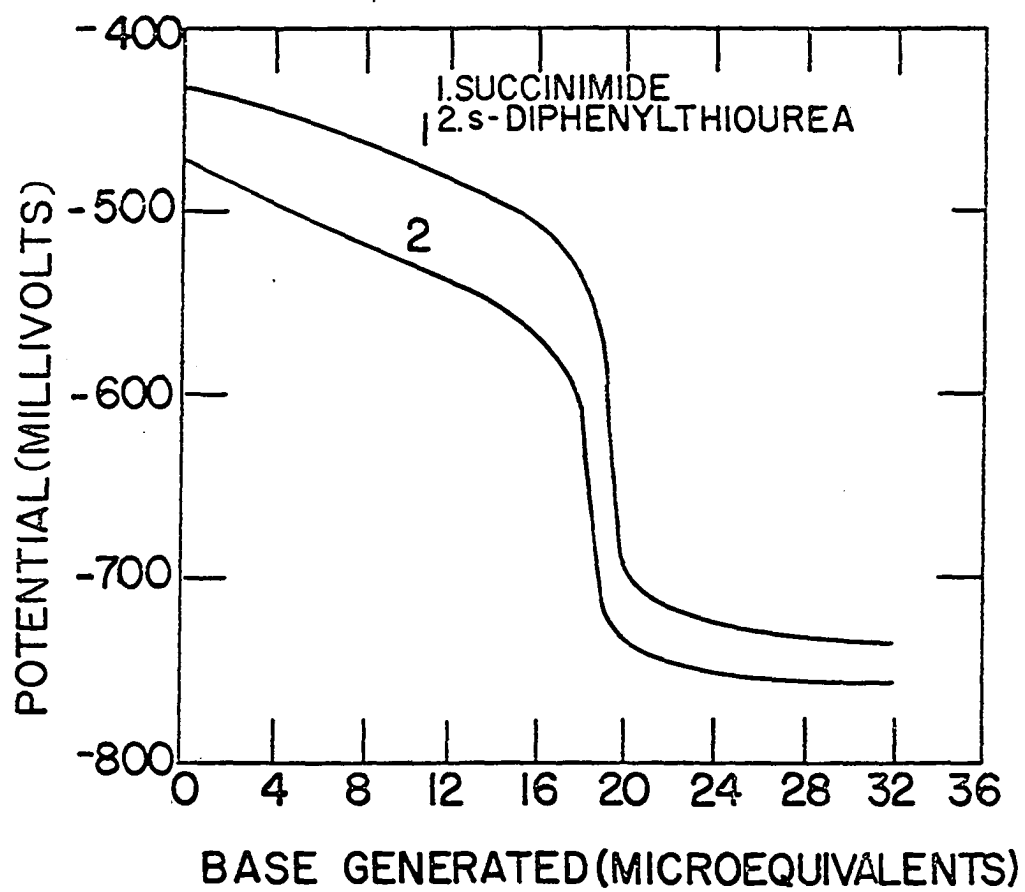


Figure 14. Titration of imides in acetone with electrolytically generated titrant

DISCUSSION OF RESULTS

General Considerations

A thin piece of transparent sheet plastic with a 1 cm^2 opening was used along with the ion exchange membranes that separated the anode and cathode compartments in the plexiglas cell used for indicator end points. This set-up was designed to reduce the membrane area exposed directly to the catholyte and thereby reduce the possibility of diffusion of generated hydroxide ions through the membrane. When highly dissociated acids were titrated some way had to be provided to impede the flow of cations, particularly hydrogen ions, through the ion exchange membrane. Even though the membranes were not 100% permselective, the reduced area plus the use of anion exchange membranes made cation flow through the membrane virtually impossible. Furthermore the use of the large bulky quaternary ammonium cation as electrolyte with a concentration greatly exceeding that of hydrogen ions also limited the passage of cations through the ion exchange membrane. Even though the sheet plastic may not have been absolutely necessary it served as an extra precautionary measure. Either the anion exchange membrane separator or the combination anion and cation exchange membrane separator was used in the plexiglas cell. Indicator end point results were excellent regardless of the separator used in the titration assembly. Ho and Marsh (24) used both anion and cation exchange membranes

together inside their electrode isolation cell so that the same cell could serve for the titration of both acids and bases.

The 0.1M supporting electrolyte concentration for the cathode compartment was chosen so that it greatly exceeded that of any acid concentration titrated. A 0.01M solution increased greatly the voltage across the generating electrodes but the current efficiency was not increased by the use of a 1.0M solution. Feldberg and Bricker (12) stated that the internal resistance drop across the generating electrodes must not be dependent upon the amount of material to be titrated. The relatively large supporting electrolyte concentration assured that the larger fraction of the current through the membranes was carried by the electrolyte rather than by the species generated or by the species titrated. It was important to maintain a constant generating current in order to have reasonable success with the coulometric titrations. A large generating electrode surface area and a relatively large electrolyte concentration were employed in this work to help achieve a high current efficiency. The large electrode area was also important to minimize electrode polarization.

The purification of the tertiary butyl alcohol solvent by fractional distillation probably reduced the water content below the 0.15% level but this reduction had no significant effect on the percent recovery of acids titrated. Preliminary

titrations of p-toluenesulfonic acid in tertiary butanol that had been distilled 3 times from sodium metal gave indicator end point results that were no different than similar titrations in undistilled tertiary butanol. The three distillations from sodium resulted in a solvent with 0.04% water. A polarographic grade tetrabutylammonium bromide is recommended preferable to a nonpolarographic grade. A spectrographic grade acetone was used because the solvent blank was reduced by more than one-half when compared to the blank of reagent grade acetone.

A separate blank value was determined for each test solution but this could be avoided if the volume and quality of electrolyte solution as well as the extent of deaeration with nitrogen were kept constant. A small current setting was used for titrations of blanks to potentiometric end points because this made it easier to get complete and meaningful blank titration curves owing to the small size of the blanks. The current setting was not so important for blank titrations to indicator end points. The important things were that the same setting be used for the blank as for the sample and that the rate of stirring be the same for both titration of the blank and titration of the sample. A fairly rapid rate of stirring was used for indicator end points to prevent any local build-up of base. Indicator reactions had to be rapid so indicators were selected on the basis of the sharpness of

their color changes. More than one indicator was usable in some cases but the sharpness of the color change increased the accuracy of titrations.

The potentiometric end point detection method is desirable when colored compounds like 2,4-dinitrophenol are titrated or when the indicator of choice is electroreducible at the platinum cathode. The potentiometric method is also valuable in cases when the indicator molecules may adhere to the membrane surface by reason of exchange or adsorption. The latter problem did not arise because the indicator concentrations were not high. The indicator method is superior when time required for titrations is at a minimum. Because of the relatively short time required for an indicator end point this method of detection is suitable when routine analyses are required. A third advantage of the indicator method is that it can be adapted to spectrophotometric detection of the end point.

The concentration range that was studied encompassed about 50 microequivalents with 10 microequivalents being the lower limit and 60 microequivalents being the upper limit. Since the coulometric method is well suited for micro quantities this range was ideal. Other factors also contributed to the choosing of this range. There was a loss in precision and accuracy when samples smaller than 10 microequivalents were titrated under the usual conditions. When quantities larger than 60 microequivalents were titrated under the usual

conditions there was a large increase in time required for titrations and there was a greater chance for interdiffusion and side reactions to occur.

The coulometric technique as described in this writing was used for miscellaneous purposes. It was used as a method of standardization of acids. The normal value of a hydrochloric acid solution as determined by the coulometric technique compared favorably with the conventional volumetric method. The coulometric technique was used also for the determination of the approximate degree of purity of organic compounds. The degree of purity of oleic acid was determined as well as the approximate degree of purity of an iminodi-acetic acid derivative that was prepared in the laboratory.

The success of this work now makes it possible to utilize the combined wealth of knowledge of nonaqueous acid-base titrations and coulometric analyses to their fullest capacity.

Variations in Titration Assemblies

A titration assembly may be considered to consist of both the titration cell and the generating and measuring electrode systems. Although the assemblies described for use with tertiary butyl alcohol were very useful and met the minimum requirements, a need was seen for the development of a more versatile system or systems. In order to meet this need efforts were made to create simple flexible assemblies that could be interchanged and would be available to most any

researcher.

One desirable feature of the assemblies used is that titrations in tertiary butanol with indicator end points can be performed, if necessary, in the cell designed for potentiometric end points as well as in the plexiglas box. However, the large size of the platinum generating electrode used in the cathode compartment for potentiometric end points makes it difficult to have continuous effective stirring and the platinum color makes a poor background for detecting indicator color changes. For these reasons it is more advantageous to use the plexiglas box for continuous titrations in tertiary butanol with indicator end points.

The plexiglas tubing used as anode compartment in the assembly for potentiometric end points is attacked by methanol. The effect of the methanol is cracking of the tubing walls with eventual leakage of anolyte. The compartment must then be discarded and another one prepared. This is problematic and time consuming and does not avail the assembly to numerous routine titrations in tertiary butanol. Glass was not selected as the material for the anode compartment because it was difficult to affix the membrane permanently to the end of glass tubing, even with roughened edges. Ultrafine glass frits were eliminated originally because of their high electrical resistance in tertiary butanol solvent. The problem now was to find suitable material and design an anode compartment that would be resistant to attack by methanol and

other organic solvents. Kel-F was chosen as the resistant material and the anode compartment was machined from solid Kel-F rod. The final product was a piece of hollow Kel-F tubing, threaded on one end, and approximately the same dimensions as the plexiglas tubing. This tubing was fitted with a Kel-F screw cap having a hole in its top. A 12 cm. disc of anion exchange membrane was placed inside the top of the screw cap to cover the hole and the union of the screw cap containing the membrane disc with the threaded tubing comprised the complete anode compartment. The screw cap had to be slightly larger in diameter than the tubing in order to attain rigidity and the hole in the cap was cut in such a way that the membrane surface was always flush with the top of the cap. Results obtained with the Kel-F anode compartment were good. Any problems associated with the use of an adhesive to affix the ion exchange membrane to the plexiglas tubing were eliminated. Thus an anode compartment was created that would be usable in any solvent that did not attack the ion exchange membrane.

The titration cell described by Marple and Fritz (31) is excellent for research requiring constant, accurate, and reproducible potentials but the design may be too sophisticated for occasional use. For titrations requiring only end point results with no regard to potentials the simple glass-calomel measuring electrode system used by Pritchett (36) is recommended. The coulometric titration of acetoacetanilide

and benzoic acid in tertiary butyl alcohol verified that good titration curves could be obtained by using this simplified electrode system. The titration curves for generated base and perchloric acid in Figure 4 and Figure 6 respectively provide additional proof of the usefulness of the simple glass-calomel system. With a small combination glass-calomel electrode it is possible to titrate acids in tertiary butyl alcohol to potentiometric end points in two additional assemblies, the plexiglas box and the cylindrical glass cathode compartment used for titrations in acetone. The Kel-F anode compartment works well in the cylindrical glass cathode compartment and, if necessary, a tall form 30 ml. beaker may be used as cathode compartment.

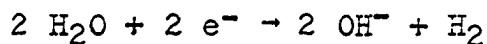
The rectangular plexiglas cell has the disadvantage that its use is limited to a very few solvents. The methanol solvent used in the anode compartment does not attack the 1/4 inch walls of the plexiglas cell very readily but solvents like benzene, acetone, and pyridine dissolve the plexiglas in less time than is required to titrate a 20 microequivalent acid sample. In order to make the rectangular cell design adaptable to more solvents a more resistant material has to be used. Glass was selected as the resistant material and a rectangular cell similar to the plexiglas cell was made from two square Barnes dropping bottles. The top and one side was cut from each bottle to form 1/2 of the cell. The two halves

were then assembled to form the titration cell with an anion exchange membrane to separate the anode and cathode compartments. Thicker cell walls were desired but the 2 mm. walls provided by the Barnes dropping bottles were strong enough to withstand pressure exerted by the wing nuts to hold the membrane intact and to form a leak proof cell.

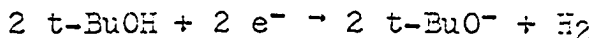
Possible Secondary Electrode Reactions

In many cases, the reverse of the desired reaction occurs at the second electrode, or the product of the reaction at this electrode may interfere with the reaction of primary interest. In such instances it is only necessary to isolate the second electrode in a separate compartment. In other cases side reactions (reactions other than the primary reaction) may occur at the electrode of interest. These side reaction products may or may not be of the same type as the desired product of the primary reaction. In any event, side reactions do alter the composition of the solution in which reactions of interest are taking place and they can cause error.

There are two possible cathode reactions when tertiary butyl alcohol is used for titrations in the cathode compartment. One is the reduction of water to give hydroxide ions.

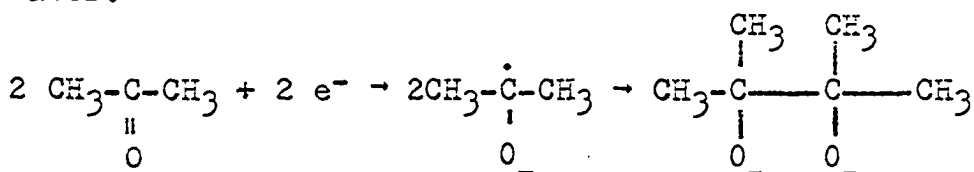


The other is the reduction of tertiary butyl alcohol to give tertiary butoxide ions.

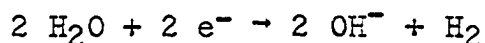


The basic species generated at the cathode may be hydroxide ions, tertiary butoxide ions or a mixture of the two depending on the water content of the alcohol.

The number of possible electrode reactions and subsequent reactions in the cathode compartment is increased when acetone solvent is used for titrations. The formation of the dianion of pinacol via transitory ketyls of acetone is a possibility if the acetone solvent contains little or no water.



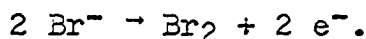
If the acetone solvent contains a sufficient amount of water the water may be reduced to form hydroxide ions.



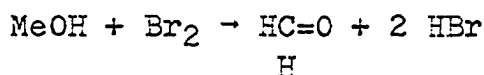
It is difficult to observe the evolution of hydrogen gas at the cathode when a large 19.3 cm² platinum sheet is used. However, when a smaller platinum cathode (4 cm²) is used hydrogen gas readily evolves from the electrode surface. This may be explained partly by the fact that the hydrogen produced can reduce acetone directly to isopropyl alcohol or pinacol and not be seen in the gaseous form. The reduction of ketones to secondary alcohols may be brought about catalytically with hydrogen and a platinum catalyst (35, p. 198). The large surface of the 19.3 cm² platinum sheet probably makes

it a more effective catalyst than the small 4 cm² sheet, thus less hydrogen is observed at the large electrode. A further minor reaction is possibly the direct electrolytic reduction of acetone to isopropyl alcohol and pinacol, according to White (48), but he concludes that this will result in a complete loss of current as regards alkali formation.

The primary reaction at the platinum anode is the oxidation of bromide ions to bromine by the reaction



The methyl alcohol medium in the anode compartment gives rise to another possible reaction.



The reaction of methyl alcohol with bromine is a very slow reaction and probably takes place only to a negligible extent. That is, the reaction is not so extensive that its products interfere with the overall primary anode reaction or with the role of the ion exchange membranes in the coulometric process.

Role of Ion Exchange Membranes in Coulometry

General considerations

Feldberg and Bricker (12) and Hanselman and Rogers (21) provided excellent discussions on the use of ion exchange membranes in coulometry. The main role of the ion exchange membrane in this study was that of separator in the electrolysis cell. In other words the membrane was used as a selec-

tive bridge to prevent contamination of the titrated solution in the cathode compartment by products of the anode reaction.

Separation of the anodic and cathodic reaction products is particularly difficult when working with highly mobile hydronium or hydroxyl ions in the coulometric titration of acids or bases. The properties of the membranes make them superior separators when compared to other more conventional separators such as sintered-glass discs or agar gel salt bridges. The membranes are nearly 100% permselective. That is, they possess the ability to allow passage of ions of similar charge while excluding ions of opposite charge. This characteristic is an advantage whether acids or bases are being titrated. The membranes offer low resistance to the passage of electrical current while impeding the flow of solvent between compartments. The low dielectric constant of tertiary butyl alcohol demands that the separator possess low electrical resistance. The membranes possess high burst strength and are of rugged construction. These qualities impede attack of the membranes by oxidizing agents, strong bases, and gases.

The same membrane pieces were used repeatedly without noticeable breakdown in structure, testifying to their physical stability. Actually, the same membranes will last for long periods of time provided they are stored in distilled water when not in use. Upon drying, the membrane volume

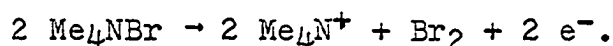
shrinks and cracking can occur. When stored in water the membranes are always ready for immediate use by merely drying the excess moisture off the membrane surface. When a large number of consecutive titrations were performed there seemed to be a noticeable change in efficiency with time. This change in efficiency apparently resulted from dehydration of the membrane surfaces by the organic solvents on both sides of the membrane. The effect of dehydration was even more apparent in acetone solvent, and this precluded the use of ion exchange membranes for titrations in acetone. The membranes were wetted intermittently during a series of successive titrations, and this action seemed to help maintain a high level of efficiency.

Conceivably an anion or cation exchange membrane may be used in the titration of either an acid or base but the extent to which this is true probably depends on the nature of the system being studied and the degree of efficiency desired. For instance, Feldberg and Bricker (12) were unsuccessful in titrating acids using anion exchange membranes. Their failure was reportedly a result of protonation of tertiary amine groups on the membranes by the acid, and recovery was always low. In this work better results were obtained when an anion exchange membrane separator was used rather than a cation exchange membrane separator. High results generally were obtained for most acids when the cation

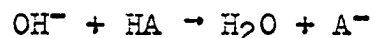
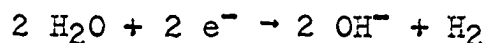
exchange membrane was used as separator. Good results were obtained when both anion and cation exchange membranes were used together as a separator in the electrolysis cell. However, the acid had to be titrated in the compartment of the cell which faced the anion exchange membrane in order to obtain good results consistently. The acid recovery was again high if the cathode compartment were adjacent to the cation exchange membrane. Explanations for this membrane activity as applied to the tertiary butyl alcohol system employed in this study are presented below.

Cation exchange membrane separator

The problem to be resolved is how will current be passed through the membrane while maintaining electrical neutrality in both compartments. The pertinent reaction in the anode compartment is



Pertinent cathode compartment reactions are



where HA is any acid being titrated. Note that the formation of free bromine in the anode compartment takes bromide ions out of solution and leaves the anolyte electrically unbalanced or rich in Me_4N^+ ions. On the other hand the reactions in the cathode compartment leave the catholyte rich in A^- and Br^- . One way to maintain or restore electrical neutrality is

to allow Me_4N^+ ions to transfer across the membrane from the anode compartment to the cathode compartment. Another way to restore neutrality is to allow A^- and/or Br^- to transfer across the membrane from the cathode compartment to the anode compartment. However, the excess supporting electrolyte insures that Br^- transfers in preference to A^- or OH^- if no acid, HA , is present to use the base as rapidly as it is generated.

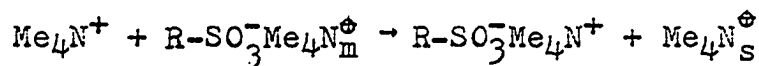
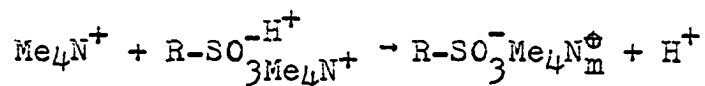
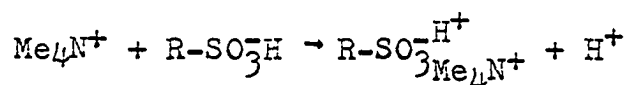
Considering the fact that a catex membrane separator is being used there is high resistance to the transfer of Br^- across the membrane and neutrality would be restored mainly by the transfer of Me_4N^+ . It may be assumed also that the bulk of the current is carried across the membrane by the transfer of the tetramethylammonium cation from the anode compartment to the cathode compartment because ions must carry the current. If the Me_4N^+ ion transfers across the membrane this cation should be detectable in both compartments and all of the H^+ ions on the membrane should be replaced eventually by Me_4N^+ ions if the electrolysis proceeds long enough. Indeed this is the case as determined experimentally.

A plexiglas cell was used in the experiment under conditions similar to those employed for coulometric acid titrations in tertiary butyl alcohol. The diagram below shows that the major difference was that isopropyl alcohol was used as solvent in the cathode compartment and no acid sample was added.

<u>anode compartment</u>		<u>cathode compartment</u>
75 ml. 0.1 M Me ₄ NBr in MeOH Pt anode	catex membrane	100 ml. 0.1 M Bu ₄ NBr in i-PrOH Pt cathode

It is significant that Me₄N⁺ is insoluble in isopropanol. Electrolysis was allowed to proceed for 2 3/4 hours at 0.02 current setting with the entire cell immersed in an ice bath. A white precipitate was observed to form in the cathode compartment during electrolysis and persisted until the coulometric current source was turned off. The white precipitate was examined and considering the make-up of the entire system the conclusion was that the precipitate was tetramethylammonium bromide which is insoluble in isopropyl alcohol.

For further clarity the membrane may be represented as R-SO₃⁻H⁺ where R is the portion of the membrane comprising copolymers of vinyl compounds. The reaction sequence



is an attempt to show what probably happens between the catex membrane and Me₄N⁺. The subscripts m and s refer to membrane and solution respectively and are to indicate that the Me₄N⁺

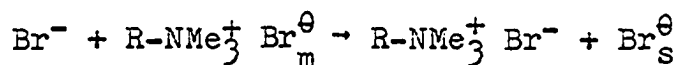
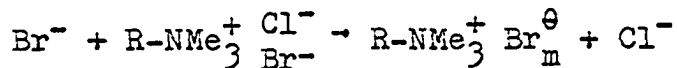
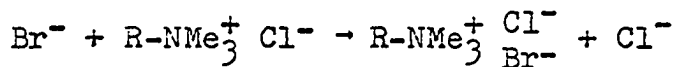
ions that are attached to the resin may later be found in solution in the cathode compartment.

The above reaction sequence is not intended to conclude that no Me_4N^+ cation originating in the anode compartment could find its way to the cathode compartment without first being stopped by and attached to a SO_3^- site in the membrane. However, certain other factors do preclude the direct transfer of Me_4N^+ from the anode compartment to the cathode compartment. The first of these factors stems from Rechnitz's studies on glass electrode response (37). The movement of the cation completely through the membrane probably would be too slow to maintain the required rate of current flow. The second factor is related to the first but stems from steric and size effects. Aside from the naturally slow movement through the membrane the bulky size of the Me_4N^+ ion and small pores of the exchange membrane would tend to prevent or impede direct transfer of the ion through the membrane. The last factor stems from experimental results but is again related to the first two. The high acid recovery or low current efficiency experienced when the cation exchange membrane was used to separate the compartments of the electrolysis cell may well be explained on the basis of poor transfer of cations through the membrane. It has not been explained in any other way. Even if the ion exchange mechanism prevailed the steric and size effects would impede the exchange process.

Anion exchange membrane separator

The reactions in the anode and cathode compartments are the same during electrolysis with an anex membrane separator as when a catex membrane separator is used. The same reasoning applies to the maintaining of current flow and electrical neutrality but it must be concluded that Br^- is responsible for this action. Rapid stirring of the catholyte during a titration was important to prevent the possibility of any local build-up of hydroxyl ions and their subsequent transfer across the anion exchange membrane. The fact that an anion exchange membrane is used as separator along with other considerations precludes the use of Me_4N^+ as current carrier or electrical neutralizer.

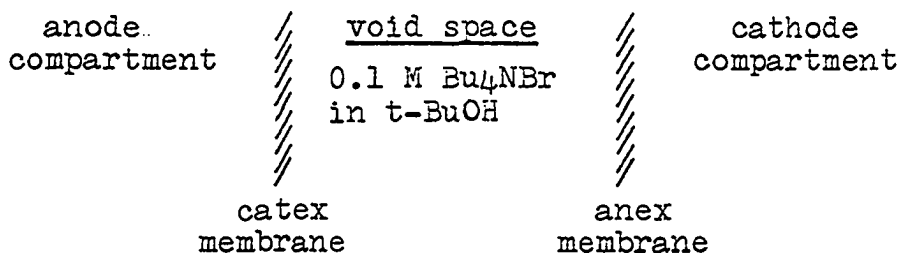
The anex membrane may be represented as $\text{R-NMe}_3^+\text{Cl}^-$ where R is the portion of the membrane comprising copolymers of vinyl compounds and Me is methyl. The following reaction sequence is only an attempt to show what probably happens between the anex membrane and Br^- assuming that movement of the anion completely through the membrane is too slow to maintain the necessary rate of current flow.



The bromide ion is relatively mobile and this could account for the good recovery when an anex membrane serves as separator of the electrolysis cell. The anex membranes also contain some tertiary amine groups. Even if H^+ protonates the tertiary amine groups low results should not be obtained permanently as suggested by Feldberg and Bricker (12). After several titrations all amine groups should be protonated, thus allowing all additional acid samples placed in the titration cell to be recovered. The good results obtained after using the same anex membrane continuously supported this opinion.

Combination anex and catex membrane separator

When anion exchange and cation exchange membranes are used jointly as separator each membrane functions as if it were used singly, only the total resistance is increased. The major difference in the titration cell is the void space that exists between the two membranes.



The void space between the membranes has to be filled with electrolyte solution in order to assure a high current efficiency. To maintain electrical neutrality in the anode compartment after loss of Br^- , the Me_4N^+ ion is transferred across the catex membrane into the void space. Likewise Br^-

transfers across the anion membrane from the cathode compartment to maintain electrical neutrality in that compartment. In effect tetramethylammonium bromide is formed in the void space. This idea is supported by the fact that a slight cloudiness appears in the tertiary butyl alcohol solution in the void space after using the cell for extended periods of time without changing the solution in the void space. Tetramethylammonium bromide is relatively insoluble in tertiary butyl alcohol.

Effect of Water on Titrations in Acetone

Experiments were conducted in this research to show graphically the effects of water on titrations in acetone. Conditions and procedures for titrating the benzoic acid samples were the same as the general procedures described earlier in this writing except that a known amount of water was added to each electrolyte test solution before titration of the acid sample. Approximately 20 microequivalents of benzoic acid were used as the acid samples for this study.

Figure 15 shows the outcome of the coulometric titrations of benzoic acid samples in acetone with varying water content. The overall effect of water was in accord with expectations. The potentials increased to more positive values with increasing water concentration. In effect the whole curve was shifted upward on the millivolt scale but there was no noticeable shifting along the microequivalent

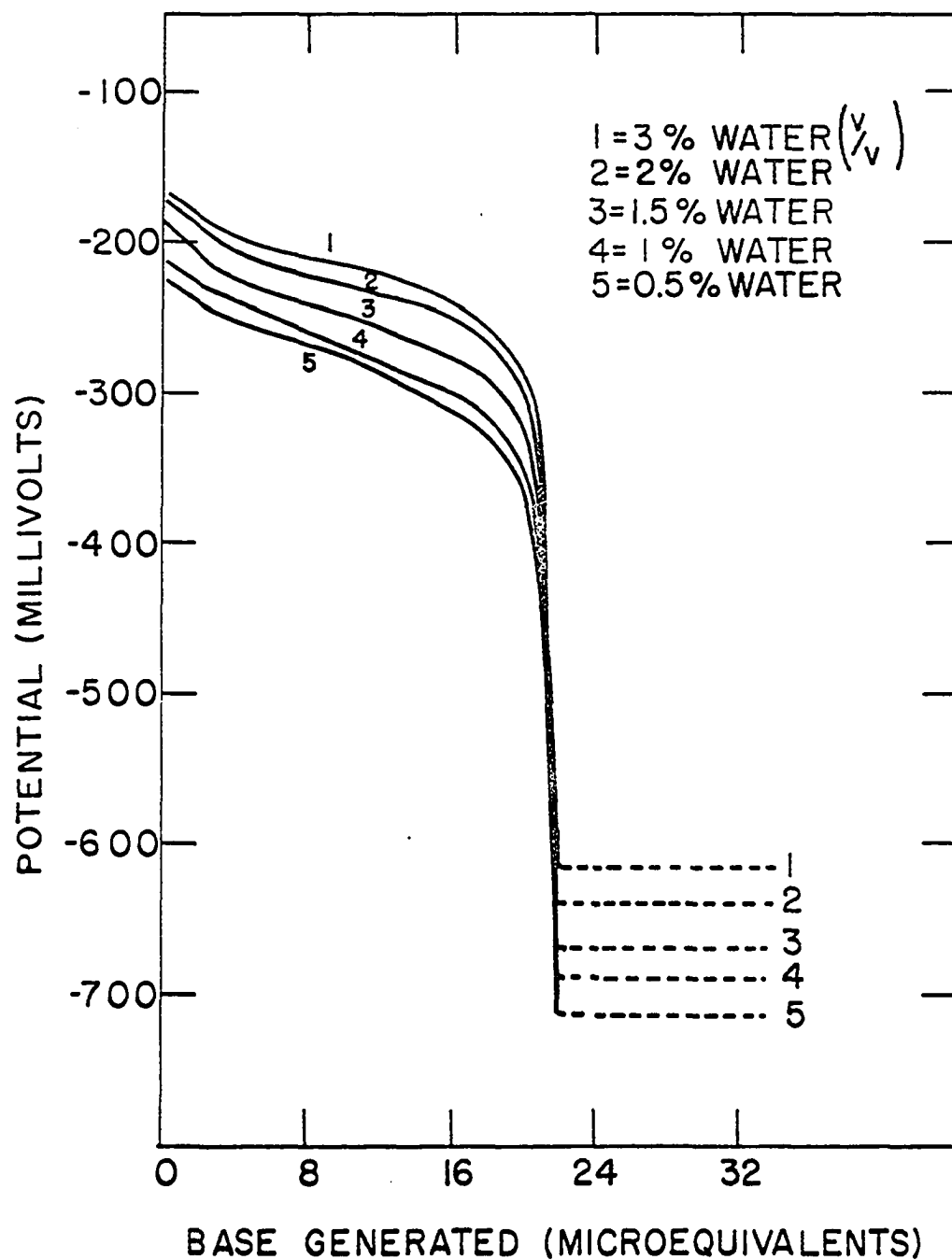


Figure 15. Effect of water on potentials during titrations in acetone solvent

scale. It was observed that there was very little, if any, shift in potentials at the same point of titration until the water content exceeded 0.8%. Theoretically it was concluded that the effect of water, within the concentration range of 0.35 to 0.8%, on the coulometric titration of weak acids in acetone is negligible. However, the shift in potentials with a water concentration greater than 0.8% was noticeable to a greater extent. It was concluded with certainty that very weak acids cannot be titrated with accuracy in acetone containing high concentrations of water.

The added water in the acetone seemed to stabilize potentials until the end point was reached. Afterwards there was increased potential drift with increasing water content. The sharpness of end points was not affected significantly by the added water but this effect probably would be more noticeable if very weak acids were titrated. The lower plateaus on the titration curves in Figure 15 were exaggerated in order to show clearly the difference in potential readings after adding the same amount of base (22 microequivalents) to each test solution.

Suggestions for Future Work

The value of having a fairly large concentration of supporting electrolyte in the cathode compartment has been discussed. Any catholyte concentration ranging from 0.1 to 1.0 M would be sufficient for titrations under the conditions

described in this writing but an intermediate concentration is recommended, particularly when the assembly for potentiometric end points is employed. This would decrease the voltage across the generating electrodes and help to stabilize the current.

Although depletion of ions at the generating electrodes was no problem in this investigation, its effects will become increasingly more noticeable as attempts are made to titrate large amounts of acids. The effects of polarization can be decreased by stirring the solutions and by increasing the electrolyte concentrations. Polarization is more likely to occur at the anode than at the cathode and more likely in the potentiometric end point assembly than in the indicator end point assembly. Constant mechanical stirring of the anolyte would be problematic but agitation of the anolyte with the platinum anode after taking several potential readings would be possible. This agitation along with a 2 or 3 fold increase in anolyte concentration should be sufficient to eliminate any effects of polarization that may arise. Actually agitation of the anolyte can be achieved best by bubbling nitrogen through the solution. A U-tube would suffice to take nitrogen from the same source to agitate the anolyte and deaerate the cathode compartment.

Some method of further purification of the spectrographic grade acetone would reduce the solvent blank considerably, if

desirable. Reduction in the water content of the acetone would be recommended if extensive titrations are to be performed in this solvent. The common drying agents may be used to dry the acetone but White (48) recommended Dow desiccant 812 as a great improvement over Drierite or molecular sieves. The new Dow desiccant, an ion exchange resin in the potassium form, is very clean, effective, and readily regenerated.

Some effort was made to titrate large quantities of acids in this research but many of the details were not worked out completely. This possibly could be accomplished with modifications in the present technique. One suggestion would be to use a different ion exchange membrane to separate the compartments. A membrane having lower electrical resistance is recommended owing to the increased electrical requirements of the higher current settings used to titrate milliequivalent amounts. Further, the concentration of both anolyte and catholyte should be increased. Water should be used as solvent in the anode compartment to lessen the changes of dehydration of the membrane when electrolysis proceeds for extended periods of time.

Solvent systems other than tertiary butyl alcohol and acetone were investigated only to a small extent. Preliminary studies showed that dimethylsulfoxide and mixed dimethylsulfoxide-tertiary butyl alcohol solvents required further study before their merits as solvents for coulometric titra-

tions of acids could be established. It was observed that the ion exchange membranes were attacked readily by the dimethylsulfoxide. It was possible to generate base in pyridine in a glass cell and observe an indicator color change but no quantitative determinations were attempted.

Research efforts to generate titrant in solution while simultaneously recording changes in potentials met with only limited success. There were some indications that continuous recordings could be made but the potential breaks at end points were not sharp enough to classify the graphs as good potentiometric titration curves. A Heath pH Recording Electrometer was used in the study. The large induction effects resulting from the electric field were picked up by the glass indicating electrode and overshadowed any minute change in potential resulting from addition of basic titrant to the test solution by the coulometric process. In order to achieve this goal a different generating electrode design along with grounding of the glass electrode may well be worth the effort. An alternative project would be to use a battery powered current source to generate titrant at a slow rate. This would minimize induction effects owing to the lower electric field.

The coulometric preparation of a basic titrant for use in conventional volumetric methods was investigated. This showed some promise of success but also required additional

detailed study. For future work it is recommended that a polarographic grade tetrabutylammonium bromide be used as electrolyte and that all solvents be purified. Tetraethylammonium bromide is obtainable in a polarographic grade and may be used as a substitute for the butyl salt. The ethyl salt has the disadvantage of being relatively insoluble. It was found to be soluble in water, methanol, and isopropanol but was only slightly soluble in acetone and tertiary butyl alcohol, two important solvents for acid titrations. The use of a portable plastic dry box for preparation of the base is recommended in order to reduce the level of carbon dioxide surrounding the electrolysis cell.

SUMMARY

The weaknesses and limitations of previous research on coulometric titrations in nonaqueous systems were discussed. Titration assemblies and procedures were designed for the coulometric titration of acids in tertiary butyl alcohol and acetone solvents. Both visual indicator and potentiometric end point detection methods were employed in tertiary butanol, but only potentiometric end points were employed in acetone solvent. Titrations of mineral acids, carboxylic acids, dicarboxylic acids, enols, imides, phenols, and sulfonic acids were successfully performed by electrolytic generation of a basic titrant at a platinum cathode. Sample sizes ranged from approximately 10 to 60 microequivalents and the acid titrations gave excellent titration curves as well as excellent recovery. Variations in titration assemblies were proposed and the effect of water on titrations in acetone was investigated.

The quality of the basic titrant was questioned and subsequent research led to a high quality titrant. A review of possible reactions involved in the titration process resulted in the conclusion that the hydroxide ion was the species generated at the cathode and, in effect, tetrabutylammonium hydroxide was the basic titrant.

Both anion and cation exchange membranes were employed in this investigation to separate the anode and cathode com-

partments of the electrolytic cells. Some experimental results verified the theories that were proposed for the role of the ion exchange membranes in the coulometric process.

In general, any acid or acidic compound of the types mentioned may be titrated successfully by one of the proposed schemes provided it is soluble in the solvent of choice and is not electroreducible at a platinum cathode.

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