

ACID-BASE TITRATIONS OF AROMATIC SULFINIC ACIDS  
IN NONAQUEOUS SOLVENTS

by

DAVID LOUIS WETZEL

A. B., Augustana College, 1956

---

A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

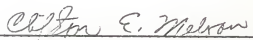
MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE UNIVERSITY  
Manhattan, Kansas

1963

Approved by:

  
\_\_\_\_\_  
Major Professor

LD  
2668  
T4  
1963  
W54  
C. 2  
Document

11.

# TABLE OF CONTENTS

INTRODUCTION. . . . .	1
LITERATURE REVIEW . . . . .	1
The Nature of Sulfinic Acids . . . . .	1
Analytical Methods . . . . .	3
Nonaqueous Analytical Acid-Base Systems. . . . .	6
EXPERIMENTAL. . . . .	7
Apparatus. . . . .	7
Chemicals. . . . .	8
General Titration Procedure. . . . .	11
Preparation of Titrant Solutions . . . . .	12
Preparation and Purification of Sulfinic Acids and Their Salts. . . . .	13
RESULTS AND DISCUSSION. . . . .	17
Effect of Titrant Variation. . . . .	17
Effect of Solvent Variation. . . . .	24
Separation of Sulfinic-Sulfonic Acid Mixtures. . . . .	29
Solvent Survey . . . . .	29
CONCLUSIONS . . . . .	37
ACKNOWLEDGMENT. . . . .	39
LITERATURE CITED. . . . .	40

## INTRODUCTION

In the analytical chemistry of sulfinic acids the general application of neutralization titrations as a method of functional group analysis has been disappointing. This has been attributed to the lack of specificity for the sulfinic acid group, and the generally low solubility of these compounds in water.

The purpose of the present investigation has been to find a system in which neutralization reactions could be studied quantitatively without solubility problems or interferences from other acidic groups, and if possible to establish a general method for the determination of sulfinic acids. The need for separation of sulfinic-sulfonic acid mixtures appeared especially significant due to the presence of sulfonic acid as a contaminant of sulfinic acids. Existing analytical methods based on other reactions have limitations or inconveniences which detract from their general applicability.

## LITERATURE SURVEY

### The Nature of Sulfinic Acids

Sulfinic acids are notorious for their instability and the ease with which they undergo autoxidation. The corresponding sulfonic acid which is a final product of both the decomposition and autoxidation processes as noted below is a potential source of interference in the quantitative study of the acidic properties of sulfinic acids.



Complete decomposition of sulfinic acid samples stored under an inert atmosphere at room temperature has been noted in a matter of weeks. The corresponding thiosulfones have been isolated and identified as a major product of this process. Feigl (16) has noted a general order of increasing stability as follows: short chain aliphatic, long chain aliphatic, aromatic. Godfrey (19) has indicated that among aromatic sulfinic acids, the disulfinic acids, where the two groups are in contact with each other, appear to be especially unstable and nucleophilic substituent groups on the ring tend to affect stability and acidity adversely. The unique stability of 1,4-butanedisulfinic acid recently reported by Beachem and coworkers (3) is cited as an interesting contrast to the general trend.

These acids are usually isolated and stored in the form of their salts which are considerably more stable than the free acids. A similar stabilization is apparent in amphiprotic solvents of reasonably polar nature, for example, water or methanol. Godfrey (19) reported that an ether solution of benzenesulfinic acid exposed to the air showed only the  $-\text{SO}_3\text{H}$  functional group in the ultraviolet spectrum of a methanol solution. A similar sample was stored in methanol solution under inert atmosphere at  $40^\circ \text{C}$  for two months with no change.

Structural considerations take into account tautomeric forms of the  $-\text{SO}_2\text{H}$  group as discussed by Feigl (16). Infrared and ultraviolet spectral data obtained by Detoni and Hadzi (13,14) favored the structure (I) for



I



II

sulfinic acids, gave evidence for resonance  $\text{O S:O}^- \leftrightarrow \text{O:S O}^-$  of the ionized sulfinic group, and indicated the polymeric nature of the undissociated form.

Bredereck and coworkers (4) confirmed the existence of (I) in polar and non-polar solvents by ultraviolet spectroscopic analysis, however, the infrared spectra of solid acids and their carbon tetrachloride solutions showed absorption corresponding to S-H bonding as in (II). Dissociation of free sulfinic acid was evident in methanol and in water but this action was repressed in 0.5 N aqueous hydrochloric acid. Bredereck et al (5) also observed that in organic solvents of increasing basicity, sulfinic acid had correspondingly lower rates of decomposition.

#### Analytical Methods

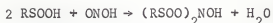
Methods of sulfinic acid analysis are summarized in the Treatises of Wilson and Wilson (41), Organic Analysis (13), and Kolthoff and Elving (25). In addition, the work of Ponzini (32) should be included.

Iron (III) Salt Methods. The amount of iron(III) consumed in the reaction with sulfinic acid to form a voluminous insoluble complex of the formula  $(\text{RSO})_3\text{Fe}$  is found by various standard iron determination procedures. Precipitated iron is weighed after ignition as iron(III) oxide or excess iron in the filtrate is titrated, for example with

standard potassium dichromate. The precipitation reaction was reported by Thomas (37). Details of analysis are given by Krishna and Singh (27).

The specificity of insoluble complex formation according to Feigl (16) is dependent upon direct connection of the  $-SO_2H$  group to an aromatic nucleus limiting the usefulness of this method to aromatic sulfinic acids. Quantitative separation is the primary problem encountered by the analyst using this method. Dal Nogare (13) has indicated that the precipitate dissolves in a large excess of iron(III) chloride, is difficult to handle because of its bulk, and tends to retain extraneous iron(III) ions.

Nitrite Titration Method. The method is based on the reaction reported by Koenigs (24).



An acid or salt sample is dissolved in water, cooled to  $0^\circ\text{C}$ , strongly acidified and titrated with 0.2 N sodium nitrite to a starch-iodide external indicator. No interferences were reported, however the slightest excess of nitrite irreversibly converted the solid hydroxylamine product to the corresponding amine oxide  $(\text{RSOO})_3\text{NO}$ . Ponzini (32) reported this method for aromatic acids and Marvel and Johnson (31) used it for aliphatic acids. The low temperature requirement, formation of a solid product, use of an external indicator, and oxidation of the product are probable weak points of this method.

Oxidation Methods. Sulfinic acid is oxidized to the corresponding sulfonic acid by various oxidizing agents. Allen (2) used permanganate for colorimetric and potentiometric titration of aliphatic sulfinates in

basic solution. The potentiometric results varied with ionic strength and some disulfone formation was noted. Slightly soluble salts were titrated just below the boiling point of the solution. Ackerman (1) used sodium hypochlorite to titrate samples at 15° C to an external starch-iodide end point. Prior separation of sulfite and sulfate was accomplished using barium chloride and standardization with sodium arsenite was required every two hours. In the manometric method of Krishna and Das (26)  $I_2$  was produced from a mixture of potassium iodate and sulfinic acid in potassium iodide. The iodine was used to liberate oxygen from alkaline hydrogen-peroxide which was then measured manometrically. The proper ratio of sample to reagents and extremely pure reagents were required.

Neutralization Titration Method. The strength of sulfinic acids can generally be described as being greater than the corresponding carboxylic acids and less than the corresponding sulfonic acids. Various sulfinic acids have been titrated with aqueous alkali to phenolphthalein and potentiometric end points. Sluggish end points and erratic results have been reported in some cases. The acidity of the sulfinic acids has not been extensively used for analytical purposes, due primarily to problems of solubility and lack of specificity due to interference by acid contamination or the presence of other acidic functional groups. Recent success of non-aqueous potentiometric methods in solving similar problems of solubility while differentiating between various acids in a mixture suggests a similar course might be appropriate for the establishment of a general method for the determination of the sulfinic acid functional group.

## Nonaqueous Analytical Acid-Base Systems

Only recently has the theory of acid-base equilibria in nonaqueous solvents been put on a quantitative basis. This is summarized by Bruckenstein (25), also in a more brief form by Laitinen (28). Unfortunately, however, very few constants have been established, particularly regarding titrations in basic solvents; therefore, one must resort to an empirical approach to the establishment of an analytical method.

Various systems involving different combinations of solvents, of titrant solutions, and electrodes or indicators have been used. These are summarized along with discussions of their applicabilities by Fritz (17), Wilson and Wilson (40), Bruckenstein (25), Riddick (33), and Streulia (36).

Of particular interest in the titration of mixtures of acids of varying strengths is the work of Cundiff and Markunas (7) who titrated acid mixtures potentiometrically in various solvents with a solution of tetrabutylammonium hydroxide in benzene-methanol using an improved calomel electrode and a glass electrode. Harlow and coworkers (22), as well as Fritz and Yanamura (18) used similar electrode systems and solvents but preferred to use quaternary ammonium bases in isopropyl alcohol solution as titrants. Continued investigations by Cundiff and Markunas (8,9,10,11,12) Harlow (20,21) and others (30,39) have resulted in refinement of the experimental procedures and further contributions to the knowledge of these systems.

From the review of existing sulfinic acid analytical methods it is



apparent that none of them could be considered ideal. The need for use of large samples, prior separations, extreme temperatures, highly unstable titrants or external indicators imposes serious limitations on the applicability of the method. A simple, direct titration at room temperature with freedom from interferences and elimination of solubility problems would appear preferable.

## EXPERIMENTAL

### Apparatus

All potentiometric measurements were made using a Leeds and Northrup 7401 pH indicator, equipped with a Leeds and Northrup glass electrode and a fiber-type Beckman No. 1170 calomel electrode in which the aqueous saturated potassium chloride solution was replaced with a solution of absolute methanol saturated with potassium chloride.

The literature accompanying this instrument indicates that the maximum limits of error are  $\pm 5$  millivolts in the 0 to 700 millivolts range and  $\pm 10$  millivolts in the 0 to 1400 millivolts range. Reproducibility of individual readings in these ranges are respectively 1.0 and 2.0 millivolts.

The titration cell consisted of a round polyethylene container with a polyethylene lid snapped on to provide a snug fit. The dimensions of the cell were very near that of an ordinary 150 ml beaker. Holes were bored in the lid for the electrodes, the buret, a nitrogen inlet tube and exhaust. The lid was mounted in place on the electrodes. A 10 ml class A microburet provided with a teflon stopcock was used which was calibrated

in 0.05 ml units.

The titrant reservoir consisted of a flexible polyethylene bottle connected to the buret with polyethylene tubing in such a way that the only air which entered either the buret or the reservoir passed through a succession of drying tubes containing indicating drierite, magnesium perchlorate, and Ascarite.

A Perkin-Elmer Infracord Model 137 equipped with sodium chloride optics was used to obtain infrared spectra.

A Beckman Model KF-3 aquameter was used for the Karl Fischer reagent titrations.

#### Chemicals

Pyridine. Baker purified pyridine was shaken with, and stored over absorbtion alumina (Fisher Scientific Co., No A-540) to remove any water and acidic impurities. In excess of 40 grams of alumina per liter of pyridine was used in this procedure as recommended by Gundiff and Markunas (7). Quantities no greater than 500 ml at a time were decanted from the alumina and filtered by gravity through a column of diatomaceous earth supported by 3 plugs of pyrex glass wool. Alternately suction filtration through a fine sintered glass funnel covered with a  $\frac{1}{2}$  inch layer of diatomaceous earth was also used. Dry nitrogen was bubbled through the purified pyridine which was protected from atmospheric carbon dioxide and moisture by Anhydrone and Ascarite. The pyridine thus prepared had an acidity blank of less than 0.05 ml of 0.1 M tetrabutylammonium hydroxide per 100 ml.

Benzene. Thiophene free benzene was dried over metallic sodium ribbon and distilled from a flask containing anhydrous phosphorus pentoxide.

Dry Methanol. Reagent grade methanol was dried by distillation with a 6 foot,  $\frac{3}{4}$  inch diameter, glass-bead packed fractionating column. The undistilled methanol had an average water content of 0.20% by weight and the average distillate had less than 0.01% water by weight as determined by Karl Fischer titration.

Water. Ion free water used for the preparation of silver oxide was prepared by running distilled water through a column of mixed-bed ion exchange resins, previously treated as described by Samuelson (34).

Tetrahydrofuran. Reagent grade tetrahydrofuran (Matheson) stabilized with 1% hydroquinone was distilled in an all glass column just prior to use.

Diethyl Ether. Anhydrous diethyl ether was dried over metallic sodium and distilled.

Dry Nitrogen. Commercial nitrogen was passed through two concentrated sulfuric acid scrubbing towers, a 10 inch tower of potassium hydroxide pellets, another 10 inch tower containing magnesium perchlorate and finally a 2 inch long plug of glass wool as a filter.

Dry Carbon Dioxide-Free Air. Air from a compressed air line was passed through a series of 10 inch columns containing calcium chloride, concentrated sulfuric acid and potassium hydroxide pellets and glass wool.

Chemicals Used Without Further Treatment. All chemicals listed here are reagent grade or the best grade available unless otherwise specified.

silver nitrate (Fisher)  
acetonitrile (Fisher)  
dimethylformamide (Fisher)  
ethylenediamine 95% (Eastman)  
1,4-dioxane (Eastman)  
n-butyl alcohol (Eastman)  
t-butyl alcohol, tech.  
nitrobenzene, tech. (Baker)  
chlorobenzene (Eastman)  
dimethylsulfoxide (Crown Zellerbach)  
cyclohexanone (Eastman)  
di-isobutylketone, tech.  
dimethylaniline, tech.  
n-hexylamine (Matheson)  
ethyl acetate, anhydrous (Baker)  
chloroform (Baker)  
p-toluenesulfonic acid, anhydrous (Matheson)  
benzenesulfonic acid  $1\frac{1}{2}$  H<sub>2</sub>O, practical (Eastman)  
benzoic acid (Fisher)  
tetra-n-butylammonium iodide (Eastman)  
tetramethylammonium bromide (Eastman)  
tetraethylammonium bromide (Eastman)  
cetyldimethylethylammonium bromide (Baker)  
trimethylbenzylammonium chloride (Commercial Solvents)  
trimethylphenylammonium iodide (Eastman)  
2,5-dimethylbenzenesulfonyl chloride (Eastman)  
p-nitrobenzenesulfonyl chloride (Matheson)  
benzenesulfonyl chloride (Eastman)  
p-toluenesulfonyl chloride (Eastman)  
n-nitrobenzenesulfonyl chloride (Eastman)  
alumina, adsorption 80-200 mesh (Fisher A-540)

## General Titration Procedure

A sample of appropriate size to require 5-10 ml of titrant was accurately weighed into a polyethylene container which served as a titration vessel. The container was immediately fitted into position and purged for 3-5 minutes with a stream of dry nitrogen. 50 ml of solvent were delivered to the vessel through an exhaust port in the lid. The magnetic stirrer was set in motion and the initial potential was recorded 4-6 minutes after the solvent was introduced. The titrant was added from a 10 ml microburet at a steady rate with readings taken at regular intervals of volume addition. In the vicinity of the equivalence potential, the addition increments were reduced to 0.05 ml and continued until a potential maximum was reached.

The glass electrode was treated after each determination by rinsing it with 3-6 ml hydrochloric acid and distilled water. It was then soaked for at least 2-3 minutes in distilled water. Just prior to each titration both electrodes were rinsed thoroughly with dry methanol. The methanol was evaporated in the stream of nitrogen prior to the addition of the titration solvent. The polyethylene titration vessels were emptied immediately after use and rinsed twice with methanol. Prior to use they were rinsed with dry acetone. Pipets used were also rinsed with methanol and acetone and dried with a stream of dry, carbon dioxide free air.

Improved stirring action was obtained using a thin stirring bar which was just slightly shorter than the diameter of the bottom of the flask. The electrode rinsing was found to be a necessary procedure since progressively smaller titration breaks were noted during a series of identical

titrations when no rinsing was done.

The polyethylene containers were preferred as titration flasks because they showed little tendency to pick up moisture and were convenient for direct introduction of solid samples. A borosilicate glass beaker was substituted when materials of unknown solvent properties were titrated.

#### Preparation of Titrant Solutions

Tetrabutylammonium hydroxide-methoxide titrant was prepared by the improved method described by Cundiff and Markunas (12) with the addition of a final treatment with activated charcoal as suggested by Marple and Fritz (30) for removal of complexed silver. 30 grams of reagent grade  $\text{AgNO}_3$  were dissolved in 5 ml of carbonate-free water. 55 ml of 4 N carbonate-free NaOH were added and then shaken vigorously. It was then filtered under a nitrogen atmosphere through a medium porosity sintered-glass funnel. The precipitated silver oxide was washed with 750 and 250 ml portions of boiling water, then with 300 and 100 ml portions of methanol. 40 grams of tetrabutylammonium iodide were dissolved in 95 ml of methanol in a 1-liter flask. The solution was chilled in a salt-ice bath to  $5^\circ\text{C}$  before the freshly precipitated, methanol-moist, silver oxide was added. The flask was then flushed with nitrogen, tightly stoppered and replaced in the salt-ice bath. The reaction was allowed to proceed for one hour with frequent, vigorous shaking, replacing the flask in the salt-ice bath after each shaking. 90 ml of benzene were added to the flask, it was reflushed with nitrogen, restoppered, shaken vigorously and replaced in the

salt-ice bath for fifteen minutes. It was then filtered through a fine porosity sintered-glass funnel. During this process approximately 300 ml benzene were added through the filter to assure maximum recovery of the base. Activated charcoal was added to the filtrate which was allowed to stand for twenty-four hours with periodic shakings during the first portion of this time. Finally the solution was filtered under nitrogen and diluted to 1 liter in a volumetric flask.

Trimethylphenyl, tetraethyl, cetyldimethylethyl, trimethylbenzyl and cetyltrimethylammonium hydroxide-methoxide titrant solutions were prepared from their quaternary ammonium halides in smaller quantities by the method just described. These preparations were made simultaneously from the same fresh batch of methanol moist silver oxide.

Previous titrant preparations in which the precautions of low reaction temperature, careful exclusion of carbon dioxide and use of high purity quaternary ammonium salt were not observed, resulted in solutions of a light yellow hue which had a lower concentration of base than had been expected. Slight but significant anomalies were noted when using these titrants.

#### Preparation and Purification of Sulfinic Acids and Their Salts

Sodium p-Toluenesulfinate. Sodium p-toluenesulfinate was prepared by reduction of p-toluenesulfonyl chloride with powdered zinc as described by Whitmore and Hamilton (40). The sulfonyl chloride was converted to the zinc p-toluenesulfinate which reacted with excess sodium carbonate to produce sodium p-toluenesulfinate. Steam was bubbled through the reaction

mixture until the odor of the *p*-toluenesulfonyl chloride was no longer evident. The crystal crop grown from the saturated solution obtained by evaporation to the first slight crust formation was bottled and stored in the refrigerator. Subsequent crystal crops containing progressively larger quantities of impurities were saved for further purification. Purity of the sodium salt was dependent upon complete removal of unreacted materials and slow crystallization.

Sodium Benzenesulfinate. Sodium benzenesulfinate was prepared by sodium sulfite reduction of benzenesulfonylchloride as described in part by Smiles and Bere (35). In the reference cited, the free acid is produced by direct acidification of the reduction reaction mixture. However, the purity of the product thus obtained was unsatisfactory for analytical use, and the following modifications were made in the synthesis and work-up. One mole of sodium sulfite was dissolved in 600-650 ml of warm water and filtered, which resulted in a nearly saturated solution.

0.5 mole of benzenesulfonylchloride was added slowly from a dropping funnel with vigorous stirring while the solution was kept alkaline by addition of 50% sodium hydroxide. After approximately one-fourth of the benzenesulfonylchloride had been added and two distinct phases were present, the mixture was heated on a hot plate but was not boiled. Addition of the benzenesulfonylchloride was continued at a liberal enough rate to maintain the reaction temperature and slightly alkaline conditions were faithfully maintained throughout the reaction by the addition of 50% sodium hydroxide by the dropper-full. Stirring was then continued for some time until a clear single phase system resulted. When the reaction was essentially



complete and the reaction mixture had started to cool, it was reheated gently just prior to the passing in of steam. The steam was passed in vigorously and stirring continued until the odor of sulfonylchloride was no longer apparent.

Additional steam distillation was continued at a moderate rate for five to ten minutes while the temperature of the reaction mixture was increased to begin the evaporation process. Alkalinity of the mixture was assured during all of the heating processes, steaming, evaporation, etc. to minimize decomposition. Also, the evaporation was carried out with the hot plate turned on low to avoid overheating or bumping.

When precipitation just barely started the solution was rapidly filtered with a fluted filter through a preheated funnel. The filtrate was allowed to come to room temperature  $25^{\circ}$  slowly. (A previous attempt was made to effect crystallization at this point by placing the solution in the refrigerator overnight. This resulted in a slush of product and sodium sulfite hydrate which made separation impossible.) The sodium benzenesulfinate crystallized in transparent plates and additional yield was obtained by lowering the temperature to approximately  $15^{\circ}$  C. The solution was filtered with mild suction and the precipitate was alternately washed with ice water and filtered repeatedly until no odor was evident. The fairly pure product was bottled and stored in a refrigerator.

The washing process resulted in the sacrifice of  $1/3$  to  $1/2$  of the precipitate, depending on the purity of the sulfinate product and the quantity of inorganic sulfur compounds originally precipitated with it. High purity of the sodium sulfinates was considered essential for preparation

of pure acids because conditions of the acid precipitation makes purification at that stage more difficult. Infrared spectra of both sodium sulfinates obtained in potassium bromide pellets were used as a check of purity in general and variations between crystal fractions.

Benzenesulfinic Acid and p-Toluene Sulfinic Acid. Preparation of the free acids from the corresponding freshly prepared pure sodium salts was accomplished by dissolving the salts in slightly more than a minimum of water and cooling in ice to approximately  $0^{\circ}$  C. While adding 3-6 M hydrochloric acid, the solution was kept in the ice bath and stirred between additions of acid to dissolve any precipitate which may have formed. When the solution was acid to congo red, addition was continued dropwise until the precipitate no longer dissolved with stirring. From this point on, acid was allowed to run down the side of the container so that it would come into gradual contact with the solution and maximize the time of crystallization.

When additional acid resulted in no more crystallization the ice cold solution was filtered immediately and the precipitate was stirred with just enough ice water to make a slush. This process of washing was continued until the precipitate was essentially odor free. In the case of compounds prepared via the sodium sulfite reduction, excessive washing steps were avoided by leaving the precipitate in the refrigerator overnight in contact with the wash water.

Preliminary drying of the free acid was accomplished by suction filtration, pressing between sheets of filter paper and blowing dry nitrogen over the crystals which were covered by an inverted funnel. The time

of air drying was quite arbitrary since further drying was accomplished by freezing the product in a dry ice-acetone bath and pumping the sample down to slightly less than 0.001 mm Hg in a short vacuum line equipped with two dry ice-acetone traps and a McLeod gauge. Dryness was indicated by pressure measurement. Excessive pumping, once a pressure of less than 0.001 mm had been reached, was definitely avoided.

The freeze drying technique was adopted to minimize decomposition during the drying process. This problem is well known (40) and has been mentioned by Burkhard and coworkers (6) as a probable cause for disagreement of independently determined constants which appear in the literature of sulfinic acids. Desiccation even under nitrogen appeared to hasten decomposition, and treatment with anhydrous magnesium carbonate in ether solution followed by precipitation with petroleum ether gave no better results. Final recrystallization from dimethyl ether and butane has been recommended by Godfrey (19) however the use of such low-boiling solvents for this purpose could hardly be considered experimentally ideal.

Success of the freeze drying technique was predictable on the basis of the nature of sulfinic acids previously described. Contact with a polar solvent was maintained to provide stabilization of the acid and during the eventual removal of the solvent low temperature was maintained by the sublimation process.

## RESULTS AND DISCUSSION

### Effect of Titrant Variation

A wide variety of quaternary ammonium titrants have been prepared in

several solvents by different methods for use in nonaqueous titrations. Since the basicity of amines and the solubility of their salts are dependent upon the substituent groups attached to the nitrogen, it appeared necessary to determine the susceptibility of sulfinic acid titration to variations in titrants. The following list of quaternary ammonium salts includes a representation of symmetrical alkylammonium cations of varying sizes, the presence of the benzyl group, the phenyl group, and the massive cetyl group.

Tetramethylammonium bromide  
Tetraethyl ammonium iodide  
Tetra-n-butyl ammonium iodide  
Trimethylbenzylammonium chloride  
Trimethylphenylammonium iodide  
Cetyldimethylethylammonium bromide

The relative insolubility of the tetramethylammonium bromide in dry methanol made conversion to the hydroxide-methoxide form by the silver oxide method ineffective since both reactants were in the solid phase. Further preparation of anhydrous tetramethylammonium titrant was abandoned because there was little reason to expect that the salts formed upon neutralization would have an improved solubility.

Approximately 0.1 N titrant solutions were prepared from the other quaternary ammonium halides listed above by the silver oxide method previously described including such precautions as exclusion of carbon dioxide and treatment with activated charcoal. The filtered solutions were bubbled with nitrogen and stored at room temperature.

Benzenesulfinic and p-toluenesulfinic acids were freshly prepared, purified and dried as previously described. Quantitative results of titrations of these samples with three of the titrants are summarized in Table 1.

Pyridine was used as the titration solvent for this series of determinations because of its excellent dissolving power, its large potential range and particularly its freedom from interaction with strong acids as reported by Cundiff and Markunas (9).

Figure I gives the typical inflections obtained in the titrations of benzene sulfinic and *p*-toluenesulfinic acids with the three titrants used in this series. Very little difference was observed in titration characteristics with the use of different titrants. The different titration curves had the same shape, approximately the same potential break and no identifiable trend in relative neutralization potentials.

Table 1. Comparison of the use of different titrants in the determination of *p*-toluenesulfinic acid and benzenesulfinic acid in pyridine.

Titrant	<u><i>p</i>-Toluenesulfinic Acid</u>			<u>Benzenesulfinic Acid</u>		
	Sample mg.	Titrated acid mg.	Acidity %	Sample mg.	Titrated acid mg.	Acidity %
TBAH	88.76	87.97	99.1	77.66	76.87	99.1
	72.84	73.15	100.4	81.54	79.93	98.2
	85.09	84.81	99.7	85.19	84.39	99.1
CDMEA	102.8	102.9	100.1	103.1	102.4	99.4
	101.7	101.7	100.0	100.3	100.2	99.8
	106.0	106.3	100.3			
TBAH	102.5	103.1	100.5	102.7	101.2	98.5
	101.0	100.3	99.4	101.6	100.4	98.8
	101.6	101.6	100.0	100.9	99.0	98.1

TBAH - trimethylbenzylammonium hydroxide in benzene-methanol

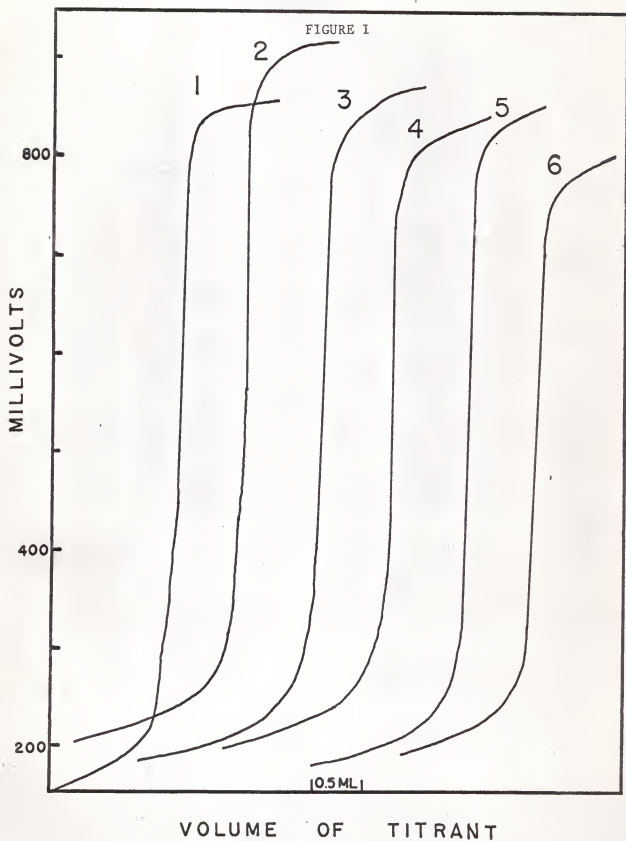
CDMEA - cetyldimethylethylammonium hydroxide in benzene-methanol

TBAH - tetra-*n*-butylammonium hydroxide in benzene-methanol

EXPLANATION OF FIGURE I

Typical inflections of benzenesulfinic and p-toluenesulfinic acids in pyridine with various titrants

Curve	Titrant	Sample
1	CDMEAH	Benzenesulfinic acid
2	CDMEAH	<u>p</u> -toluenesulfinic acid
3	TMBAH	Benzenesulfinic acid
4	TMBAH	<u>p</u> -toluenesulfinic acid
5	TBAH	Benzenesulfinic acid
6	TBAH	<u>p</u> -toluenesulfinic acid



The apparent acidity values reported on Table 1, are based upon the average of standardizations against benzoic acid determined potentiometrically before, in between and after titrations of both acids. The titrants were used in the order in which they are listed in the table. From Table 1, the variance between titrant classes does not appear significant in comparison to the variance within solvent classes. In the case of *p*-toluenesulfinic acid a comparison of deviations found in Table 2 shows greater deviations within titrant classes in two of the three cases. The ratio of variance between titrant classes to variance within titrant classes found in Table 3 is 0.486. This is an estimate of the statistical F value which is compared to a value of 5.14 found in statistical tables of F values at 2 and 6 degrees of freedom at the 95 per cent confidence level. In this case it was concluded that the ratio F was not significant. The analysis of variance as applied here is described in detail by Laitinen (29).

Repeated attempts to titrate benzoic acid and sulfinic acids with trimethylphenyl ammonium titrant were unsuccessful. A light brown color and an amine like odor suggested that complete decomposition of the titrant had occurred. A similar odor was noted for the tetraethylammonium titrant, and precluded its use.

These observations of decomposition are in direct agreement with a recent report by Harlow (21) on stabilities of similar titrant solutions.



Table 2. Comparison of deviations in titrations of *p*-toluenesulfonic acid.

Titrant	Acidity R	Mean Acidity	Deviation within titrant classes			Deviation between titrant classes		
			d	d <sup>2</sup>	Σd <sup>2</sup>	d	d <sup>2</sup>	Σd <sup>2</sup>
TBAH	99.1	99.73	0.6	0.36	0.85	0.21	0.044	0.132
	100.4		0.7	0.49				
	99.7		0.0	0.00				
CDMEAH	100.1	100.13	0.0	0.00	0.05	0.19	0.036	0.108
	100.0		0.1	0.01				
	100.3		0.2	0.04				
TBAH	100.5	<u>99.97</u>	0.5	0.25	<u>0.61</u>	0.03	0.001	<u>0.003</u>
	99.4		0.6	0.36				
	<u>100.0</u>		0.0	0.00				
	899.5	99.94			1.51			0.243

TBAH - trimethylbenzylammonium hydroxide in benzene-methanol

CDMEAH - cetyldimethylethylammonium hydroxide in benzene-methanol

TBAH - tetra-*n*-butylammonium hydroxide in benzene-methanolTable 3. Analysis-of-variance for trimethylbenzyl, cetyldimethyl ethyl and tetrabutylammonium titrants with three determinations of *p*-toluenesulfonic acid in each class.

Source of Variation	Sum of squares	Degrees of freedom	Variance
between titrant classes	0.243	2	0.1215
within titrant classes	<u>1.510</u>	6	0.2500
	1.753	8	0.219
Ratio of variances = 0.486			

### Effect of Solvent Variation

Previous results have indicated that pyridine is a satisfactory solvent for titrations of samples containing sulfinic acid as the only acid, however, other solvents with a lesser leveling power are of more use for acid mixtures.

The solvents quantitatively compared to pyridine for titrations of sulfinic acids were dimethylformamide, tetrahydrofuran, and a 9:1 benzene-methanol mixture identical to that used as the titrant solvent. The titrant used was 0.1 N tetrabutylammonium hydroxide-methoxide in benzene-methanol and the results of this series of determinations appear in Table 4.

A direct quantitative comparison between results in different solvents is not possible due to sample decomposition which took place in the course of this series of determinations. The first obvious evidence of decomposition was the appearance of a distinct odor. The decomposition was confirmed by final titration of the benzenesulfinic acid in pyridine which was also the first solvent used. The final titrations in pyridine, performed on successive days with restandardization of titrant for each titration, plainly indicated a continual decline in the acidity of the sample. The age of the samples, progression of the decomposition reaction past the initiation stage and repeated exposure to the atmosphere at room temperature, are explanations which may be offered for the decline in acidity which was not nearly as obvious in the previous titrant variation series.

Speculation concerning explanation of abnormally high acidity values observed in the benzene-methanol solvent system for both acids is focused upon a possible solvent-solute interaction. Presumably the methanol in the solvent mixture constitutes an excess sufficient to cause predominate amphiprotic solvent characteristics. Van der Heidje and Dahmen (39), working in the concentration range of approximately 0.01 N, observed that apparent acidity of uncharged oxygen acids in amphiprotic solvents was enormously enhanced.

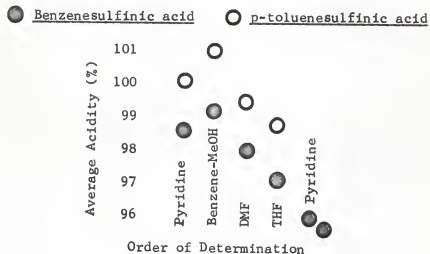
From Figure II the nearly parallel effect on both acids is apparent and the difference in acidity values obtained in other solvents can be explained by decomposition of the sample.

Typical titration curves from this series appear in Figure III. No difference was noted between the curves for benzenesulfinic acid (not shown) and those for *p*-toluenesulfinic acid. A slight anomaly is apparent in the curves for tetrahydrofuran in the form of an abnormal rise in the region of the half-neutralization point. This, in no way, interfered with the detection of the end point.

Table 4. Titrations of benzenesulfinic acid and *p*-toluenesulfinic acids in various solvents.

Solvent	<u>Benzenesulfinic Acid</u>			<u>p-Toluenesulfinic Acid</u>		
	Sample mg.	Titrated acid mg.	Acidity %	Sample mg.	Titrated acid mg.	Acidity %
Pyridine	102.7	101.2	98.5	102.5	103.1	100.5
	101.6	100.4	98.8	101.0	100.3	99.4
	100.9	99.0	98.1	101.6	101.6	100.0
Benzene- Methanol	103.3	102.7	99.3	101.6	102.8	101.2
	101.4	100.3	98.9	100.8	101.8	101.0
	102.3	101.0	98.8	101.1	101.9	100.8
Dimethylform- amide	102.1	100.2	98.2	106.6	105.7	99.2
	101.7	99.3	97.7	102.4	101.4	99.1
	102.0	99.8	97.9	100.0	99.7	99.7
Tetrahydro- furan	100.5	98.0	97.5	108.2	106.8	98.8
	101.5	97.4	96.1	108.2	106.8	98.8
	101.7	98.9	97.4	103.2	101.7	98.5

FIGURE II

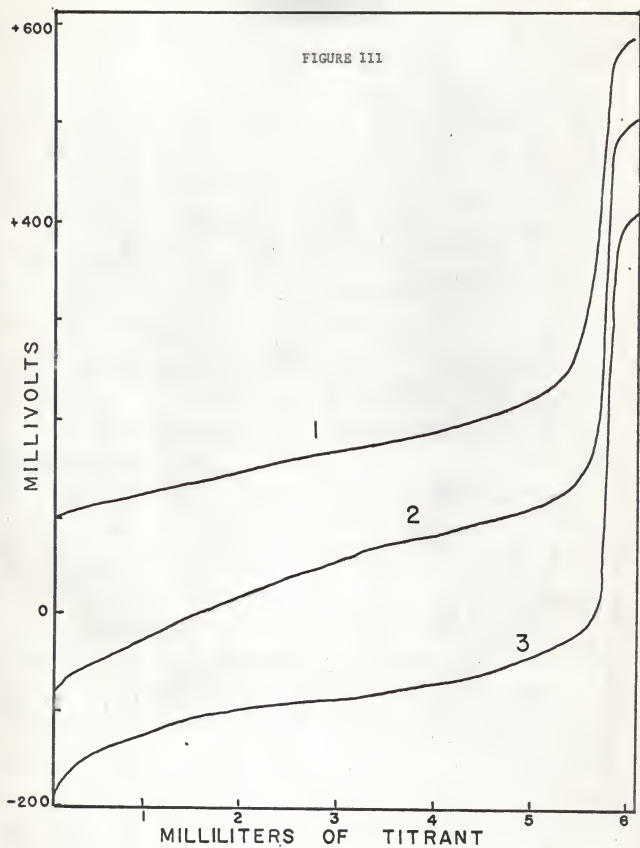


EXPLANATION OF FIGURE III

Typical titration curves for *p*-toluenesulfonic acid  
in various solvents

Curve	Solvent
1	dimethylformamide
2	tetrahydrofuran
3	Benzene-methanol

FIGURE III



### Separation of Sulfinic-Sulfonic Acid Mixtures

The ionization constant in water of benzenesulfinic and benzenesulfonic acids have been reported as  $1 \times 10^{-2}$  and  $2 \times 10^{-1}$  respectively (6,23). Two inflections were noted in the titration curves of these mixtures in pyridine, however, a much more definite separation was obtained in tetrahydrofuran which has a larger range of potential than pyridine, but does not have as great a leveling effect. Separation of sulfinic-sulfonic mixtures has been successful with benzene-methanol, tertiarybutyl alcohol, dimethylformamide, and dimethylsulfoxide as indicated on Figure IV. Separation in chlorobenzene was unsuccessful.

### Solvent Survey

Several solvents representing different functional groups and wide variance of basicity and dielectric constants were used for titrations of the benzene sulfinic and/or p-toluene sulfinic acid samples. The titration curves obtained provide a qualitative survey of the feasibility of using various solvent types. The characteristics under particular scrutiny for each system included the sharpness and size of the potential break, the available overall potential range, the relative half neutralization potentials, the steadiness of electrode response and occurrence of anomalies. 0.1 N tetrabutylammonium hydroxide titrant was used in this series of titrations. The ratio of approximately 0.7 millimoles of sample per 50 ml of solvent was maintained in order that a comparison of successive titrations at the same stages of neutralization would have nearly the same solvent mixture composition ratios and solute concentrations.

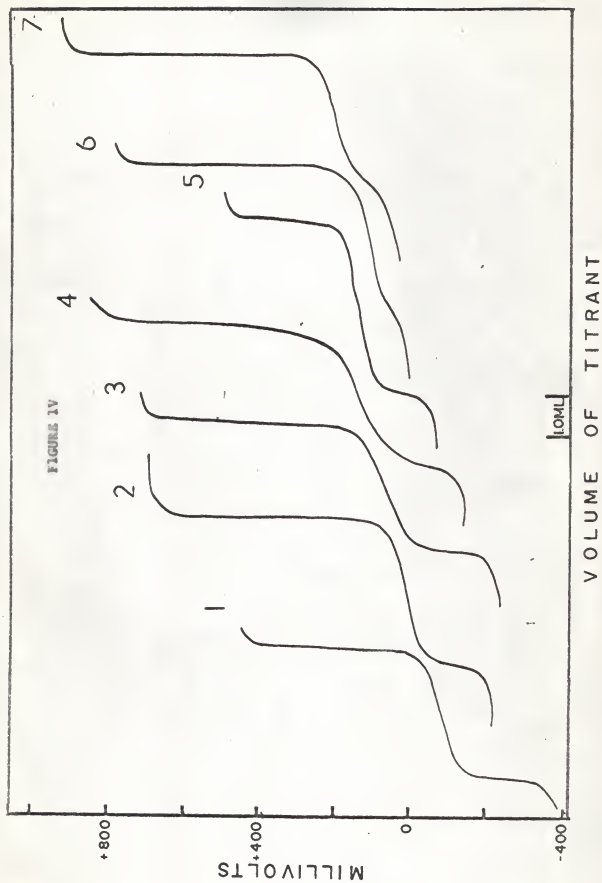
# EXPLANATION OF FIGURE IV

Titration of sulfinic-sulfonic acid mixtures in various solvents with 0.1 N tetrabutylammonium hydroxide-methoxide in 9:1 benzene-methanol

Curve	Solvent	Sample
1	Benzene-methanol	p-toluenesulfinic-sulfonic acids
2	Tertiarybutyl alcohol	Benzenesulfinic-sulfonic acids
3	Tetrahydrofuran	p-toluenesulfinic-sulfonic acids
4	Dimethylformamide	p-toluenesulfinic-sulfonic acids
5	Dimethylsulfoxide	Benzenesulfinic-sulfonic acids
6	Pyridine	Benzenesulfinic-sulfonic acids
7	Pyridine	p-toluenesulfinic-sulfonic acids

Note: An average of 50 points were taken to establish each curve.





The effects of the benzene-methanol mixture upon properties of the titration solvents used represented an unknown variation which was minimized, however not eliminated.

A comparison of the quantitative results of this series of titrations was not possible since in most instances single titrations were performed without the benefit of standardization in the particular solvent used or adequate solvent blank determinations. Solvents in which a usable inflection occurred are listed in Table 5.

The following solvents dissolved the samples but were unsatisfactory for use with the present potentiometric titration system. Plots of the potentiometric responses observed are found in Figure V. A small overall potential range was the limiting factor in the basic solvents ethylenediamine and *n*-hexylamine; also in the neutral solvents cyclohexanone and di-isobutyl ketone. Poor stability of potentials resulted with the use of the solvents of low dielectric properties, chloroform (not shown) and 1,4-dioxane.

In addition to the sulfinic acids for which quantitative data has been presented, samples known to contain the following acids have been titrated in pyridine resulting in a similar potentiometric response.

*p*-nitrobenzenesulfinic acid

*m*-nitrobenzenesulfinic acid

2,5-dimethylbenzenesulfinic acid

Table 5. Solvents in which a usable inflection occurred in order of increasing apparent basicity.

Substance	Category	Dielectric Constant	Dipole Moment	Figure Reference
ethyl acetate*	inert	6.4	1.78	VI-8
dimethyl sulfoxide*	inert			VI-2
chlorobenzene	inert	5.708	1.67	VI-4
nitrobenzene	inert	35.74		VI-3
acetone	inert	21.20	2.95	not shown
acetonitrile	inert	37.5	3.93	VI-1
diethyl ether	inert	4.3		not shown
tetrahydrofuran	inert			III-2
methanol (benzene-methanol)	amphiprotic	33.64		III-3
n-butyl alcohol	amphiprotic	7.8		VI-5
t-butyl alcohol	amphiprotic	18.7		VI-6
pyridine	basic	12.5		I
dimethylformamide	basic			III-1
dimethyl aniline	basic	4.48		VI-7

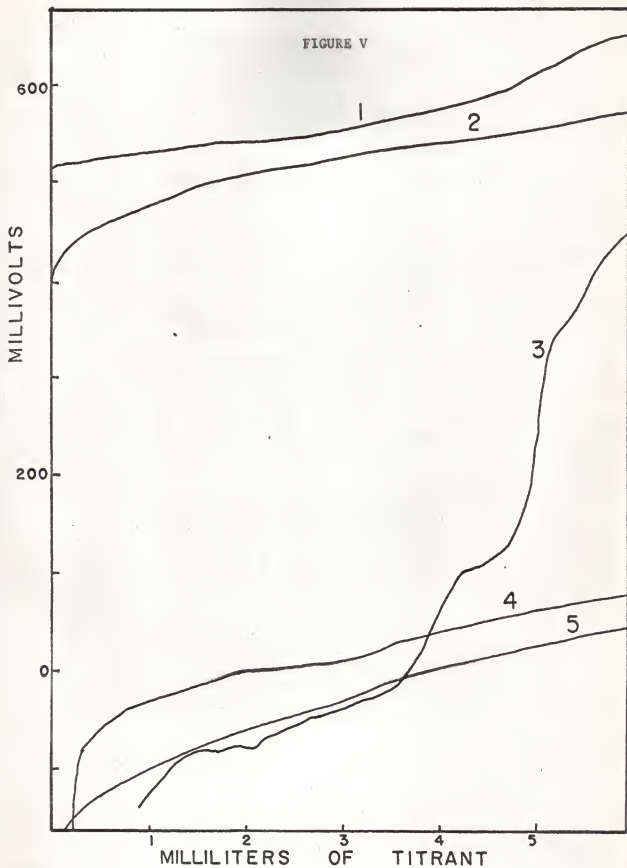
\*Relative basicity indefinite.

# EXPLANATION OF FIGURE V

Potentiometric responses observed in the attempted titrations  
of sulfinic acids in various solvents

Curve	Solvent	Sample
1	ethylenediamine	<u>p</u> -toluenesulfinic acid
2	<u>n</u> -hexylamine	<u>p</u> -toluenesulfinic acid
3	1,4-dioxane	benzenesulfinic acid
4	cyclohexanone	benzenesulfinic acid
5	di-isobutyl ketone	benzenesulfinic acid

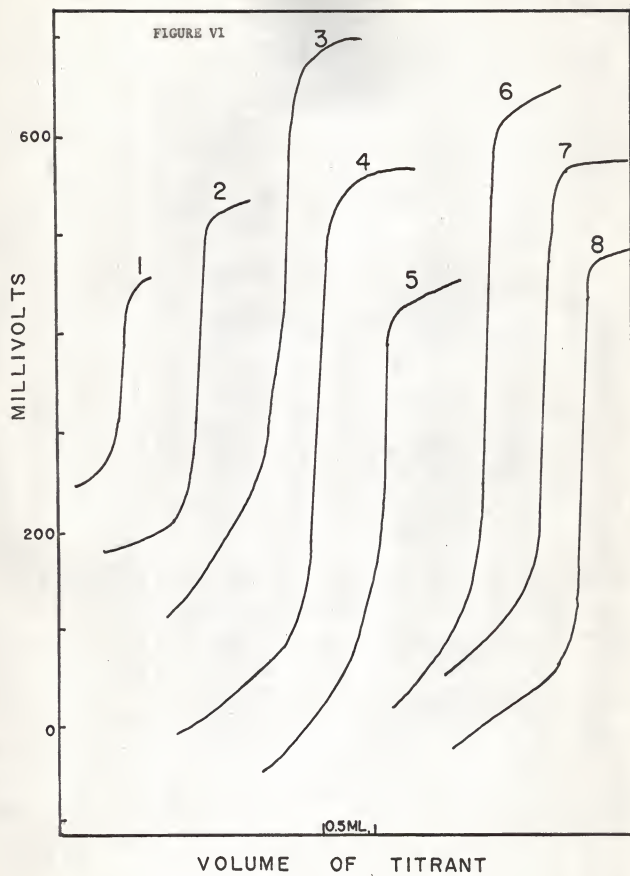
FIGURE V



# EXPLANATION OF FIGURE VI

Inflection observed in the titration of aromatic sulfinic acids in various solvents

Curve	Solvent	Sample
1	acetonitrile	<u>p</u> -toluenesulfinic acid
2	dimethyl sulfoxide	benzenesulfinic acid
3	nitrobenzene	benzenesulfinic acid
4	chlorobenzene	benzenesulfinic acid
5	<u>n</u> -butyl alcohol	benzenesulfinic acid
6	<u>t</u> -butyl alcohol	benzenesulfinic acid
7	dimethyl aniline	benzenesulfinic acid
8	ethyl acetate	<u>p</u> -toluenesulfinic acid



## CONCLUSIONS

Acid base titrations of sulfinic acids and mixtures of sulfinic and sulfonic acids with quaternary ammonium titrants in nonaqueous solvents show promise as a method for quantitative analysis. Various titrants may be used with equal confidence, and several solvent systems are available. Separation of sulfinic-sulfonic acid mixtures is readily possible.

The method of analysis adopted is essentially that proposed by Cundiff and Markunas (7) with the incorporation of recent improvements and special precautions. Acid samples dissolved in pyridine or another suitable basic or neutral solvent are titrated under a nitrogen atmosphere with approximately 0.1 N tetrabutylammonium hydroxide-methoxide in a 9:1 benzene-methanol solution. Titration end points are determined from potentiometric data obtained by using a pH meter equipped with an all purpose glass electrode and a modified commercial calomel electrode in which the saturated aqueous potassium chloride solution in the outer jacket has been replaced with a saturated solution of potassium chloride in methanol. The titrants are standardized by titration of benzoic acid to a potentiometric end point in the solvents used for the respective determinations. Variation of the tetrabutylammonium hydroxide pyridine system may be used. In the case of acid separation problems, tetrahydrofuran is a recommended solvent. When titrants of lower stability are used, refrigerated storage is advisable.

Some advantages of acid base titrations of this type include (1) the



elimination of prior separation steps, (2) all operations can be done at room temperature without solubility or sample decomposition problems and (3) 100 mg samples may be used to obtain precision comparable to that of methods requiring twenty-five times as much sample.

## ACKNOWLEDGMENT

The author wishes to thank his major professor, Dr. Clifton E. Meloan, for his encouragement, patience, constructive criticism and direction through the course of this investigation.

## LITERATURE CITED

- 1 Ackerman, Leo. Ind. Chem. Anal. Ed. 18,243-4 (1946).
- 2 Allen, P. Jr. J. Org. Chem. 7,23 (1942).
- 3 Beachem, M.T. and others. J. Am. Chem. Soc. 81,5430-35 (1959).
- 4 Brederick, H. and others. Ber. 88,438-44 (1955).
- 5 Brederick, H. Angew. Chem. 70,268-9 (1958) (C.A. 52:20013).
- 6 Burkhard, R.K., D.E. Sellers, F. DeCou, and J.L. Lambert. J. Org. Chem. 24,767-9 (1959).
- 7 Cundiff, R.H. and P.C. Markunas. Anal. Chem. 28,792 (1956).
- 8 Ibid. 30,1447.(1958).
- 9 Ibid. 30,1450 (1958).
- 10 Ibid. 33,1028 (1961).
- 11 Ibid. 34,296 (1962).
- 12 Ibid. 34,584 (1962).
- 13 Dal Nogare, S. "Organic Analysis" Vol I New York:Interscience (1953) p.378.
- 14 Detoni, S. and D. Hadzi. J. Chem. Soc. 1955,3163-9.
- 15 Detoni, S. and D. Hadzi. Bull. Sci. Conseil Acad. RPF Yougoslavie 2,44-5 (1955) (C.A. 49:12965i).
- 16 Feigl, F. "Chemistry of Specific, Selective and Sensitive Reactions" New York:Academic Press (1949) p. 289-91.
- 17 Fritz, J.S. "Acid Base Titrations in Nonaqueous Solvents" G. Frederick Smith Chemical Co. Columbus, Ohio (1952).
- 18 Fritz, J.S. and Yanamura. Anal. Chem. 29,1079 (1957).
- 19 Godfrey, John J. "The Decomposition of Sulfinic Acids" Ph.D. Dissertation, Brooklyn Polytechnical Institute (1958).
- 20 Harlow, G.A. Anal. Chem. 34,1482 (1962).
- 21 Ibid. 34,1487 (1962).

- 22 Harlow, G.A., C.M. Noble and G.E.A. Wyld. Anal. Chem. 28,787 (1956).
- 23 Heilbron, I.M. "Dictionary of Organic Compounds" Vol 1 New York: Oxford University Press (1953) p. 247.
- 24 Koenigs, C. Ber. 11,615 (1878).
- 25 Kolthoff, I.M. and Stanley Bruckenstein. "Treatise on Analytical Chemistry" Part 1. Vol 1. New York: Interscience (1959) pp. 475-540.
- 26 Krishna, S. and B. Das. Quant. J. Indian Chem. Soc. 4,367 (1927).
- 27 Krishna, S. and H. Singh. J. Am. Chem. Soc. 50,792 (1928).
- 28 Laitinen, H.A. "Chemical Analysis" New York: McGraw-Hill Book Company, Inc. (1960) pp. 57-83.
- 29 Ibid. pp. 556-560.
- 30 Marple, L.W. and J.S. Fritz. Anal. Chem. 34,796 (1962).
- 31 Marvel, C.S. and R.S. Johnson. J. Org. Chem. 13,822-29 (1948).
- 32 Ponzini, S. Farm. Sci. e tec. (Pavia) 2,198-9 (1947) (C.A. 42:3701).
- 33 Riddick, John A. Anal. Chem. 32,172R (1960).
- 34 Samuelson, Olof. "Ion Exchangers in Analytical Chemistry" New York: John Wiley (1953).
- 35 Smiles, S. and C. Bere. "Organic Synthesis" Coll. Vol I New York: John Wiley (1946) p. 7.
- 36 Streuli, C.A. Anal. Chem. 34,302R (1962).
- 37 Thomas, J. J. Chem. Soc. 95,343 (1909).
- 38 Truce, W.E. and A.M. Murphy. Chem. Rev. 48,69 (1951).
- 39 Van der Heidje, H.B. and E.A.M.E. Dahmen. Anal. Chim. Acta. 16,378 (1957).
- 40 Whitmore, F.C. and F.H. Hamilton. "Organic Synthesis" Coll. Vol. I New York: John Wiley (1946) p. 492.
- 41 Wilson, C.L. and D.W. Wilson. "Comprehensive Analytical Chemistry" Vol. 1B New York: Elsevier (1960) p. 748.

ACID-BASE TITRATIONS OF AROMATIC SULFINIC ACIDS  
IN NONAQUEOUS SOLVENTS

by

DAVID LOUIS WETZEL

A. B., Augustana College, 1956

---

AN ABSTRACT OF A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE UNIVERSITY  
Manhattan, Kansas

1963

#### ABSTRACT

p-Toluene sulfinic acid and benzenesulfinic acid have been determined by potentiometric titration with quaternary ammonium bases in several non-aqueous solvent systems using a glass and a modified calomel electrode.

Twenty different solvents were tried for titrations of sulfinic acids. Titration curves were obtained for 14 of these in which a significant inflection was observed.

No significant variance was noted in the quantitative results or titration characteristics of either acid between the use of tetra-n-butylammonium, trimethylbenzylammonium and cetyldimethylethylammonium bases in a dry 9:1 benzene-methanol solution. Dry acid-free pyridine was the titration solvent. The relative stabilities of the various quaternary ammonium bases was evident by the decomposition of the trimethylphenyl and the tetraethylammonium hydroxide-methoxide titrant solutions which were prepared and stored under the same conditions as the three titrants used successfully.

Titrations with tetrabutylammonium hydroxide titrant in pyridine, benzene-methanol, dimethylformamide and tetrahydrofuran were without interfering anomalies. Abnormally high acidity values for samples of both benzenesulfinic and p-toluenesulfinic acids in the benzene-methanol solvent mixture were the only obvious evidence of solvent interference. Precision within each solvent was comparable to the precision in the other solvents and with one exception the variance of sample acidity between different solvent systems corresponded to sample decomposition.

Two inflections were observed in the titration of benzene and p-toluene sulfinic-sulfonic acid mixtures in tetrahydrofuran, pyridine, dimethylsulfoxide, tertiarybutyl alcohol, dimethylformamide, and a 9:1 benzene-methanol solvent mixture.

A procedure for determination has been recommended which utilizes a rapid direct titration, and does not require preliminary separation, external indicators, highly unstable titrants, extreme temperatures or large samples.

The freeze drying vacuum technique has been used successfully to dry sulfinic acid samples with a minimum of decomposition.