[CONTRIBUTION FROM THE LABORATORY OF INORGANIC CHEMISTRY, DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Electrical Conductivities of Mixtures of Sulfuric Acid, Acetic Acid and Water

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Introduction

As part of the general program of acidity studies from this Laboratory, a rather careful investigation has been made of the highly acid homogeneous system: sulfuric acid, acetic acid, water. The study has included measurements of conductivities, electromotive forces, vapor pressures and colorimetric measurements. Some freezing points have been determined, and the results of others recalculated. Other investigators who have recently studied certain aspects of this problem include Hall and Conant,[1] Hall and Werner,[2] Hantzsch and Langbein,[3] Hutchison and Chandlee,[4] Hammett and Deyrup,[5] James Kendall,[6] La Mer and Eichelberger[7] as well as Dr. Sprinkle and Mr. Freeman of this Laboratory.

The present paper describes the conductance measurements, and is divisible into three parts: (I) the conductance of dilute solutions of sulfuric acid in acetic acid; (II) concentrated solutions, and (III) conductivities in the ternary system sulfuric acid–acetic acid–water.

I. Dilute Solutions

A. Apparatus and Materials.—The resistances were measured by means of a Jones[8] bridge manufactured by Leeds and Northrup. A simple Hartley oscillator with a 201A tube, operating at 1400 cycles per sec., was used, as well as a two-stage transformer-coupled audio frequency amplifier and head phones. The oscillator and amplifier were separated from the bridge and each other and (with all leads) completely shielded. Absolutely silent minima and precisions of the order of 10^{-6} were readily obtained. Standard Oil Company "Finol" was used in the thermostat, which was heated by a bare wire and controlled by a mercury-in-glass regulator with oscillating contact. The bath was set at 25 ± 01° with a B. S. standard thermometer and held a constant temperature within 0.005°. The cells were made of glass with platinum electrodes and were of the usual design. Their constants were obtained by means of the 0.01D solution of Parker[9] prepared from "equilibrium" water and purified potassium chloride. Solutions were made up and kept with every care to exclude moisture before and during the measurements.

Acetic acid was prepared by fractional distillation in an all-glass still of glacial acid obtained from the Niacet Chemical Company. That used had a melting point of 16.63° and a specific conductance (κ) of 3×10^{-8}. In the course of its preparation freezing

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[1] Hall and Conant, THIS JOURNAL, **49**, 3047 (1927).

[2] Hall and Werner, *ibid.*, **50**, 2367 (1928).

[3] Hantzsch and Langbein, *Z. anorg. allgem. Chem.*, **204**, 193 (1932).

[4] Hutchison and Chandlee, THIS JOURNAL, **53**, 2881 (1931).

[5] Hammett and Deyrup, *ibid.*, **54**, 2721 (1932).

[6] Kendall, *ibid.*, **43**, 1826 (1921).

[7] La Mer and Eichelberger, *ibid.*, **54**, 2763 (1932).

[8] Jones and Josephs, *ibid.*, **50**, 1049 (1928); see also Dike, *Rev. Sci. Instruments*, **2**, 379 (1931).

[9] Parker, THIS JOURNAL, **46**, 312 (1924).

points as high as 16.65° were recorded and values of κ as low as 1.05×10^{-8}. There is not a simple relationship between maximum freezing point and minimum conductance. This point is being further studied.

Sulfuric acid was obtained by mixing reagent quality fuming acid with 95% acid until a maximum freezing point of 10.46° was reached. This acid had $\kappa = 1.02 \times 10^{-2}$, which may be compared to the values 0.97×10^{-2} obtained by Hantzsch and by Bergius,[10] and 1.04×10^{-2} obtained by Lichty.[11]

Acetic anhydride from Merck was fractionally redistilled. The corrected boiling point was 138.2° and $\kappa = 1.94 \times 10^{-7}$.

B. Results.—The results are shown in Table I. No solvent correction has been made, and it is probable that none should be made. V is the molar dilution in liters, and λ is as usual $1000 V\kappa$. The results are calculated for sulfuric acid as a uni-univalent electrolyte as it certainly is in these solutions.[1,4,7]

In order to detect possible errors and because of the interest attached to such measurements, the effects of water and of acetic anhydride on the conductance were studied. For the former, acetic acid containing a very small amount of water (0.08% by the freezing point curve of Richmond and England)[12] was used as solvent. The results are shown in Table II.

TABLE I

CONDUCTIVITY OF SULFURIC ACID IN ACETIC ACID AT 25°

M. p. of solvent, 16.63°; sp. cond. 3×10^{-8}

Soln. no.	Concn. mole/l.	$\sqrt{\text{Concn.}}$	V, liter/mole	Sp. cond. $\kappa \times 10^6$	Mol. cond.
1 d	0.924	0.9612	1.083	1531	1.653
2 d	.7345	.8570	1.362	856.1	1.165
3 d	.2220	.4712	4.505	26.52	0.1194
4 d	.1105	.3324	9.050	6.142	.0553
5 v	.1075	.3280	9.300	6.075	.05651
6 v	.02231	.1493	44.83	1.017	.04562
7 v	.01115	.1056	89.66	0.6274	.05625
8 v	.005576	.07465	179.3	.4012	.07194
9 v	.002788	.05287	358.6	.2848	.1021
10 v	.001394	.03732	717.3	.1943	.1394
11 v	.000697	.02644	1434.6	.1468	.2105

TABLE II

THE CONDUCTIVITY OF SULFURIC ACID IN "WET" ACETIC ACID

M. p. of solvent, 16.47°; sp. cond. 8.2×10^{-8}

Soln. no.	Concn. mole/liter	$\sqrt{\text{Concn.}}$	V, liter/mole	Sp. cond. $\kappa \times 10^6$	Mol. cond.
1 v	0.08078	0.2842	12.38	6.21	0.07688
2 v	.04038	.2009	24.76	2.801	.06936
3 v	.02019	.1421	49.52	1.477	.07311
4 v	.01010	.1005	99.04	0.9279	.09189
5 v	.005048	.07106	198.1	.6113	.1212

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(10) Hantzsch, *Z. phys. Chem.*, **61**, 257 (1908); Bergius. *ibid.*, **72**, 338 (1910).

(11) Lichty, THIS JOURNAL, **30**, 1834 (1908).

(12) Richmond and England, *Analyst*, **51**, 283 (1926).

Addition of acetic anhydride also caused an increase in the specific conductance. Thus a 0.119 M solution of sulfuric acid in acetic acid had $\kappa = 7.21 \times 10^{-6}$, while when it was made 0.0357 M in acetic anhydride, κ rose to 8.01×10^{-6}. A 0.107 M solution of acetic anhydride in acetic acid had a κ of only 3.91×10^{-8}.

From these facts it is evident that the conductivities recorded in Table I are very near minimum values, and that the solutions contained neither water nor acetic anhydride in appreciable amounts. The data of Tables I and II and also those of Hantzsch and Langbein[3] and of Jones[13] are shown in Fig. 1. A possible reason for the difference between our results and those of the other investigators is suggested by our measurements on "moist" acetic acid solutions. Incomplete drying of the solvent produces just such a fairly uniform increase in conductance as is shown by the other measurements. In Fig. 1 the anomalous decrease of λ with dilution (often previously noted for all types of electrolyte in this solvent) is clearly seen. The complete conductivity curve (not shown, *cf.* Fig. 3), also shows a maximum value of λ in more concentrated solutions. These peculiarities have been discussed by Walden[14] and by Bjerrum[15] among others.

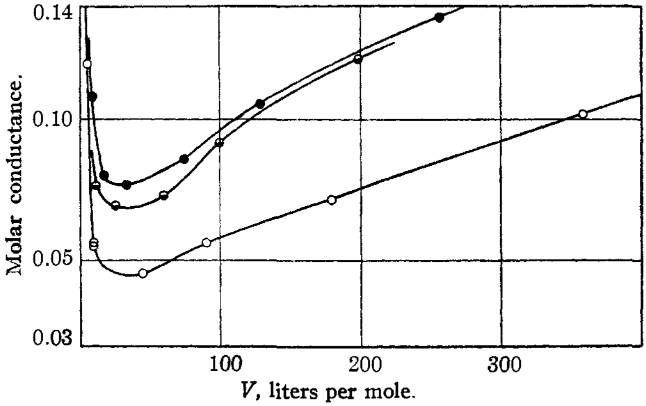

Fig. 1.—Molar conductance of sulfuric acid in acetic acid at 25°: ⊙, Voge; ◒, Voge, solvent containing 0.08% H_2O; ●, Hantzsch and Langbein.

In the most dilute solutions the variation of λ with V is more nearly what would be expected from an ordinary weak electrolyte. A test of this type of behavior is furnished by a plot of $C\lambda$ against $1/\lambda$.[16] If the Ostwald dilution law is obeyed, such a plot should yield a straight line from which both K and λ_0 might be derived. Figure 2 shows such a plot for the five

(13) Jones, *Am. Chem. J.*, **16**, 1 (1894).

(14) Walden, "Leitvermögen der Lösungen," II, III.

(15) Bjerrum, *Ber.*, **62**, 1091 (1929).

(16) Kraus, "Properties of Electrically Conducting Systems," The Chemical Catalog Company, New York, 1922, p. 54.

most dilute solutions of Table I. It is seen that from the conductimetric viewpoint sulfuric acid is a typical weak electrolyte in the most dilute solutions. It is not possible, however, to determine λ_0 or K with any degree of precision from measurements on such high-resistance solutions as these. Even if the accuracy of the measurements were greatly increased this would not be possible. Walden[14] has given two useful generalizations which should establish the order of magnitude of λ_0. These are $\eta\lambda_0$ = const., and $\lambda_0 \partial\lambda/\lambda\partial t$ = const. where η = viscosity and $\partial\lambda/\lambda\partial t$ is the temperature coefficient of the conductivity. By comparison with water as a solvent, these lead to the values $\lambda_0 = 280$ and $\lambda_0 = 70$, respectively, for the conductivity at infinite dilution of $H^+(HSO_4^-)$ in acetic acid. Use of these figures gives values for K ranging in the one case from 3.3 to 3.9×10^{-10} and in the other from 5.3 to 6.2×10^{-9}. While these figures are very approximate, they probably indicate the correct order of magnitude for the dissociation constant.

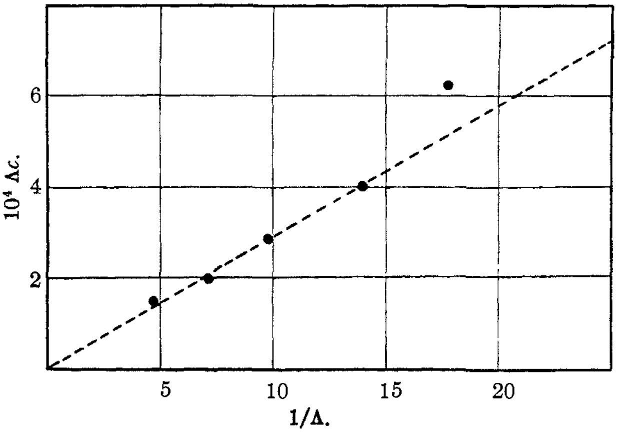

Fig. 2.—Sulfuric acid in acetic and the dilution law.

II. Concentrated Solutions and the Complete Conductivity Curve for the System H_2SO_4–CH_3COOH

This system has been investigated over a small range by Jones[13] and by Hantzsch and Langbein.[8] For these measurements a cell in the shape of an inverted Y was used which had a constant of 18.684 and to which varying amounts of liquid could be added without affecting the cell constant. The procedure adopted was as follows. The cell was cleaned, rinsed, dried at 140° and flushed with dry air. It was then weighed, filled with one component, and weighed again. The other component was added in successive portions from a weight buret, and the two were mixed in the glass-stoppered cell; after cooling at 25° in the thermostat, the conductivity was measured.

In Table III the results are shown. Here the mole fractions are calculated from the weights in air against brass because of the low absolute

TABLE III

SPECIFIC CONDUCTANCES FOR THE SYSTEM H_2SO_4–AcOH AT 25°

Soln. no. n	Mole fract. H_2SO_4 N_2	Sp. cond. $K \times 10^2$	n	N_2	$k \times 10^2$
1	0.000	0.00265	11	0.372	1.113
2	.01282	.00265	12	.404	1.139
3	.04155	.08561	13	.523	1.540
4	.0520	.1531	14	.639	2.945
5	.1133	.6658	15	.737	5.394
6	.175	1.009	16	.835	7.450
7	.258	1.128	17	.929	7.116
8	.277	1.126	18	.960	5.452
9	.307	1.116	19	.990	2.573
10	.325	1.111	20	1.000	1.0

accuracy. The conductivity curve is shown in Fig. 3, together with the viscosity curve of Drucker and Kassel.[17] It adds a little to the favorable evidence for the molecular compound AcOH·H_2SO_4 of which Kendall[6] finds indications in an unpublished freezing point curve, but which Lehrman could not crystallize.[18]

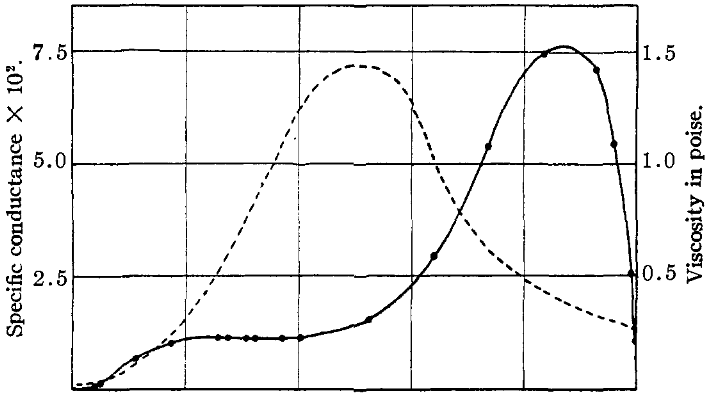

Fig. 3.—Conductance and viscosity of AcOH–H_2SO_4 mixtures: ——— specific conductance curve for the system H_2SO_4–AcOH at 25°; - - - - viscosity curve from Drucker and Kassel at 15°.

Complete explanation of the form of the curve is not possible, but the following factors may be pointed out. Solutions of acetic acid in sulfuric acid conduct better than those of sulfuric acid in acetic acid because of the much higher dielectric constant of sulfuric acid, although this must be

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(17) Drucker and Kassel, *Z. physik. Chem.*, **76**, 367 (1911).

(18) Lehrman, *Trans. Am. Inst. Chem. Engrs.*, **18**, 187 (1926).

partially offset by its greater viscosity. Equal rate of change of conductance in opposite directions caused by increasing concentration and decreasing ionization of acetic acid accounts for the pronounced maximum on the sulfuric acid side. The slight maximum on the acetic acid side doubtless has a similar explanation. The slight central minimum, while apparently arising from the increased viscosity at this point, cannot be separated in origin from the associative tendencies which cause the latter. Kendall[19] has given an excellent discussion of such systems and has pointed out our very incomplete knowledge of them.

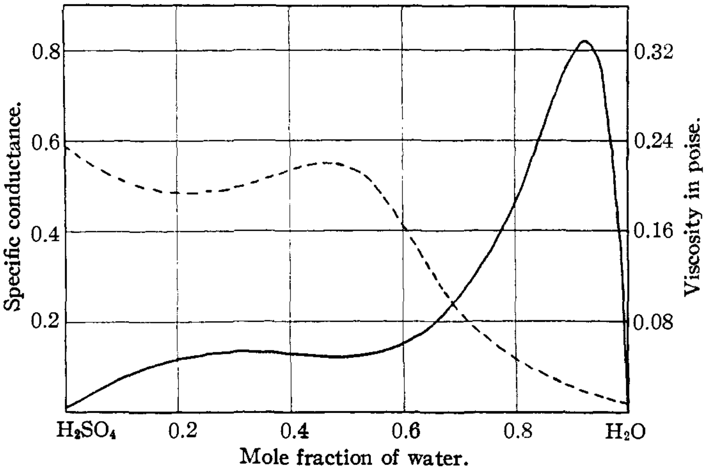

Fig. 4.—Conductance and viscosity of H_2SO_4–H_2O mixtures: ——— specific conductances for the system H_2SO_4–H_2O at 25° (Kohlrausch); - - - - viscosities for the system H_2SO_4–H_2O at 25° ("I. C. T.").

Conductivity curves[20] for the related systems H_2SO_4–H_2O and CH_3CO-OH–H_2O are of almost exactly the same form as that for this system. They are shown, corrected to 25°, and with their viscosity curves, in Figs. 4 and 5.

III. Conductivities for the Three Component System H_2SO_4–H_2O–AcOH

In the hope of more closely relating the highly acid solutions involved, and because of the rather novel interest attached to such measurements, the three component system H_2SO_4–H_2O–AcOH was next investigated conductimetrically. Almost no data exist on such mixtures; a few points of Jones[18] which lie quite close together and which were determined at an unspecified temperature are the only ones to be found in the literature.

In this portion of the research precision was less essential; hence the

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[19] Kendall, Ref. 6, and previous papers.

[20] Landolt-Börnstein, "Tabellen," Hw II, pp. 1075–77.

following procedure was adopted. Mixtures of acetic acid and sulfuric acid were made up by weight in cell 7. Water was then added from a microburet, and on mixing and cooling to 25° the conductivity was measured. The composition of all mixtures was calculated from the weight in air.

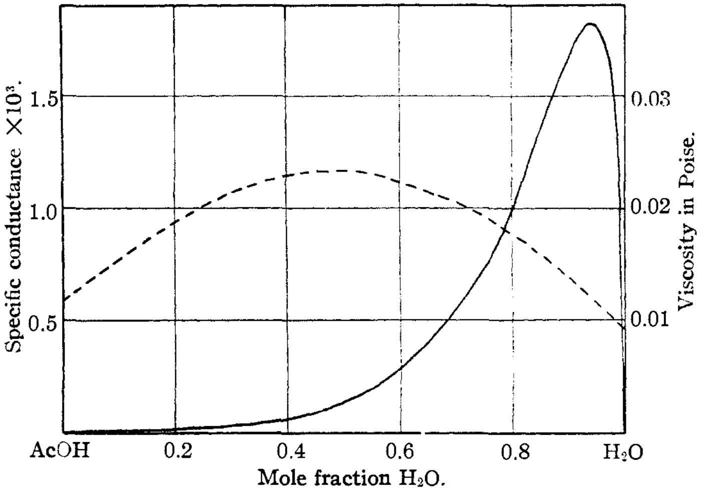

Fig. 5.—Conductance and viscosity of AcOH–H_2O mixtures: ——— specific conductances for the system AcOH–H_2O at 25° (Kohlrausch); - - - - - viscosities for the system AcOH–H_2O at 25° ("I. C. T.").

Results are shown in Table IV, and in Fig. 6 by means of iso-conductive lines. This diagram indicates the interplay of the many factors determin-

TABLE IV

CONDUCTIVITIES IN THE SYSTEM H_2SO_4–AcOH–H_2O AT 25°

Series	No.	Mole fract. H_2SO_4	Mole fract. AcOH	Sp. cond. × 10^2	Series	No.	Mole fract. H_2SO_4	Mole fract. AcOH	Sp. cond. × 10^2
I	1	0.210	0.709	1.180	IV	1	0.592	0.377	2.478
	2	.185	.625	1.397		2	.536	.342	2.568
	3	.140	.472	3.168		3	.470	.300	2.90
	4	.101	.341	8.09		4	.387	.246	3.99
	5	.079	.267	13.14		5	.316	.201	6.28
	6	.0646	.218	17.41		6	.252	.161	10.90
	7	.0475	.160	22.7		7	.194	.123	20.17
II	1	.350	.589	1.22		8	.150	.096	31.3
	2	.266	.449	2.21	V	1	.830	.120	6.654
	3	.204	.344	4.82		2	.751	.109	6.56
	4	.152	.256	11.02		3	.667	.097	6.29
III	1	.469	.454	1.598		4	.599	.087	6.13
	2	.419	.406	1.93		5	.527	.076	6.26
	3	.371	.360	2.429		6	.404	.0585	8.60
	4	.314	.305	3.567		7	.316	.046	14.01
	5	.249	.242	6.653		8	.196	.028	33.7
	6	.167	.162	14.44					

ing conductivity in such solutions. Here the trough may be related to loose compound formation or other associative phenomena, while the maxima serve to indicate roughly the points of greatest ion concentration. More complete explanation of these conductivities is not possible at present.

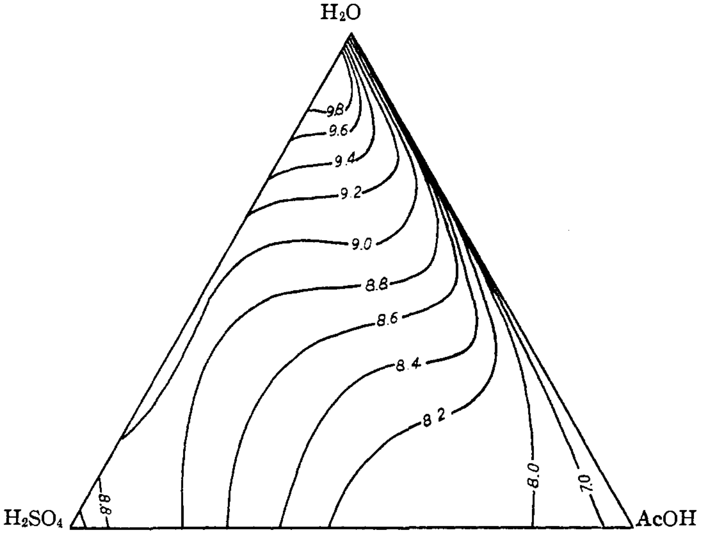

Fig. 6.—Iso-conductive lines showing log specific conductance + 10 for the system H_2SO_4–H_2O–AcOH at 25°; concentrations are in mole fractions.

Attempts to extend the study to the more general system SO_3–H_2O–Ac_2O were not successful. On adding acetic anhydride to 30% fuming sulfuric acid, chemical reaction took place and the solution turned orange in color. It was noted that the resistance was increased on adding the acetic anhydride but no quantitative conclusions could be drawn. These data will be discussed further in later papers dealing with the thermodynamic properties of the system.

Summary

1. The conductance of dilute solutions of sulfuric acid in acetic acid has been carefully redetermined. It is shown that the solute behaves as a typical weak electrolyte and its dissociation constant is tentatively calculated as 10^{-9}.

2. The complete conductance curve is determined for the binary system H_2SO_4–CH_3COOH and discussed in connection with similar curves for the systems H_2SO_4–H_2O and H_2O–CH_3COOH.

3. The complete conductance diagram is given for the system H_2SO_4–CH_3COOH–H_2O.

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