

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA, MINNEAPOLIS, MINNESOTA]

Calculated and Experimental Conductometric Titration Curves of Intermediately Strong Acids and Bases in Acetonitrile¹

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RECEIVED AUGUST 17, 1962

An equation has been derived for the calculation of conductometric titration curves of intermediately strong acids with aliphatic amines in acetonitrile as a solvent. The calculations require a knowledge of the dissociation constants $K_{\text{BH}^+\text{AHA}^-}$ of the conjugate salt, $K_{\text{BH}^+\text{A}^-}$ of the simple salt, of the conjugation constant K_{AHA^-} , and of ionic mobilities. Good agreement between calculated and observed conductances has been found in the titration of varying concentrations of sulfuric acid with *n*-butylamine and of 3,5-dinitrobenzoic acid with triethylamine (Fig. 2 and 3). From the solubility of potassium 3,5-dinitrobenzoate in solutions of varying concentration of the parent acid the conjugation constant K_{AHA^-} was found to be equal to 1.7×10^4 while the solubility product of the salt is 5.3×10^{-8} at 25°. A list of other determined constants is given in Table IV. The maximum in the conductometric titration curves is found at 50% neutralization of the acid when K_{AHA^-} is very large and $K_{\text{BH}^+\text{A}^-}$ small.

Introduction

Several conductometric acid-base titrations in non-aqueous solvents have been reported in the literature, but no quantitative interpretation of the titration curves has been given. In solvents of low dielectric constant the dissociation of ion-pairs is highly incomplete and values of dissociation constants of salts formed and of ion mobilities must be known in order to calculate the conductance. Moreover, in solvents of very low dielectric constant ion triplets and quadruplets can be formed, which makes a calculation of the equilibrium conditions very complicated. In solvents which are non-hydrogen bond donors (inert solvents) anions are stabilized by conjugation with the conjugate undissociated acid: $\text{A}^- + \text{HA} \rightleftharpoons \text{AHA}^-$, and a knowledge of the conjugation constant and of the dissociation constant of the salt BH^+AHA^- is required in order to calculate the concentration of all ionic species. As a matter of fact, the over-all shape of the titration curves in inert solvents depends much more on the conjugation of the anion A^- than on the dielectric constant.

Pioneer work on conductometric titrations of acids and bases in benzene and dioxane as solvents has been carried out by Maryott.² In the titration of trichloroacetic acid with diethylamine in these solvents the conductance was found to rise to a maximum well before the equivalence point and then to decrease to a very low value in the neighborhood of the equivalence point. The maximum was attributed to a stabilization of the trichloroacetate ion with undissociated acid, the conjugate salt being considerably more dissociated than the normal salt.

Maxima of the above nature were also described and interpreted by Harlow and Bruss³ in the conductometric titration of several phenols with tetra-*n*-butylammonium hydroxide in the truly inert solvents benzene, toluene, and gasoline.

Extensive studies on the conductometric titration of acids and bases in non-aqueous solvents have been reported by van Meurs and Dahmen,⁴ who concentrated particularly on the titration of dibasic acids. For several reasons maxima of the type discussed above were not observed. An excellent qualitative interpretation of titration curves of relatively weak acids and bases in acetone and acetonitrile as solvents has been given by Bryant and Wardrup.⁵

(1) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 49-(638)519. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(2) A. A. Maryott, *J. Res. Natl. Bur. Std.*, **38**, 527 (1947).

(3) G. A. Harlow and D. B. Bruss, *Anal. Chem.*, **30**, 1836 (1958).

(4) N. van Meurs and A. M. F. Dahmen, *Anal. Chim. Acta*, **19**, 64 (1958); **21**, 10, 193 (1959); *J. Electroanal. Chem.*, **1**, 458 (1960).

(5) P. J. R. Bryant and A. W. H. Wardrup, *J. Chem. Soc.*, **169**, 895 (1957).

In the present paper calculated titration curves of sulfuric acid (as monobasic acid) with *n*-butylamine and of 3,5-dinitrobenzoic acid with triethylamine in acetonitrile have been compared with the experimental curves.

In order to calculate the titration curves it is necessary to know the conjugation constant

$$K_{\text{AHA}^-} = [\text{AHA}^-]/[\text{HA}][\text{A}^-] \quad (f_{\text{AHA}^-} \cong f_{\text{A}^-}) \quad (1)$$

and the mobilities and concentrations of the various ionic species. For bisulfate the constant K_{AHA^-} has been determined in a previous paper.⁶

The conjugation constant for the dinitrobenzoate ion has been calculated from the solubility of potassium 3,5-dinitrobenzoate in solutions of various concentrations of 3,5-dinitrobenzoic acid. Dissociation constants $K_{\text{BH}^+\text{A}^-}$ of simple salts BH^+A^- and mobilities of the ions composing the salt have been calculated from Fuoss and Kraus plots,⁷ constructed from conductance measurements of the appropriate salts.⁸

The dissociation constant $K_{\text{BH}^+\text{AHA}^-}$ of the conjugate salt $n\text{-BuNH}_3^+\text{HSO}_4^-\text{H}_2\text{SO}_4$ has been estimated using data from titration curves. Even though the concentration of $\text{BH}^+\text{A}^- \dots \text{HA}$ is at a maximum at 50% titrated, the concentration of A^- may not be negligible at this point, especially when K_{AHA^-} is small and $K_{\text{BH}^+\text{A}^-}$ is relatively large as compared to the conjugate salt. As a first approximation it has been assumed that between zero and thirty-five per cent neutralization of the acid only the conjugate salt $\text{BH}^+\text{A}^- \dots \text{HA}$ with its corresponding ions are present in the solution. A Fuoss and Kraus plot of the conductance data in this region in the titration of sulfuric acid with *n*-butylamine was made which yielded an approximate value of $K_{\text{BH}^+\text{AHA}^-}$

$$K_{\text{BH}^+\text{AHA}^-} = [\text{BH}^+][\text{AHA}^-]f^2/[\text{BH}^+\text{AHA}^-] \quad (f_{\text{BH}^+} = f_{\text{AHA}^-} = f) \quad (2)$$

The calculations were repeated by correcting for the approximate concentration of A^- and BH^+A^- .

The dissociation constant of the conjugate salt $\text{Et}_3\text{NH}^+\text{DNB}^-\text{HDNB}$ (DNB denotes 3,5-dinitrobenzoate) could not be estimated from the early portion of the titration curves because of formation of considerable amounts of undissociated salt. The dissociation constant of this salt is only of the order of 10^{-5} (see Table IV). In order to estimate the dissociation constant of $\text{Et}_3\text{NH}^+\text{DNB}^-\text{HDNB}$ the conductance of solutions of the amine in a large excess of the acid was determined. From a Fuoss and Kraus plot the equivalent conductance at infinite dilution and the dissociation

(6) I. M. Kolthoff and M. K. Chantooni, Jr., *J. Phys. Chem.*, **66**, 1675 (1962).

(7) R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **55**, 476, 2387 (1933).

(8) I. M. Kolthoff, S. Bruckenstein and M. K. Chantooni, Jr., *ibid.*, **83**, 3927 (1961).

constant of the conjugate salt were found. The viscosity of the solutions in the large excess of acid was considerably greater than that of the solvent and a viscosity correction has been applied.

In all calculations it was assumed that the limiting Debye-Hückel expression $-\log f = 1.53 \sqrt{\mu}$ (μ is ionic strength) holds and that $f_+ = f_-$.

Considering the complex of equilibria involved and the limitation of the Debye-Hückel expression, reasonable agreement between calculated and experimental titration curves can be expected only in very dilute solutions.

Calculation of Titration Curves.—From the electro-neutrality rule we find a relation in mixtures of a monobasic weak acid and its salt in the titration range between zero and 100% neutralized

$$[\text{BH}^+] = [\text{A}^-] + [\text{AHA}^-] \quad (3)$$

$[\text{H}^+]$ being negligibly small.

The dissociation constant of the sample salt BH^+A^- is given by

$$K_{\text{BH}^+\text{A}^-} = [\text{BH}^+][\text{A}^-]/[\text{BH}^+\text{A}^-] \quad (4)$$

where $f_{\text{BH}^+} = f_{\text{A}^-} = f$.

Equation 5 is obtained by substituting equations 2 and 4 into equation 3

$$[\text{BH}^+] = (1/f) \times \frac{\sqrt{K_{\text{BH}^+\text{A}^-}[\text{BH}^+\text{A}^-] + K_{\text{BH}^+\text{AHA}^-}[\text{BH}^+\text{AHA}^-]}}{2f^2} \quad (5)$$

Under conditions of quantitative acid-base reaction, the total salt concentration c_s equals the amount of base added.

$$c_s = [\text{BH}^+] + [\text{BH}^+\text{A}^-] + [\text{BH}^+\text{AHA}^-] \quad (6)$$

Substituting equation 6 into equation 5 and simplifying, equation 7 is obtained

$$[\text{BH}^+] = \frac{-K_{\text{BH}^+\text{A}^-} \pm \sqrt{K_{\text{BH}^+\text{A}^-}^2 + 4f^2\{K_{\text{BH}^+\text{A}^-}c_s + (K_{\text{BH}^+\text{AHA}^-} - K_{\text{BH}^+\text{A}^-})[\text{BH}^+\text{AHA}^-]\}}{2f^2} \quad (7)$$

In the calculation of the titration curve an approximate value of $[\text{BH}^+\text{AHA}^-]$ from $K_{\text{BH}^+\text{AHA}^-}$ at a given fraction titrated is introduced into equation 7 and $[\text{BH}^+]$ calculated, using the experimentally determined constants $K_{\text{BH}^+\text{A}^-}$ and $K_{\text{BH}^+\text{AHA}^-}$. Knowing $[\text{BH}^+]$ and c_s and using the approximate value of $[\text{BH}^+\text{AHA}^-]$, $[\text{BH}^+\text{A}^-]$ is calculated from equation 6. This value of $[\text{BH}^+\text{A}^-]$ and also f^2 and $[\text{BH}^+]$ are introduced in equation 4 to calculate $[\text{A}^-]$.

Next, $[\text{AHA}^-]$ is calculated by substituting the values of $[\text{A}^-]$ and $[\text{BH}^+]$ in equation 3. Knowing $[\text{A}^-]$ and $[\text{AHA}^-]$, $[\text{HA}]$ is calculated from equation 1. The relation, applicable at any point during the titration, between the initial concentration c_a of the acid and the various species is given by

$$c_a = [\text{HA}] + [\text{A}^-] + 2[\text{AHA}^-] + [\text{BH}^+\text{A}^-] + 2[\text{BH}^+\text{AHA}^-] \quad (8)$$

Equation 8 is solved for $[\text{HA}]$ upon substituting the calculated values of $[\text{A}^-]$, $[\text{AHA}^-]$, $[\text{BH}^+\text{A}^-]$ and $[\text{BH}^+\text{AHA}^-]$. When the same value of $[\text{HA}]$ was found from equations 8 and 1, the correct value of $[\text{BH}^+\text{AHA}^-]$ had been used in equation 7.

If the difference between the two values of $[\text{HA}]$ was too great, all calculations were repeated using a corrected value for $[\text{BH}^+\text{AHA}^-]$. From the known concentrations of all species and their mobility the conductometric titration curves could be calculated.

In all instances mobilities of the ions were calculated from the values at infinite dilution, using the Onsager⁹ equation $\lambda = \lambda_0 - [0.735\lambda_0 + 115]\sqrt{c}$

(9) L. Onsager, *Physik. Z.*, **27**, 388 (1926); **28**, 277 (1927).

The constants in this equation were obtained using the values of 36 and 0.345 cp. for the dielectric constant and viscosity of acetonitrile, respectively, at 25°.

Experimental

Chemicals. Acetonitrile.—Purified and dispensed as previously described.⁸ The specific conductance of purified solvent was 1 to 2×10^{-7} ohm⁻¹ cm.⁻¹. The purified solvent was 2 millimolar in water as determined by Karl Fischer titration and 2×10^{-6} M in ammonia as determined by spectrophotometric titration with picric acid at 410 m μ .⁸

Sulfuric Acid.—Prepared as previously described.⁸

3,5-Dinitrobenzoic Acid.—Eastman Kodak White Label product was recrystallized from water-ethanol mixture and dried at 70° *in vacuo* over barium oxide for six hours; m.p. 204°; lit. value¹⁰ 204–205°. Assay of the acid by alkalimetric titration with standard sodium hydroxide in water-alcohol mixture (9:1) gave 99.8% of the theoretical value.

n-Butylamine. Triethylamine.—Eastman Kodak White Label products were shaken over Merck Reagent Grade potassium hydroxide pellets for 24 hours, then distilled at atmospheric pressure. Boiling points at 760 mm. were 76 and 89° for n-butylamine and triethylamine, respectively; literature values,¹⁰ 78 and 89°. These bases were stored in a nitrogen atmosphere.

n-Butylammonium Picrate.—Twenty g. of Eastman Kodak White Label picric acid was dissolved in 30 ml. of U.S.P. 95% ethanol, 200 ml. of conductivity water added and the solution neutralized with n-butylamine introduced from a buret using methyl red as external indicator. The resulting solution was taken to dryness over a steam bath and the residue recrystallized from a benzene-ethanol mixture (1:4) and dried for five hours at 70° *in vacuo*; m.p. 147°. Analysis of the salt by spectrophotometric titration of a 0.00333 M solution in acetonitrile with 0.489 M perchloric acid (in anhydrous acetic acid) in a 1.8 cm. cell at 480 and 490 m μ gave 100.5% of the theoretical value.

Tetraethylammonium 3,5-Dinitrobenzoate.—Five g. of Eastman Kodak White Label 3,5-dinitrobenzoic acid was dissolved in 200 ml. of Merck Reagent Grade acetone and 30 ml. of conductivity water added. This solution was neutralized with 1 M aqueous tetraethylammonium hydroxide prepared as previously described.⁸ Phenolphthalein served as external indicator. The resulting solution was taken to dryness over a steam bath and the product recrystallized from a 1:1 benzene-ethanol mixture. The salt was dried at 80° *in vacuo* for two days. It had a tan color. A 0.1 M solution of the recrystallized salt in acetonitrile was a bright red, due to traces of m-dinitrobenzene as impurity in the acid. After two recrystallizations of the salt (see above) the impurity was removed and solutions of the salt in acetonitrile were a light yellow.

Five ml. of 1.94×10^{-3} M tetraethylammonium 3,5-dinitrobenzoate in acetonitrile was titrated spectrophotometrically at 410 m μ with 0.489 M perchloric acid (in anhydrous acetic acid) in the presence of 6.1×10^{-6} M o-nitro-p-chloroaniline as indicator. The purification of the indicator base is described elsewhere.⁸ All absorbances were corrected for the absorbance found in the absence of indicator. Analysis by spectrophotometric titration gave 101.3% of the theoretical value. Conductometric titration of 5 ml. of 0.00194 M salt in acetonitrile with 0.489 M perchloric acid gave a purity of 100.5%.

Potassium 3,5-Dinitrobenzoate.—Ten g. of Eastman Kodak White Label 3,5-dinitrobenzoic acid was dissolved in 30 ml. of U.S.P. ethanol, 30 ml. of conductivity water added and the solution neutralized with aqueous potassium hydroxide solution, using brom thymol blue as external indicator. The neutralized solution was evaporated to dryness on a steam bath. The salt was washed with acetonitrile and dried at atmospheric pressure at 70°.

Conductivity Measurements.—An Instruments RC-1B Model conductance bridge operated at 60 cycles/sec. was used in all conductance measurements. When necessary, a 0.1 μ f. external decade condenser was introduced in the circuit. Unplatinized electrodes were used in oblong shaped conductivity cells (provided with 12/18 glass stoppers) having cell constants of 0.224 and 0.670. The former cell was employed in all conductance measurements except in the conductometric titration of 0.0561 M sulfuric acid and of 0.062 M dinitrobenzoic acid, when the latter cell was employed. Cell constants were determined with 0.01 and 0.001 M aqueous potassium chloride solution in the conventional way. The measurements were carried out in a light kerosene bath maintained at $25.00 \pm 0.02^\circ$.

Procedure for Conductometric Titrations.—For titrations of sulfuric acid the desired amount of anhydrous sulfuric acid was dispensed from a 0.1 ml. Gilmont microburet into 5 ml. of acetonitrile previously pipetted into the conductance cell. Volume correction upon the addition of sulfuric acid is negligible.

(10) "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1961.

For titration of 3,5-dinitrobenzoic acid the solid acid was weighed out into the cell and acetonitrile was added to a mark etched onto the neck, corresponding to a volume of 5.18 ml.

Only freshly prepared solutions of sulfuric and 3,5-dinitrobenzoic acid were used. The amine titrant was introduced from a 0.1 ml. Gilmont microburet previously calibrated and the conductivity reading taken immediately after mixing. Volume corrections for addition of titrant were negligible.

Density of 3,5-Dinitrobenzoic Acid Solutions.—The density of 0.0617 *M* and 0.350 *M* 3,5-dinitrobenzoic acid solutions were determined at 25° by means of a pycnometer of 5.809 ml. capacity and equipped with capillary side arms. The capacity was determined from the weight of the pycnometer filled with conductivity water at 25.00 ± 0.01°. All weighings were corrected for air buoyancy.

Viscosity of 3,5-Dinitrobenzoic Acid Solutions.—The viscosity of 3,5-dinitrobenzoic acid solutions relative to pure acetonitrile was measured with an Ostwald viscometer of 15.5 ml. capacity. The efflux time was 73.7 sec. with acetonitrile at 25°.

The conductances of triethylamine in 0.35 *M* dinitrobenzoic acid (Table II) were corrected for the viscosity effect assuming the Walden relation to hold $\eta_{\text{soln.}} \Sigma \lambda_{\text{ionsolv.}} = \eta_{\text{soln.}} \Sigma \lambda_{\text{ionsolv.}}$, where *i* denotes a particular ion and the subscripts solv. and soln. refer to pure acetonitrile and solution, respectively. In the conductometric titration the viscosity effect was negligible except in titrations of 0.0619 *M* 3,5-dinitrobenzoic acid and 0.0561 *M* sulfuric acid solutions in which η equals 0.364 and 0.363 cp., respectively, at 25°. The viscosity of the pure solvent is 0.345 cp. at 25°.

Spectrophotometric Titrations.—A 1.8 cm. Pyrex cylindrical glass stoppered cell was used in all spectrophotometric titrations. A Beckman Model B spectrophotometer operated at sensitivity 3 and slit width 0.1 to 0.3 mm. was used. Since room temperature did not fluctuate more than 0.2° during a titration, no thermostat was required.

Determination of Solubility of Potassium 3,5-Dinitrobenzoate in the Presence of 3,5-Dinitrobenzoic Acid.—The solid acid was weighed in a 10 ml. volumetric flask, approximately 50 mg. of solid potassium 3,5-dinitrobenzoate added and the flask filled to the mark with acetonitrile. The flask and contents were shaken in a mechanical shaker operated at 270 oscillations/min. for 6 hours at 29° and set aside for 10 hours in a water bath held at 25.00 ± 0.02°.

A 1 ml. aliquot of the saturated solution was pipetted into the spectrophotometer cell and 4 ml. of acetonitrile added. The solution was made 1.4 × 10⁻⁵ *M* in *o*-nitro-*p*-chloroaniline and titrated spectrophotometrically with 0.489 *M* perchloric acid (in anhydrous acetic acid) as described for the tetraethylammonium salt.

Results

Ionic Mobilities.—In previous work $\lambda_{\text{H}_2\text{SO}_4}$ was found to be 90⁸ and $\lambda_{\text{H}_2\text{SO}_4 \cdot \text{HSO}_4^-}$ 65.⁶ From Λ vs. \sqrt{c} plots of the conductance data of the rather extensively dissociated salts *n*-butylammonium picrate and tetraethylammonium 3,5-dinitrobenzoate (Table I) Λ_0 values of 188 and 186, respectively, were obtained. The experimental Onsager slopes were 3100 and 3300 as compared to the calculated slopes of 368 and 367, the difference indicating considerable association of both salts at higher concentrations. With either salt Fuoss and Kraus plots did not yield straight lines at concentrations greater than 0.001 *M*. The conductance then was greater than expected on the basis of ion pair dissociation, indicating ion triplet formation.

TABLE I
CONDUCTANCE OF SALTS IN ACETONITRILE

<i>n</i> -Butylammonium picrate <i>M</i> × 10 ⁴	Λ	Tetraethylammonium 3,5-dinitrobenzoate	
		<i>M</i> × 10 ⁴	Λ
0.833	159.0	0.387	194
1.667	150.0	0.968	162
3.33	137.0	1.94	150
8.33	121.1	3.87	142
16.67	108.5	9.68	133.4
33.3	93.4	19.4	126
		38.7	117

$\Lambda_0 = 188$

$\Lambda_0 = 186$

Using Walden's¹¹ values of 78 and 86 for λ_{Pi^-} and $\lambda_{\text{Et}_4\text{N}^+}$, we obtain $\lambda_{\text{n-BuNH}_3^+} = 110$ and $\lambda_{\text{3,5-dinitrobenzoate}} = 100$.

Mobility of AHA⁻: BuNH₃⁺HSO₄⁻H₂SO₄.—The dissociation constant of this salt was estimated from Fuoss and Kraus plots of the data in the conductometric titration curves between 0 and 35% titrated. After using the method of successive approximations discussed in the Introduction, corrected plots yielded a value of the intercept of 0.0062 and a slope of 0.0375, from which $K_{\text{BH}^+\text{AHA}^-} = 1.0 \times 10^{-2}$ and $\Lambda_{\text{0BH}^+\text{AHA}^-} = 160$ are obtained. From the previously determined values of $\lambda_{\text{0BuNH}_3^+} = 110$ and $\lambda_{\text{0H}_2\text{SO}_4 \cdot \text{HSO}_4^-} = 65^6$ we obtain a value of $\Lambda_0 = 175$. Considering the limitations in accuracy of the method of successive approximations the agreement between the two values is fair. In the calculation of the conductometric titration curves the more accurate value of $\lambda_{\text{0H}_2\text{SO}_4 \cdot \text{HSO}_4^-} = 65$ was used.

Et₃NH⁺DNB⁻·DNBH.—Table II presents conductance data corrected for viscosity effect of triethylamine in a concentration range between 0.0014 and 0.017 *M* in 0.35 *M* 3,5-dinitrobenzoic acid. All of the salt may be considered present as the conjugate form BH⁺AHA⁻. The viscosity of the 0.35 *M* dinitrobenzoic acid solution was 0.412 cp. as compared to 0.345 cp. of the pure solvent. The specific conductance of the 0.35 *M* solution of the acid was 1.46 × 10⁻⁶ ohm⁻¹ cm.⁻¹ and is negligibly small. A Fuoss and Kraus plot of the data in Table II gives an intercept of 0.00754 corresponding to $\Lambda_0 = 133$. Taking Walden's value $\lambda_{\text{0Et}_3\text{NH}^+} = 87$ we obtain $\lambda_{\text{0AHA}^-} = 133 - 87 = 46$. It is of interest to note that λ_0 of the corresponding conjugate ion of bisulfate is 65. The smaller value found for the conjugate dinitrobenzoate ion may be attributed to its larger size. The slope of the above Fuoss and Kraus plot was 0.00184, corresponding to a dissociation constant $K_{\text{BH}^+\text{AHA}^-}$ of the order of 3 × 10⁻².

TABLE II
CONDUCTANCE OF TRIETHYLAMINE IN 0.350 *M* 3,5-DINITROBENZOIC ACID

Concn. of amine (<i>M</i>)	Λ
0.0014	119.4
.0030	107.0
.0057	99.0
.0114	97.0
.0171	82.2

$\Lambda_0 = 133$

Conjugation Constants K_{AHA^-} .—For the bisulfate sulfuric acid conjugate ion the previously found⁶ value of 1.0 × 10⁸ was used. The corresponding value for the conjugated 3,5-dinitrobenzoate ion was calculated from solubility data of potassium 3,5-dinitrobenzoate in solutions of varying concentrations of the acid. The data are presented in Table III. From the

TABLE III
SOLUBILITY OF POTASSIUM 3,5-DINITROBENZOATE IN SOLUTIONS OF 3,5-DINITROBENZOIC ACID

Analytical acid concn., <i>c_a</i>	Solu- bility, <i>s</i> <i>M</i> × 10 ²	<i>f</i> ²	$K_{\text{AHA}^-} \times 10^4$
0	0.314 ^a	0.930	..
0.00302	1.80	.739	(3.2)
.00600	2.45	.714	2.1
.0106	2.94	.680	1.4
.0190	4.52	.617	1.5
.0347	7.38	.540	2.0
		Av.	1.7 (neglecting top value)

^a K_{sp} taken as 5.3 × 10⁻⁸.

solubility of the salt in pure solvent a value of the solubility product $K_{\text{sp}} = 5.3 \times 10^{-8}$ was calculated. The values of K_{AHA^-} are given in the last column and were

(11) P. Walden and E. J. Birr, *Z. physik. Chem.*, **144**, 269 (1929).

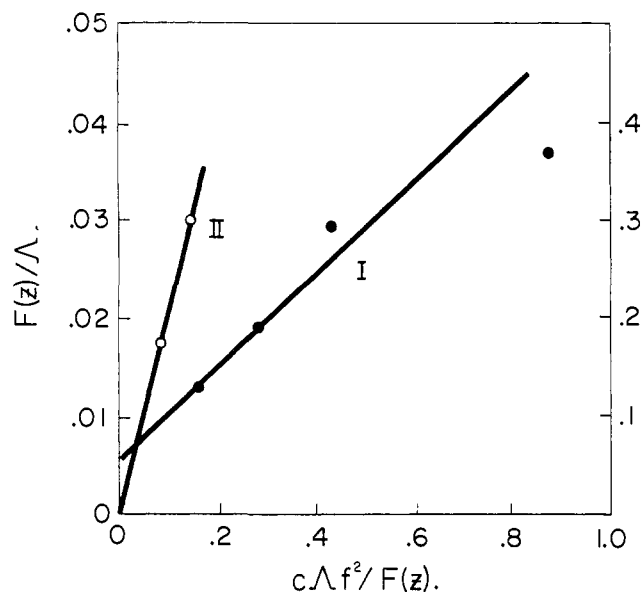


Fig. 1.—I, Fuoss and Kraus plot of *n*-butylammonium bisulfate (at 100% titrated), slope = 0.0480, intercept *ca.* 0.005; II, Fuoss and Kraus plot of triethylammonium 3,5-dinitrobenzoate (at 120% titrated), slope = 1.99, intercept *ca.* 0. Left-hand scale refers to I, right-hand scale to II.

found from the expression⁶

$$K_{\text{AHA}^-} = \{s - [K^+A^-]\}^2 / K_{\text{sp}}(c_a - c_a)$$

in which *s* is the solubility of the salt and *c_a* the analytical concentration of the acid. The salt K^+AHA^- was assumed to be completely dissociated in saturated solution of KA in the presence of acid.

The value of the concentration of the undissociated salt $[K^+A^-]$, a constant, was found from the dissociation constant of the salt, $K_{K^+A^-}$. The equivalent conductance of the saturated solution in pure solvent was found equal to 138. Taking Walden's¹¹ value of $\lambda_{0K^+} = 86$ and of $\lambda_{03,5\text{-dinitrobenzoate}^-} = 100$, we find $\lambda_{0K^+A^-} = 186$ and $K_{K^+A^-} = 2.6 \times 10^{-4}$.

Dissociation Constants of BH^+A^- ($K_{BH^+A^-}$). $BuNH_3^+HSO_4^-$.—A Fuoss and Kraus plot was made of the conductance of solutions in the conductometric titration at 100% neutralization (considering the acid as monobasic). The acid and base are strong enough that acid-base dissociation of the salt can be neglected.

The plot in Fig. 1 has an intercept of 0.051 and a slope of 4.8×10^{-2} , corresponding to a dissociation constant of 5×10^{-4} .

$Et_3NH^+DNB^-$ —In the titrations of 3,5-dinitrobenzoic acid with triethylamine there is slight disproportionation of the salt into acid and base at 100% neutralization. This is evident from the decrease of the conductance upon further addition of base (Fig. 3). After addition of the equivalent of 120% base to the acid the conductance became constant. A Fuoss and Kraus plot was constructed (Fig. 1) from the data of the conductance at the point where the equivalent of 120% of base was added. The salt appears to be slightly dissociated and the intercept is too small to provide an accurate value for $\lambda_{0Et_3NH^+A^-}$. However, its value is found from the values of $\lambda_{0Et_3NH^+}$ and λ_{0A^-} given above and is equal to 186. From this and the slope of the plot of 1.98, $K_{Et_3NH^+A^-}$ is calculated to be 1.2×10^{-5} .

Calculated and Experimental Titration Curves.—The results obtained in the neutralization of sulfuric acid with *n*-butylamine are presented in Fig. 2 and 3,5-dinitrobenzoic acid with triethylamine in Fig. 3. No effort has been made to analyze the curves with sulfuric acid (Fig. 2) beyond 100% neutralization (to

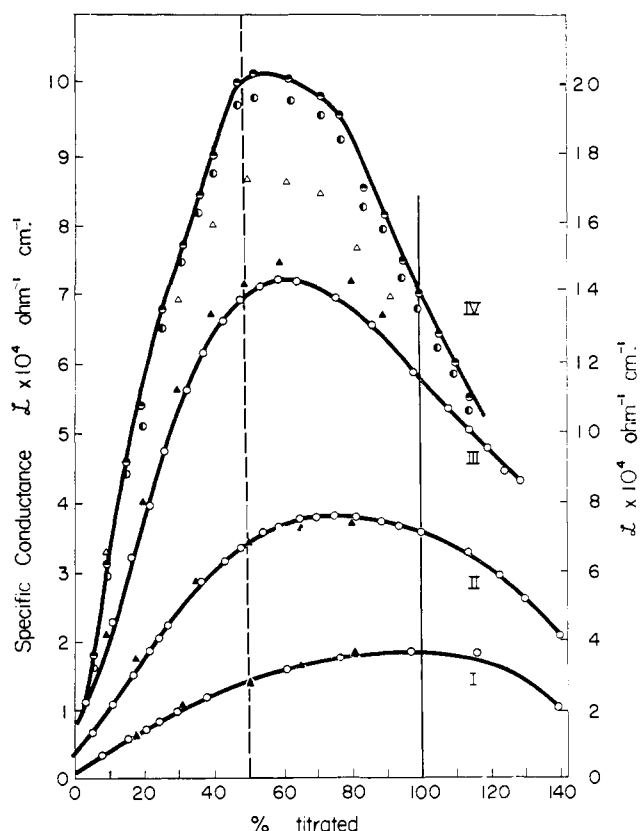


Fig. 2.—Conductometric titration of sulfuric acid with *n*-butylamine: I, 0.00261 *M* H_2SO_4 ; II, 0.00744 *M* H_2SO_4 ; III, 0.0187 *M* H_2SO_4 ; IV, 0.0561 *M* H_2SO_4 . Curves I, II and III, O, experimental points, curve IV O experimental points uncorrected for viscosity, ● corrected for viscosity; ▲ calculated points, curves I, II and III; Δ curve IV. Left hand scale refers to curves I, II and III and right hand scale to curve IV.

bisulfate). The decrease in conductance beyond this point is attributed to formation of very slightly dissociated normal sulfate $(BH^+)_2SO_4^{2-}$. The decrease is more pronounced the more concentrated the solution. At all sulfuric acid concentrations used precipitation of the normal sulfate occurred after addition of the equivalent of 130 to 150% of base to the acid.

A summary of the constants used in the calculation of the theoretical curves is given in Table IV. As is

TABLE IV
CONSTANTS USED IN CALCULATION OF TITRATION CURVES

	$H_2SO_4-n-BuNH_2$	3,5-Dinitrobenzoic acid- Et_3N
$K_{BH^+A^-}$	$5.0 \times 10^{-4}{}^a$	$1.2 \times 10^{-5}{}^a$
K_{AHA^-}	1.0×10^{3b}	1.7×10^{2b}
$K_{BH^+AHA^-}$	1.0×10^{-2c}	3.0×10^{-2c}
λ_{0BH^+}	110 ^d	88 ^e
λ_{0AHA^-}	65.0 ^f	46 ^g
λ_{0A^-}	90.0 ^h	100 ^h

^a From conductance data at 100% titrated; ^{a'} at 120% titrated. ^b From solubility data of alkali metal salt in presence of acid. ^c From conductance data from 0 to 30% titrated; ^{c'} from Table II. ^d From conductance data of $n-BuNH_3^+Pi^-$. ^e From Walden's conductance data of $Et_3NH^+Pi^-$. ^f From ref. 6. ^g From Table II. ^h From conductance data of Et_3NA (Table I).

evident from the Introduction, the calculations are fairly involved. As an example we present in Table V the calculated values of the ionic species and of the total conductance in the titration of 0.0187 *M* 3,5-dinitrobenzoic acid with triethylamine. Good agreement between calculated and experimental conductances is found except in the titration of 0.0561 *M* sulfuric acid,

TABLE V
CALCULATED TITRATION CURVE OF 0.0187 M 3,5-DINITROBENZOIC ACID WITH TRIETHYLAMINE

% titrated	[BH ⁺] M × 10 ³	f ^a	[BH ⁺ A ⁻] M × 10 ³	[A ⁻] M × 10 ³	[BH ⁺ A ⁻] M × 10 ³		[HA] M × 10 ³	λ _{BH⁺}	λ _{A⁻}	λ _{AHA⁻}	λ _{BH⁺AHA⁻} ^a	Specific conductance	
					M × 10 ⁴	M × 10 ³						L _{calcd.} × 10 ⁴	L _{ob.d.} × 10 ⁴
10	1.33	0.80	0.52	0.60	0.47	1.32	15.5	121	1.61	1.90
20	2.33	.72	1.28	0.92	1.30	2.32	12.7	116	2.71	2.83
30	3.00	.67	2.41	1.44	2.0	2.98	11.0	114	3.42	3.38
50	3.27	.66	5.85	3.26	2.3	3.24	5.9	114	3.74	3.71
70	2.85	.67	10.0	6.31	1.7	2.70	2.7	77	90	38	..	3.28	3.20
85	1.38	.72	13.2	11.3	0.9	1.92	0.9	79	91	39	..	2.46	2.34

^a Contribution of A⁻ to conductance neglected.

where the experimental values (corrected for viscosity) near the maximum are about 20% higher than the calculated values. This difference probably can be attributed to ion triplet formation.

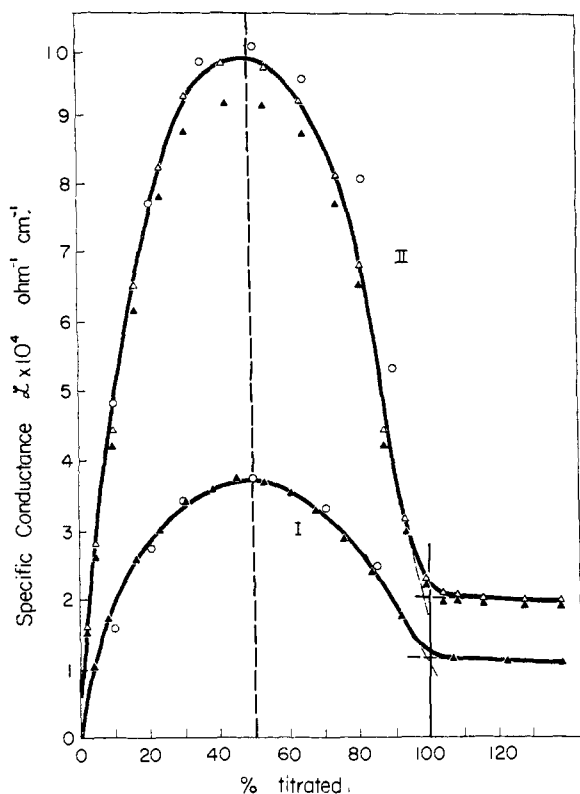


Fig. 3.—Conductometric titration of 3,5-dinitrobenzoic acid with triethylamine: I, 0.0187 M acid; II, 0.0619 M acid; ▲ experimental points, Δ corrected for viscosity in II, ○ calculated points.

Discussion

A general qualitative statement can be made regarding the location of the maximum in conductometric titration curves in acetonitrile of moderately strong acids with moderately strong bases. When the contribution of A⁻ to the conductance remains much smaller than that of AHA⁻ up to 70 to 80% titrated, the maximum appears at 50% neutralization or close to the right of this point. A large value of K_{AHA⁻} and a small value of K_{BH⁺A⁻} are favorable in obtaining a large ratio of [AHA⁻]/[A⁻]. This is the situation in the titration of 3,5-dinitrobenzoic acid (Fig. 3), where the pronounced maximum is found at 50% neutralization. When the above conditions do not hold the maximum becomes less pronounced and shifts in the direction of the equivalence point. (Compare the titration curves of 0.0187 M sulfuric and 3,5-dinitrobenzoic acids in Fig. 2 and 3 and the values of K_{BHA} and K_{AHA⁻} in Table IV.)

For a given acid-base titration system at a given percentage neutralized [A⁻]/[AHA⁻] increases with dilution, as is evident from equation 1. The maximum then shifts closer to the end-point and becomes less acute with increasing dilution. Ultimately, no maximum is found, as is evident from the shape of the titration curves of very dilute sulfuric acid solutions (Fig. 2).

In the conductometric titration of 3,5-dinitrobenzoic acid with triethylamine (or similar bases) an approximate end-point is found at the point where the conductance becomes almost constant. An end-point closer to the equivalence point then is found from the point of intersection of the horizontal conductance line beyond 120% neutralization and the line which is tangent to the titration curve at 80 to 85% (referred to the first approximate end-point; see dotted lines in Fig. 3). The error in locating the end-point is within 1 to 2%. The tangent should not be drawn in the immediate vicinity of the end-point because of acid-base dissociation of the salt.