[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Analytical Determination and Conductance of Sulfuric Acid in Anhydrous Acetic Acid

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An accurate method of analyzing very dilute solutions of sulfuric acid in anhydrous acetic acid is essential for cryoscopic studies of such solutions. The customary acid-base titration is impossible because of the acid nature of the solvent. Gravimetric determination as barium sulfate is not feasible because of the possibility of adsorption of acetic acid on the precipitate. The corresponding conductivity titration, however, yielded a satisfactory analytical method. To avoid the introduction of foreign ions which would disturb the conductivity, barium acetate was selected as the source of barium ion.

The specific conductances of acetic acid–water mixtures were investigated to find the most suitable dilution where the errors caused by absorption of moisture during titration are at a minimum. The specific conductances (Table I) when plotted against percentage of acetic acid (Fig. 1) yield a curve with a maximum at about 18% acetic acid, which falls off sharply on each side of this point, flattening out at about 80% acetic acid with an asymptotic approach to the abscissa. An 18% solution should therefore be least sensitive to variations in water content. Unfortunately, the conductivity titration curves for this solvent yielded a poorly defined intersection (Fig. 2A). For a solvent of 50% acetic acid and 50%'water, the initial points obtained with small additions of the barium acetate solution when plotting the reciprocal of the resistance against the amount of solution, fell on a straight line (Fig. 2B), but after the equivalence point was passed all the points were on a curve. The conductivity titration curves obtained in 75% acetic acid to 25% water mixture yielded an intersection sufficiently well defined to give a precision of two or three parts per thousand (Fig. 2C).

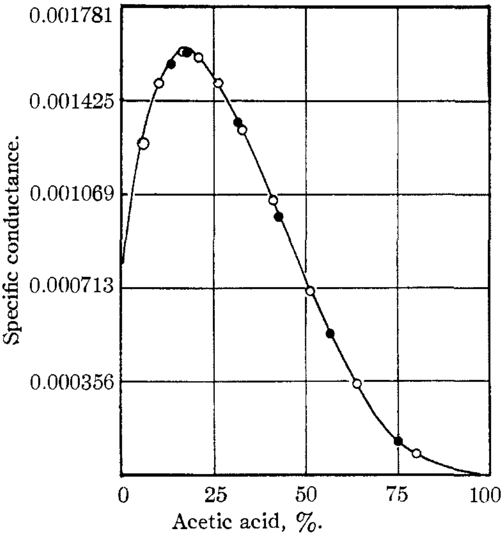

Fig. 1.—Specific conductance of acetic acid–water mixtures.

A conductivity cell of 200 cc. capacity with electrodes 1 sq. cm. in area is suitable for titrations of 0.005 molal sulfuric acid (the most dilute analyzed). The barium acetate solution was prepared by dissolving Kahlbaum c. p. barium hydroxide in the calculated amount of pure acetic acid and water, and was standardized conductimetrically in the same manner as it was to be used. The final procedure involved placing 50 cc. of 0.01000 *M* aqueous sulfuric acid in the conductivity cell, adding 150 cc. of pure acetic acid—a considerable contraction in volume occurs—and titrating the contents with 0.5 *M* barium acetate solution from a weight buret in approximately 100-milligram portions.

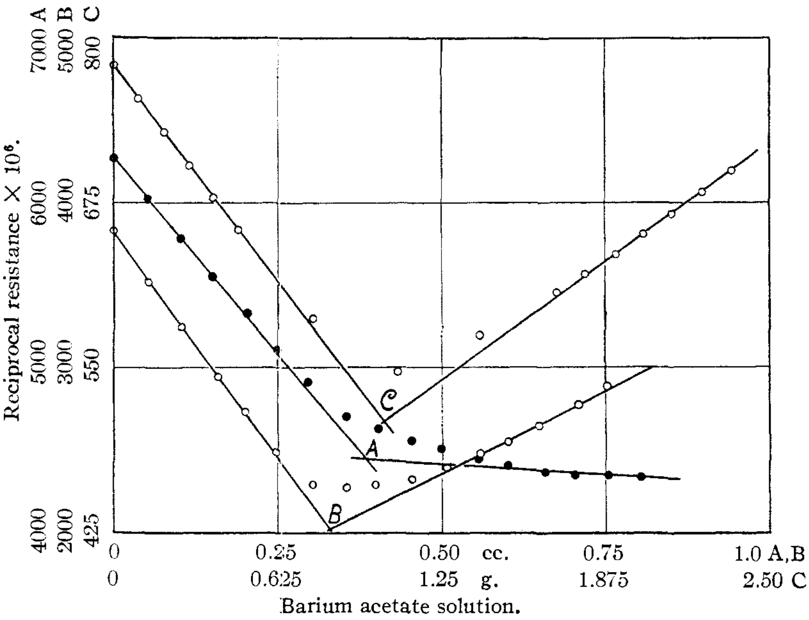

Fig. 2.—Conductivity titrations of sulfuric acid in: (a) 20% acetic acid–80% water; (b) 50% acetic acid–50% water; and (c) 75% acetic acid–25% water solvents.

The exact point of intersection was determined algebraically from the equations fitting the linear portions of the experimental curves of the type illustrated in Fig. 2C.

It is important that the determination of the unknown be carried out under approximately the same conditions as employed in standardizing the known solution, because of "electrolyte effects." Thus, if the concentration of the sulfuric acid was doubled, the barium acetate required would not be exactly twice that for the first solution. However, if the concentrations of sulfuric acid in duplicate experiments agreed to within 5%, the titers checked to 0.2%. The resistances of the known and un-

TABLE I

SPECIFIC CONDUCTANCE OF ACETIC ACID-WATER MIXTURES AT 25°

Acetic acid, %	Specific conductance, mhos
	Series A
100	1.4×10^{-8}
75	0.000136
56.2	.000537
42.2	.000984
31.6	.001333
23.7	.001392
17.8	.001611
13.3	.001563
	Series B
100	1.4×10^{-8}
80	0.000077
64	.000346
51.2	.000700
41.0	.001042
32.8	.001312
26.2	.001492
21.0	.001588
16.8	.001613
10.1	.001492
6.0	.001260

TABLE II

MOLAL CONDUCTANCE AT 25° OF SULFURIC ACID IN ANHYDROUS ACETIC ACID

(M. p. 16.60°; $\kappa = 1.4 \times 10^{-8}$ mhos)

Molality	Molal conductance
	Series 1
0.00502	0.106
.00496	.0842
.00946	.0686
.00987	.0701
.0494	.0498
.0510	.0530
.0982	.0701
	Series 2
0.1003	0.0707
.1001	.0748
.0481	.0552
	Series 3
0.01004	0.0730
.01947	.0543
.01948	.0540
.0369	.0507
.0400	.0532
.0795	.0560
.0805	.0557

known solutions must also agree within 10% of each other in order to obtain the precision desired. A preliminary determination is therefore necessary.

Conductance measurements also were carried out on solutions of sulfuric acid in anhydrous acetic acid. The results are given in Table II and plotted in Fig. 3. The curve follows the general type predicted by Walden[1] for solvents of low dielectric constant. A Washburn type of cell was used for these measurements.

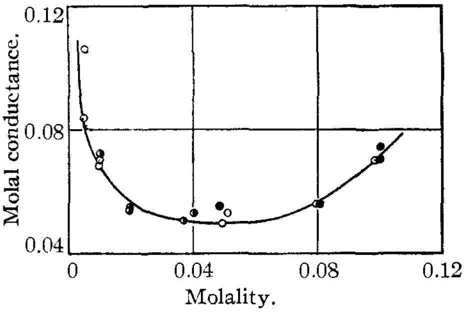

Fig. 3.—Molal conductance of sulfuric acid in anhydrous acetic acid.

Since completing this work (Spring, 1932), Hall and Voge[2] have published the complete conductance curve for the binary system H_2SO_4-CH_3COOH (m. p. 16.63° and $\kappa = 3 \times 10^{-8}$ mhos at 25°). Our curve parallels theirs very closely, but is displaced above it by an amount which would correspond to the presence

(1) Paul Walden, "Salts, Acids and Bases," McGraw-Hill Book Co., Inc., New York, 1929.

(2) Hall and Voge, THIS JOURNAL, **55**, 239 (1933).

of only 0.02% water, if the source of the difference is attributed entirely to moisture. Our solutions stood for a few days in well-stoppered, ordinary glass bottles which had been used for acetic acid solutions for several months previously. They were protected by beakers sealed with paraffin.

The measurements were made on apparatus[3] of the a. c. bridge type consisting of the following parts: a 1000-cycle microphone hummer, a Kohlrausch slide wire (Leeds and Northrup Co.), non-inductive type resistance (Leeds and Northrup Co.), accurate to 0.05%, a variable air condenser across the resistance box to balance the capacity of the cell, and a two-stage audio amplifier with headphones matched to the frequency of the oscillator. The center of the bridge is grounded and all leads are shielded. The conductivity cell is placed in a thermostat which is constant to 0.005°.

Conclusions

1. A conductivity method is described for the precise determination of small quantities of sulfuric acid when dissolved in anhydrous acetic acid.

2. The specific conductances of the complete range of acetic acid–water mixtures have been determined.

3. The molal conductances of solutions of 0.005 to 0.10 M sulfuric acid in anhydrous acetic acid were determined. The data agree very well with the recent measurements of Hall and Voge.

(3) Kindly loaned to us by Professor J. J. Beaver of this Department.

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The Ionization Constant of Monochloroacetic Acid, at 25°, from Conductance Measurements[1]

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In sufficiently dilute aqueous solution the thermodynamic ionization constant of a weak acid, HA, is given by the equation

$$K = \gamma^2 C_i^2/(C - C_i) = \gamma^2 K' \tag{1}$$

where γ is the geometrical mean activity coefficient, C_i is the concentration of the ionized portion, and C is the total concentration of the acid. K' is the usual concentration (or dilution) constant. Evaluating γ by means of the limiting law of Debye and Hückel,[2] taking the dielectric constant for water at 25° as 78.56 (the mean of the results of Drake, Pierce and Dow[3] and Wyman),[4] we may write

$$\log K = \log K' - 1.013 \sqrt{C_i} \tag{2}$$

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(1) This paper contains material which represents part of the dissertation submitted by Theodore W. Langer to the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1931. The authors wish to acknowledge their indebtedness to Lawrence S. Darken and Harry F. Meier, who contributed the measurements on hydrochloric acid and its sodium salt.

(2) Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

(3) Drake, Pierce and Dow, *Phys. Rev.*, **35**, 613 (1930).

(4) Wyman, *ibid.*, **35**, 623 (1930).