stant nearly twice that of cellulose acetate. An explanation for this difference is suggested, based on their variation in chemical structure.

EAST PITTSBURGH, PENNA. RECEIVED MARCH 26, 1934

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

The Thermodynamic Dissociation Constant of Benzoic Acid from Conductance Measurements

BY FRANK G. BROCKMAN AND MARTIN KILPATRICK

In a contribution from this Laboratory[1] a tentative value of the thermodynamic dissociation constant of benzoic acid, obtained from conductance measurements, was reported. This paper reports a more accurate determination of this constant and compares the results with the Debye–Hückel theory.

Experimental Part

(*a*) **Alternating Current Bridge.**—The bridge used in these measurements differs in certain respects from those more recently described in the chemical literature[2] and a brief discussion of this apparatus follows.

The nucleus about which the bridge was built was a ratio box according to the design of Campbell and Shackelton.[3] The resistance boxes (carefully calibrated on a d. c. bridge by comparison with standards certified by the Bureau of Standards) were completely shielded, and resistors up to and including the 100-ohm decade were of bifilar construction. Resistances from 1000 to 10,000 ohms were obtained by the use of woven wire resistors which have the lowest time factor of any convenient resistors thus far produced. Although the ratio box is equipped with a Wagner grounding arrangement, this was not utilized in this investigation.[4] Any unbalance due to the power source was obviated by a carefully constructed power-transformer with balanced double shields. The shields surrounding the resistance boxes and the cell were removed to sufficiently great distances from the measured impedances so that the distributed capacities were negligible as shown by the absence of any variation of the measured resistance with a change in the frequency of the a. c. source from 1050 to 2730 c. p. s. In all instances the Grounded Point type bridge was employed. Complete shielding and the use of the Grounded Point type bridge much enhance the ease with which measurements can be made.

Resistance components were measured to 0.01 ohm. No resistances measured were less than 400 ohms. Electrolytic resistances greater than 10,000 ohms were shunted by a 10,000 ohm woven wire resistor and the electrolytic resistance computed.

(*b*) **Source of Alternating Current.**—The bridge was supplied alternating current from a shielded vacuum tube generator in which two type 112A tubes were used, the one as an oscillator and the other as an amplifier which serves to isolate the oscillatory system from the associated apparatus. The voltage applied to the bridge never exceeded 3 volts R. M. S. as measured by a thermocouple meter. Experimentation demonstrated that the energy dissipation corresponding to this voltage was low enough to prevent thermal changes in the measured resistance. All measurements were made at a frequency of 1050 c. p. s., but frequent checks at 2730 c. p. s. showed that no frequency error was to be found. Connections with the bridge were effected by a shielded two conductor cable.

(*c*) **Tuned Amplifier.**—The output of the bridge was fed through a shielded conductor pair to a shielded tuned two stage amplifier. Voltage amplification of a high order was obtained by feeding a type 36 screen grid vacuum tube through a tuned impedance into a type 37 triode, which in turn fed the head phones. The resonant frequency of the tuned circuit was determined by a series of fixed mica dielectric condensers.

(*d*) **Cell.**—The cell used in all measurements was a quartz-glass cell after the design of Shedlovsky.[5] The electrodes were platinized by adding successive thin layers of platinum black until the coating was just thick enough to prevent polarization with the most conducting solution to be measured. Such a condition was considered to be realized when, with the solution in the cell, no change in measured resistance occurred with a change in the frequency of the voltage source from 1050 to 2730 c. p. s. The cell was calibrated with a 0.01 "demal" solution of potassium chloride containing 0.74625_3 g. of potassium chloride in 1 kg. of water (weighed in air), which according to Parker and Parker[6] has a specific conductance of 0.0014078_9 ohm^{-1} cm.$^{-1}$ at 25°. On this basis the cell constant was 0.57386. The potassium chloride used was Kahlbaum, for analysis with guarantee, recrystallized twice from hot conductivity water and fused *in vacuo* before weighing.

(*e*) **Temperature Control.**—All measurements were carried out at 25 ± 0.003° by immersing the cell in a thermostat filled with transformer oil.

(*f*) **Conductivity Water.**—Pure water was prepared by redistillation from alkaline permanganate in a still similar to that due to Kraus and Dexter.[7] The conduc-

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[1] Kilpatrick and Chase, THIS JOURNAL, **53**, 1732 (1931).

[2] Jones and Josephs, *ibid.*, **50**, 1049 (1928); Shedlovsky, *ibid.*, **52**, 1793 (1930); Dike, *Rev. Sci. Instruments*, **2**, 379 (1931).

[3] For references see Behr and Williams, *Proc. Inst. Radio Eng.*, **20**, 969 (1932).

[4] Field, General Radio Experimenter, **4**, Jan., 1930, page 1; also, General Radio Experimenter, **6**, Sept., 1931, page 6.

[5] Shedlovsky, THIS JOURNAL, **54**, 1411 (1932).

[6] "I. C. T.," Vol. VI, p. 230.

[7] Kraus and Dexter, THIS JOURNAL, **44**, 2469 (1922).

tivity of the solvent for each experiment is reported in the tables.

(*g*) **Procedure.**—The experimental procedure followed that of Shedlovsky for very dilute solutions.[8]

(*h*) **The Conductivities of Potassium Benzoate Solutions.**—This salt was prepared from Kahlbaum benzoic acid and Baker analyzed potassium carbonate in conductivity water. It was crystallized by concentrating on a water-bath, dried at 110°, recrystallized twice from 95% alcohol and again dried at 110°. The resulting salt was anhydrous and pure as shown by comparison of the weight of potassium benzoate taken, with the weight of potassium carbonate produced by careful ignition at 500°.

In the following tabulation of results, the series designated as a, b, c and d were carried out by using buffered solutions as recommended by MacInnes and Shedlovsky[9] for the reduction of hydrolysis. The acid to salt concentration ratio was about 2.5×10^{-3}. The benzoic acid was added as the fused solid weighed upon a micro balance. To perform the corrections for the acid contribution to the conductances we used a value for the dissociation constant of benzoic acid, at the ionic strengths encountered, which was determined catalytically. The experiment designated as e was performed with unbuffered solutions. The results indicate that the effect of hydrolysis is negligible.

Using Shedlovsky's extended Onsager equation[10] and applying least squares to the Λ_0' *vs.* C line to ascertain the true Λ_0 value and the second constant in the equation, the following equation was derived. It expresses the equivalent conductivity in terms of the concentration with an average deviation of 0.07%

$$\Lambda = 105.88 - 83.87\sqrt{C} + 122.9\ C\ (1 - 0.2274\sqrt{C})$$

Table I is a compilation of the experimental results. Concentrations in all instances are expressed in molarities.

Combining this equation with Shedlovsky's[11] equations for potassium chloride and hydrochloric acid, the equation for "completely dissociated" benzoic acid is

$$\Lambda_e = 382.10 - 146.72\sqrt{C_i} + 193.5\ C_i\ (1 - 0.2274\sqrt{C_i})$$

This equation is used in calculating the dissociation constants of the acid.[12]

TABLE I

	$c \times 10^3$	Λ exptl.		$c \times 10^3$	Λ exptl.
e	0.14817	104.83	e	1.3064	102.94
d	.17340	104.66	b	2.1582	102.30
c	.21917	104.74	e	2.1812	102.17
e	.31433	104.35	d	2.2700	102.23
d	.34255	104.33	a	2.2935	102.15
c	.41719	104.39	d	3.1607	101.63
e	.47891	104.03	e	3.6409	101.19
d	.54738	103.98	b	3.7195	101.24
c	.65105	104.03	a	3.8101	101.16
e	.66011	103.70	d	3.9490	101.19
d	.78659	103.67	d	4.5616	100.86
e	.86904	103.41	a	5.1864	100.45
c	.96098	103.60	d	5.3124	100.51
d	1.0648	103.31	b	5.4760	100.33
c	1.1422	103.37	e	5.5733	100.20
a	1.2096	103.16	d	5.9731	100.21
b	1.2157	103.15	a	6.4051	99.91
d	1.2937	103.06	b	6.9894	99.67

Conductance of water:

Experiment a 4.13×10^{-7} ohm^{-1} cm.$^{-1}$
b 3.55×10^{-7} ohm^{-1} cm.$^{-1}$
c 3.50×10^{-7} ohm^{-1} cm.$^{-1}$
d 4.13×10^{-7} ohm^{-1} cm.$^{-1}$
e 3.46×10^{-7} ohm^{-1} cm.$^{-1}$

(*i*) **The Conductivities of Benzoic Acid Solutions and the Value of the Dissociation Constant.**—Benzoic acid used in these measurements was Bureau of Standards certified acid, fused and cast into rods in small diameter test-tubes. Benzoic acid is, unfortunately, relatively insoluble and the rate with which it dissolves is very slow. We were therefore forced to adopt the following procedure in preparing the stock concentrated solutions. A liter glass-stoppered Pyrex bottle was carefully cleaned, steamed and dried. A quantity of the benzoic acid was transferred from a weighing bottle and the weight of acid determined by difference. The dry Pyrex bottle with the benzoic acid was then weighed, about one liter of conductivity water was introduced and the weight again determined. This bottle with the solute and the solvent was introduced into a slowly rotating device and rotated until complete solution was effected. For a 0.015 molar solution this required about forty-eight hours. Portions of this stock solution were added from a weight buret to conductivity water weighed in the cell. This method is open to the objection that the stock solution is flowed for a comparatively long time across glass surfaces, and may thus be contaminated. This contamination increased the experimental difficulties and made the production of water with a specific conductivity of less than 2×10^{-7} ohm^{-1}cm.$^{-1}$ a necessity in order to obtain reproducible results.

Six conductance determinations were made of more concentrated solutions. These solutions were made externally to the flask-like cell, by weighing water into a clean half-liter Pyrex bottle and then adding a quantity of concentrated solution and reweighing. These solutions were,

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[8] Shedlovsky, THIS JOURNAL, **54**, 1411 (1932).

[9] MacInnes and Shedlovsky, *ibid.*, **54**, 1429 (1932).

[10] Shedlovsky, *ibid.*, **54**, 1405 (1932).

[11] Shedlovsky, *ibid.*, **54**, 1411 (1932).

[12] Davies, *Phil. Mag.*, **4**, 244 (1927).

in turn, poured directly into the cell and measured. We do not pretend that the accuracy of these measurements is as high as our experiments done in more dilute solutions because of this procedure; they are, nevertheless, exact enough to show the "medium effect" reported by MacInnes and co-workers.[13] These experiments are designated as c in the table.

Table II is a compilation of the data for the solutions of benzoic acid.

TABLE II

	$c \times 10^3$	Λ	$\sqrt{C_i} \times 10^2$	log $K_c + 5$	log $K_a + 5$
b	0.090271	212.94	0.71023	0.80539	
a	.095887	209.32	.72576	.80753	0.80019
b	.19112	166.03	.91287	.80906	.79983
a	.21148	160.14	.94315	.81007	.80054
b	.26281	147.66	1.0097	.81035	.80014
b	.38101	127.85	1.1315	.81161	.80017
a	.39045	126.60	1.1399	.81157	.80005
b	.75122	96.679	1.3823	.81409	.80012
a	.76027	96.203	1.3872	.81432	.80030
b	.99902	85.541	1.4998	.81529	.80013
a	1.0729	82.937	1.5305	.81568	.80003
b	1.2878	76.538	1.6110	.81722	.80093
a	1.3218	75.676	1.6229	.81653	.80012
a	1.4915	71.728	1.6786	.81706	.80009
b	1.4952	71.634	1.6795	.81685	.79987
a	1.7037	67.587	1.7417	.81762	
b	1.7673	66.472	1.7592	.81759	
a	1.9039	64.291	1.7959	.81805	
b	2.0494	62.173	1.8324	.81821	
b	2.5069	56.724	1.9362	.81902	
a	2.5377	56.423	1.9429	.81932	
c	3.6833	47.478	2.1479	.81996	
c	3.7186	47.212	2.1522	.81891	
c	4.4369	43.509	2.2569	.82018	
c	7.2213	34.691	2.5728	.82477	
c	13.441	25.637	3.0200	.82209	
c	14.361	24.864	3.0745	.82345	

Conductance of water: Experiment a, 1.69×10^{-7} ohm^{-1} cm.$^{-1}$; Experiment b, 1.57×10^{-7} ohm^{-1} cm.$^{-1}$; Experiments c, varied for different experiments between 3×10^{-7} and 5×10^{-7} ohm^{-1} cm.$^{-1}$

Since the theoretical treatment, by which the logarithm of the classical dissociation constant is derived as a linear function of the square root of the ion concentration, is based upon the Debye–Hückel derivation and since the latter depends upon the assumption of dilute solutions, the extrapolation of the log K_c *vs.* $\sqrt{C_i}$ line must be done with values of log K_c corresponding to low ion concentrations.

Applying least squares to all values for ion concentrations less than $(1.7 \times 10^{-2})^2$ gram-ions per liter, a value of $\bar{5}.79918$ is obtained for the intercept (*i. e.*, the logarithm of the thermodynamic dissociation constant) and 1.079 for the slope. The first value for the set designated as b is definitely at variance with the rest of the data, and the deviation is more than four times that of the average. Again applying least squares, but omitting this one value, one obtains, as log K_a, $\bar{5}.80018$ with slope of 1.011 for the log K_c *vs.* $\sqrt{C_i}$ line. The antilogarithm of $\bar{5}.80018$, 6.312×10^{-5}, is the value for the thermodynamic dissociation constant deduced from these experiments.

The last column in Table II records the log K_a value calculated from the equation

$$\log K_a = \log K_c - 1.011 \sqrt{C_i}$$

for each experimentally determined log K_c. The average deviation is ±0.00018 in the logarithm. Values calculated on the basis of the theoretical slope (1.013) are less than 0.01% from these.[14]

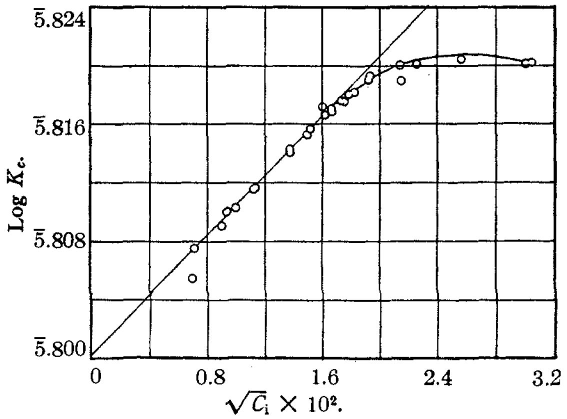

Fig. 1.

All results are represented graphically in Fig. 1. Reference to this figure shows that here, as with acetic acid and monochloroacetic acid,[13] the curve tends to display a maximum at higher concentrations, although in this case the effect is less pronounced since large concentrations cannot be investigated. It will be remarked also that the points begin to deviate from the line at approximately 1.7×10^{-2} for the square root of the ion concentration. During the progress of our research, Ives[15] published the

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[13] MacInnes, Shedlovsky and Longsworth, *Chem. Rev.*, **13**, 29 (1933).

[14] While this investigation was in progress, Jones and Bradshaw, THIS JOURNAL, **55**, 1780 (1933), published a carefully revised set of values for the standard potassium chloride solutions. Many of our calculations had been carried out at that time using the Parker values. Recalculation on the basis of these new values leads to the following results: log K_a = $\bar{5}.80071$, $K_a = 6.320 \times 10^{-5}$, slope of log K_c *vs.* $\sqrt{C_i}$ line, 0.984.

[15] Ives, *J. Chem. Soc.*, 731 (1933).

results of work on weak acids in which he reported accurate relative values of the classical dissociation constants. In this report he notes that the deviation from linearity occurs at about this same concentration. As he states, these experiments were performed principally with the view of substantiating the theoretical slope, which they do, but no great absolute accuracy was attempted. The value deduced for the thermodynamic constant is higher than ours.

Rørdam[16] extrapolated the data of Schaller[17] and reports a value of 6.61 × 10^{-5} at 25°. Larsson[18] records a value of 5.83 × 10^{-5} at 18°.

Due acknowledgment is made of a grant from the Faculty Research Committee of the University which defrayed part of the cost of the apparatus and made available the services of a mechanic.

Summary

The equivalent conductivities of solutions of potassium benzoate and of benzoic acid have been determined.

The thermodynamic dissociation constant for benzoic acid has been calculated and is 6.312 × 10^{-5}.

The results confirm the limiting law of Debye and Hückel.

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(16) Rørdam, Inaugural Dissertation, Copenhagen, 1925.

(17) Schaller, *Z. physik. Chem.*, **25**, 497 (1898).

(18) Larsson, *ibid.*, **A148**, 148 (1930).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 332]

Freezing Points of Aqueous Solutions. VII. Ethyl Alcohol, Glycine and their Mixtures[1]

BY GEORGE SCATCHARD AND S. S. PRENTISS

Thermodynamic Calculations in Solutions more Complex than Binary.—The application of chemical potentials, or activities, most interesting to chemists is the study of chemical equilibria, most of which involve mixtures of several components. Yet relatively few such systems have been studied systematically. One reason for this hiatus is the lack of a satisfactory method of interpolation. For a binary system the variation with composition at constant temperature and pressure of any property may be represented by a line, and graphic interpolation is satisfactory. A ternary system requires a surface for the same representation, and more complicated systems go beyond the limits of ordinary geometry. Some analytical expression of the results is necessary, and it is highly desirable to have one which reduces as far as possible the number of experimental points necessary for accurate interpolation.

According to the physical theory of mixtures the free energy of a quantity of fluid may be expressed as

$$\frac{F}{RT} = \sum\nolimits_i^0 n_i\left(K_i + \ln\frac{n_i}{\sum\nolimits_j^0 n_j}\right) + \frac{1}{V}\sum\nolimits_{ij}^0 \beta_{ij}n_in_j + \frac{1}{V^2}\sum\nolimits_{ijk}^0 \delta_{ijk}n_in_jn_k + \ldots \qquad (1)$$

where n_i is the number of moles of the i'th component, V the volume of the system and K_i, β_{ij} and δ_{ijk} functions only of the temperature and pressure. $\sum_{ijk}^0$ represents the triple sum $\sum_i\sum_j\sum_k$; etc., where each sum is carried over all the components. We shall later use $\sum_{ijk}$ for the same sum in which the solvent is omitted in the summation. Coefficients with the same subscripts but in different orders cannot be measured separately, so we shall represent their sum by a single one of the coefficients with the proper numerical factor. These factors are the same as the coefficients of the corresponding terms in the multinomial expansion of $(\sum_i n_i)^\nu$, where ν is 2 for the β's, 3 for the δ's, etc.[2]

The first term on the right of Equation (1) is the perfect gas term and represents the effects of the individual molecules. The second arises from the interaction of the molecules in pairs, and is just as complicated as the possible types of pairs. The third term includes the interactions in groups of three, and is as complicated as the possible types of groups of three, etc.

The volume of the system is fixed, at constant temperature and pressure, by the quantities of

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(1) Paper VI in this series appeared in THIS JOURNAL, **56**, 807 (1934).

(2) For a derivation in the simple case for which nothing beyond the β term is necessary, see: G. Scatchard, *Chem. Rev.*, **8**, 321 (1931); J. H. Hildebrand and S. E. Wood, *J. Chem. Phys.*, **1**, 817 (1933).