[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XII. The Influence of Temperature on the Conductance of Electrolytes in Anisole[1]

BY GEORGE S. BIEN[2] WITH CHARLES A. KRAUS AND RAYMOND M. FUOSS

I. Introduction

It has been shown that the conductance of many binary electrolytes as a function of concentration in solvents of moderately low dielectric constant is given by the equation[3]

$$\Lambda = \Lambda_0 \sqrt{K}/\sqrt{c}\, g + (\lambda_0 \sqrt{K}/k\, g) \sqrt{c} \qquad (1)$$

This is a simplified form of the general conductance function, and is valid approximately from concentrations where γ is negligible in comparison with unity up to the concentration corresponding to the minimum in equivalent conductance. The equation[4] is derived on the basis of the assumption that the effects of two and three ion configurations at short distances can be taken into account by postulating the equilibria

$$A^+ + B' \rightleftharpoons AB \qquad (2)$$
$$AB + A^+ \rightleftharpoons A_2B^+ \qquad (3a)$$
$$AB + B' \rightleftharpoons AB_2' \qquad (3b)$$

The equilibrium constants K for the reaction (2) and k, assumed to be the same for (3a) and (3b), have been calculated as functions of *temperature*, dielectric constant and ion size by a method which appears to be justified as a numerical approximation. (The calculation is, of course, also subject to the physical approximations implied in the model used to represent the conducting system.) Under the assumption that the ion size is independent of temperature, it is possible to calculate the conductance as a function of temperature[5] over the range of concentration where (1) applies. A comparison of results calculated in this way with observed values will thus permit a test of the general theory of electrolytes as developed in previous papers of this series.

It is the purpose of this paper to present conductance data for tetra-*n*-butylammonium nitrate and picrate in anisole, covering the concentration range 0.01 to 0.00001 N and the temperature range −33 to +95.1°, and to compare the data with theory.

Anisole was chosen as solvent for this investigation for the following reasons: it is liquid over a wide temperature range (−37.8 to 155°), is a good solvent for electrolytes of the quaternary ammonium type, can be purified (solvent conductance less than 10^{-13} mhos) and kept pure for a long time, and has a dielectric constant of 4.29 at 25°, which brings the minimum in conductance to about 0.001 N for the salts used.

With increasing temperature, the conductance at a given concentration increases, due to increased fluidity of the solvent and to increased dissociation of ion pairs, while the minimum in conductance shifts to higher concentrations. These effects are all accounted for by equations derived in the preceding papers of this series.

II. Materials, Apparatus and Procedure

Tetra-*n*-butylammonium Salts.[6]—The preparation of these salts is analogous to the preparation of the tetraisoamylammonium salts, which has already been described.[7]

Anisole.—The technical material was first fractionally distilled. The 154–155° fraction was washed with sodium hydroxide solution, followed by water, and was then dried over calcium chloride. After filtering, it was refluxed with molten sodium and again distilled. The middle fraction was stored over sodium in a still from which it could be distilled directly into the weight burets or conductance cells. The solvent conductance was 10^{-13} mhos or less.

Conductance Cells.—The conductance was first determined at 25°, using the cell and thermostat employed by Fuoss and Kraus.[8] For conductances at other temperatures, cells of a special type (Fig. 1A) were constructed. The first had plate electrodes, 2 × 2.5 cm. and a cell constant of 0.01799, determined by comparison with a cell standardized with 0.1 demal potassium chloride solution, using the data of Jones and Bradshaw.[9] The second had cylindrical electrodes, similar to those described by Fuoss and Kraus, and a cell constant of 0.002906, likewise determined by comparison. Both sets of electrodes were left bright. The purpose of the wide expansion chamber above the electrode compartment was to avoid a long column of electrolytic solution parallel to the electrode lead wires.[10]

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(1) This paper comprises a part of the subject matter of a thesis submitted by George S. Bien in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University.

(2) University Fellow at Brown University, 1932–1934.

(3) We shall use consistently the symbols employed in earlier papers of this series; in order to save space, they will not be redefined here.

(4) Fuoss and Kraus, THIS JOURNAL, **55**, 2387 (1933).

(5) Fuoss, *ibid.*, **56**, 1857 (1934).

(6) N. L. Cox, "Thesis," Brown University, 1934.

(7) Kraus and Fuoss, THIS JOURNAL, **55**, 21 (1933); Fuoss and Kraus, *ibid.*, **55**, 3614 (1933).

(8) Fuoss and Kraus, *ibid.*, **55**, 3614 (1933).

(9) Jones and Bradshaw, *ibid.*, **55**, 1780 (1933).

(10) Jones and Bollinger, *ibid.*, **53**, 1207 (1931).

The lead wires were carried up through ground glass caps, which fitted the special vapor thermostats described below.

Electrical Equipment.—The d. c. bridge described by Fuoss and Kraus was only used for the determination of solvent conductance. This was always far less than 0.1% (usually less than 0.01%) of the total conductance, but was always determined as a precaution. The resistances of the solutions were determined on a Jones type of conductance bridge. Resistances up to 3 megohms could be measured, by supplementing the resistances furnished with the bridge (90,000 ohms) by Curtis coils (100,000 ohms) or Shallcross resistors (up to 3 megohms). If no more than two of the latter are used, and if they are well spaced, the frequency variation observed was less than 0.1% between 0.4 and 2.0 kilocycles.[6] The leads (2 mm. copper wire) from the bridge to the conductance cells were carried on bakelite spacers in grounded brass tubing of 2.5 cm. diameter. Their center to center distance was 7.6 cm. A vacuum tube oscillator, two-stage amplifier and telephone completed the electric equipment.

Procedure.—Solutions were made up by adding pure solvent to weighed samples of salt in weight burets, or by diluting stock solutions in special dilution flasks. Precautions were taken to avoid contact with the atmosphere. The solution was siphoned into the conductance cell, previously filled with dry nitrogen, and the cell was then sealed. The conductance at 25° was determined in an oil thermostat regulated to 25 ± 0.002°. For −33° the cell was placed in a tube containing petroleum ether, which in turn was immersed in a bath of boiling ammonia, whose pressure was held at 776 ± 1 mm. For 0° the petroleum ether bath containing the cell was packed in ice. For temperatures above 25°, the cell was placed in vapor jackets of the design shown in Fig. 1B. Chloroform (b. p. 61.3°), benzene (b. p. 80.2°) and heptane (b. p. 95.1°) were used; the internal pressure in the stills was regulated to 760 ± 1 mm. After completing the above sequence of readings, the resistance at 25° was redetermined; final values checked the initial values within 0.2% unless decomposition occurred at the higher temperatures, in which case the determinations were discarded.

Densities.—Densities of the solvent and of several solutions at 25° were determined in a pycnometer. The values obtained were 0.9890 for pure anisole and 0.9899 for a solution containing 0.01145 mole of tetra-*n*-butylammonium picrate per kilo of anisole. The densities at other temperatures were calculated by means of the formula

$$d_t = d_{25}/[1 + 0.0_3928(t - 25) + 0.0_675(t - 25)^2] \quad (4)$$

which is based on a series of readings in a dilatometer which was calibrated with mercury.

III. Results

The conductances at −33, 0, 25, 61.3 (80.2) and 95.1° for tetrabutylammonium nitrate in anisole are given in Table I, and for the picrate in Table II. (No determinations at 80.2° were made for the latter.) In these tables *m* denotes moles of salt per kilogram of solvent; volume concentrations may be calculated by means of the density formula given above. The results are shown graphically in Figs. 2 and 3, where log Λ is plotted against log *c*. The data at temperatures other than 25° are self-consistent within about 2%.

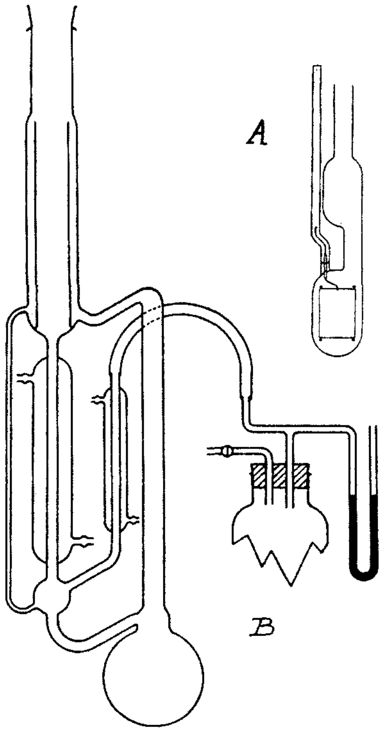

Fig. 1.—Apparatus: A, conductance cell; B, vapor jacket.

TABLE I

THE CONDUCTANCE OF TETRA-*n*-BUTYLAMMONIUM NITRATE IN ANISOLE AT DIFFERENT TEMPERATURES

	Equivalent Conductance					
$m \times 10^3$	−33°	0°	25°	61.3°	80.2°	95.1°
6.091	0.00986	0.0297	0.0522	0.0941	0.1198	....
5.430	.00932	.0279	.0489	.0895	.1130	....
4.204	.00863	.0259	.0453	.0838	.1072	0.1263
2.981	.00849	.0234	.0417	.0764	.0986	....
2.731	.00737	.0221	.0392	.0725	.0936	....
2.645	.....	....	.0390	....	....	.0116
2.318	.00715	.0214	.0382	.0709	.0917	....
1.868	.00665	.0199	.0359	.0676	.0880	.1048
1.405	.00633	.0193	.0352	.0668	.0879	.1054
1.042	.00608	.0189	.0346	.0673	.0890	.1073
0.779	.00572	.0183	.0341	.0676	.0900	.1092
.580	.00583	.0186	.0351	.0703	.0945	.1158
.435	.00569	.0187	.0360	.0737	.0996	.1223
.391	.00570	.0190	.0368	.0759	.1027	.1265
.226	.00615	.0209	.0416	.0880	.1210	.1501
.159	.00660	.0227	.0449	.1001	.1376	.1700
.113	.00705	.0251	.0515	....	....	....

IV. Discussion

Two general effects of increased temperature may be seen by inspection of the figures: the equivalent conductance at a given concentration increases with increasing temperature, and the

Table II

The Conductance of Tetra-*n*-butylammonium Picrate in Anisole at Different Temperatures

$m \times 10^3$	Equivalent Conductance −33°	0°	25°	61.3°	95.1°
11.56	0.01300	0.0434	0.0823	0.1639	0.269
6.710	.00901	.0315	.0618	.1288	.215
4.632	.00763	.0272	.0544	.1166	.203
3.103	.00694	.0257	.0525	.1154	.204
2.077	.00675	.0255	.0531	.1185	.213
2.060	.00669	.0254	.0530	.1189	.214
1.396	.00691	.0270	.0570	....	.235
1.395	.00705	.0274	.0577	.1310	.239
0.997	.00758	.0296	.0629	.1448	.265
.845	.00761	.0308	.0634	.1493	.274
.820	.00780	.0309	.0657	.1525	.285
.521	.00872	.0356	.0769	.1791	.332
.461	.00926	.0376	.0812	.1890	.356
.325	.01025	.0420	.0906	.211	.393
.187	.01342	.0551	.1192	.280	.529
.160	.01416	.0575	.1254	.293	.544
.073	.01936	.0881	.1730	.408	.759

concentration at which the minimum appears increases. Qualitatively, these effects may be easily understood: with increasing temperature, increasing fluidity and increasing dissociation of ion pairs at low concentrations increases Λ, while increasing dissociation of ion triples into free ions and ion pairs retards the appearance of the minimum.

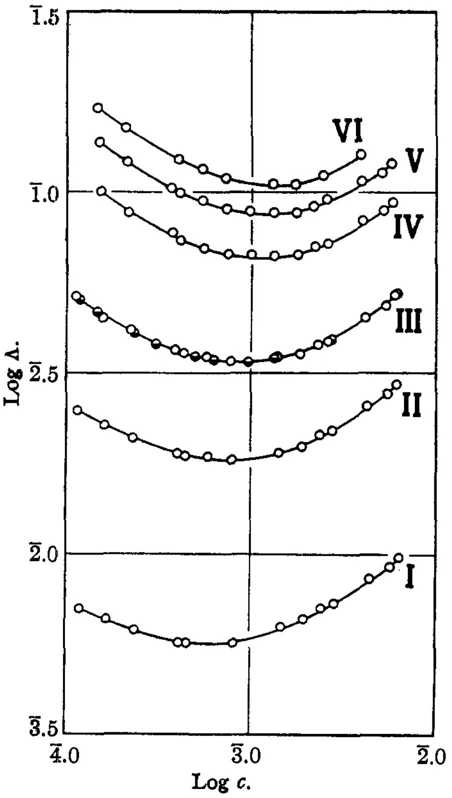

Fig. 2.—Conductance of tetra-*n*-butylammonium nitrate in anisole at −33°, Curve I; at 0°, II; at 25°, III; at 61.3°, IV; at 80.2°, V; at 95.1°, VI.

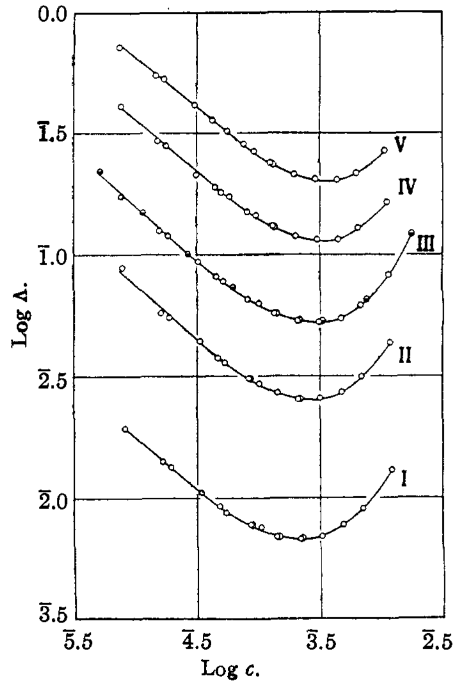

Fig. 3.—Conductance of tetra-*n*-butylammonium picrate in anisole at −33°, Curve I; at 0°, II; at 25°, III; at 61.3°, IV; at 95.1°, V.

In order to apply the previously derived expression for the temperature coefficient of Λ[11]

$$\frac{1}{\Lambda}\frac{\mathrm{d}\Lambda}{\mathrm{d}T} = \frac{\mathrm{d}\ln\varphi}{\mathrm{d}T} + \frac{1}{2T}\left(1 + \frac{\mathrm{d}\ln D}{\mathrm{d}\ln T}\right)\left(b - 1 - \frac{4}{b}\right) - \frac{1}{2T}\frac{1}{1 + k\Lambda_0/\lambda_0 c}\left(1 + \frac{\mathrm{d}\ln D}{\mathrm{d}\ln T}\right)\left(b_3 - 4 - \frac{16}{3b_3}\right)$$

it is necessary to know the dependence of the fluidity φ and of the dielectric constant D on the temperature.

For the fluidity of anisole as a function of temperature, we shall employ the equation

$$0.6741\,\varphi = (T^2 - 585.7\,T + 99{,}438)^{1/2} + T - 349.53 \quad (5)$$

This equation was calculated by the method of Bingham and Spooner[12] using 1.25 as the "association factor." At T = 298.1° this formula gives $\eta = 1/\varphi = 0.01027$, which is in good agreement with the value 0.0101 found by Baker.[13]

The temperature coefficient of D may be obtained by equations (8) and (9) of the previous paper of this series. The polarization P of anisole

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(11) Fuoss, This Journal, **56**, 1857 (1934). Equation (11).

(12) Bingham and Spooner, *Physics*, **4**, 387 (1933).

(13) Landolt-Börnstein, Erg. 1, p. 77.

as a function of temperature[14] is given by the equation

$$P = 45.73 + 3380/T$$

Our values are about 1.5% lower than Estermann's,[15] whose measurements covered the temperature range 20–50°.

The conductance data have been treated by graphical methods in order to obtain the constants K and k. Using $\Lambda_0\eta = 0.508$ for tetrabutylammonium nitrate,[16] values of Λ_0 for the various temperatures were calculated, using (5) to calculate $\eta = 1/\varphi$. Then the function $g(c)$, which approximates the time-average effects of the free ions, was calculated. Writing (1) in the form

$$\Lambda g \sqrt{c} = \Lambda_0 \sqrt{K} + (\lambda_0 \sqrt{K}/k)c$$

we note that $\Lambda_0 \sqrt{K}$ and $\lambda_0 \sqrt{K}/k$ are determined as the intercept and slope, respectively, on a plot of $\Lambda g \sqrt{c}$ against concentration. These constants, for tetrabutylammonium nitrate in anisole, are given in the second and third columns of Table III. The data for salts in anisole satisfy the conductance function (1) up to concentrations near the minimum (*i. e.*, about 0.001 N); at higher concentrations the curve begins to deviate upward from the limiting straight line. This effect is presumably due to ionic interactions which are not included in equation (1). The ratio of the intercept to the slope gives a value for $k\Lambda_0/\lambda_0$. The logarithm of this quantity was plotted against log T and differentiated graphically, giving $d \ln k/d \ln T$, since we assume that the ratio Λ_0/λ_0 is independent of temperature. Using (XI.7),[17] b_3 and hence a_3 were determined. We obtained $a_3 = 5.83 \pm 0.09 \times 10^{-8}$ cm. as the average over the five midpoints of the six experimental temperatures. With $a_3 = 5.83 \times 10^{-8}$, values of log k at the various temperatures were computed. Comparison with the experimental $k\ \Lambda_0/\lambda_0$ values gave the average value $\lambda_0/\Lambda_0 = 0.82$. Using this value of λ_0/Λ_0, k values at the experimental temperatures were calculated from the intercept–slope ratios, and then b_3 and a_3 were calculated in second approximation by means of (XI.6). These values are given in the fifth column of Table III. The average is the same as that obtained from the first approximation, but the mean error is reduced to ±0.04 Å. Finally, by means of our equation (III.6) connecting log K and $Q(b)$, and a large scale plot of log $Q(b)$ against b, b values and hence a values for the reaction (2) were calculated. The result is $a = 4.91 \pm 0.04 \times 10^{-8}$ cm. It will be noted that $a_3 > a$; this is probably due to the fact that the model we are using (uniformly charged spheres of *equal* size to represent the simple anions and cations) is inadequate. The experimental a value represents an average over the two simple ions, while a_3 represents an average over two kinds of triple ions, assumed to be present in equal concentrations, and each containing three simple ions.

A similar calculation for the picrate is summarized in Table IV. For this salt we assumed $\Lambda_0\eta = 0.434$. This is based on Cox's value for tetrabutylammonium nitrate in ethylene chloride, the difference 13.5 for the limiting conductances of tetraethylammonium picrate and nitrate in methyl alcohol,[18] and the ratio (0.0546/0.07853) of the viscosities of methyl alcohol and ethylene chloride. This calculated value is probably correct within several per cent. Since the minimum for the picrate appears at higher concentrations than for the nitrate, the various approximations involved in calculating a_3 are more doubtful; furthermore, the numerical value of the slope is smaller, so that the constant k for the picrate is less accurately determined than for the nitrate. The parameter a remains reasonably constant for the picrate, but the a_3 value shows a rather large increase with temperature. It seems probable

TABLE III

CONSTANTS FOR TETRABUTYLAMMONIUM NITRATE IN ANISOLE

t	$\Lambda_0 \sqrt{K} \times 10^4$	$\lambda_0 \sqrt{K}/k$	Λ_0	$-\log k$	$a_3 \times 10^8$	$k \times 10^{11}$	$a \times 10^8$
−33	0.650	0.115	14.22	3.336	5.79	2.08	4.88
0	2.34	.324	31.8	3.230	5.79	5.42	4.95
25	4.75	.550	49.5	3.152	5.84	9.20	4.96
61.3	10.50	.950	82.1	3.044	5.82	16.30	4.91
80.2	14.70	1.145	102.1	2.980	5.88	20.65	4.89
95.1	18.10	1.288	118.9	2.940	5.88	23.2	4.85

TABLE IV

CONSTANTS FOR TETRABUTYLAMMONIUM PICRATE IN ANISOLE

−33	1.65	0.0623	12.15	2.876	7.2	18.5	5.36
0	6.75	.187	27.2	2.742	7.6	61.5	5.55
25	14.35	.348	42.3	2.685	7.7	115	5.61
61.3	33.8	.675	70.2	2.600	7.9	232	5.62
95.1	62.8	1.03	101.7	2.516	8.2	382	5.61

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[14] We are indebted to Mr. John A. Geddes, of this Laboratory, for measurements of the dielectric constant of anisole at a series of temperatures from 0 to 75°.

[15] Estermann, *Z. physik. Chem.*, **B1**, 134 (1928).

[16] This value is based on the value 64.7 for Λ_0 obtained at 25° in ethylene chloride, for which $\eta = 0.007853$; N. L. Cox, Thesis, Brown University, 1934.

[17] We shall use this notation to refer to previously derived equations; the Roman numeral will give the number of the paper in this series and the Arabic numeral the number of the equation.

[18] Unmack, Bullock, Murray, Rust and Hartley, *Proc. Roy. Soc.* (London), **A132**, 427 (1931).

that the deviations in this case are due to the electrical asymmetry of the picrate ion and consequent failure of the spherical model. The situation may be further complicated by interaction between the charge on the picrate oxygen atom and an electron pair on the ether oxygen atom of a solvent molecule. It will be noted that the picrate curves are much steeper than the nitrate curves at concentrations above the minimum. Further work on electrolytes with unsymmetrical ion types is in progress.

Granting the validity of the equations used to compute the ionic parameters from the data, the values a and a_3 are reasonably constant. Their small variations from the mean values appear to be systematic, but it must be recalled that the following possible errors are absorbed in these parameters: (a) systematic errors produced by incorrect constants in the fluidity formula, (b) errors produced by extrapolating the polarization formula beyond the temperature range in which the dielectric constants were determined, (c) systematic deviation of the approximate function g which allows for interionic effects on mobility and activity of free ions, (d) variation of the product $\Lambda_0\eta$ with temperature,[19] and (e) all experimental errors.

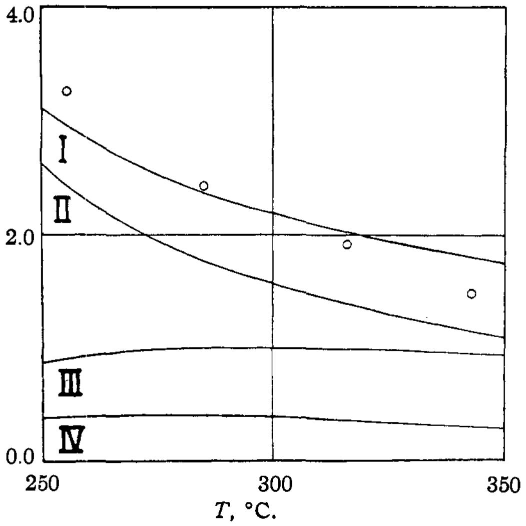

Fig. 4.—Temperature coefficients for 0.001 N tetrabutylammonium nitrate in anisole as a function of temperature: Curve I, $d \ln \Lambda/dT$; Curve II, $d \ln \varphi/dT$; Curves III and IV, dissociation constant terms.

Curve I, Fig. 4, represents the calculated temperature coefficient of conductance for a 0.001 N solution of tetrabutylammonium nitrate in anisole as a function of temperature. It is the algebraic sum of Curves II, III and IV which represent, respectively, the contributions to the temperature coefficient of the terms of (XI.11) due to viscosity, to change of K and of k. (It will be recalled that the ion-triple term is negative.) The points are experimental values, determined as chord-slopes on a log Λ–T plot.

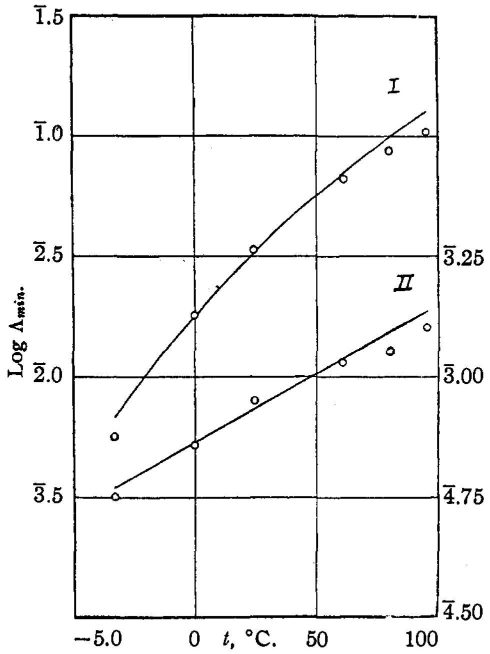

Fig. 5.—Minimum equivalent conductance and corresponding concentration as a function of temperature: curves calculated, circles observed for tetrabutylammonium nitrate in anisole.

While the deviations between the calculated and observed values at the extreme temperatures are rather large (at worst, 30% of the actual temperature coefficient), the calculated curve does reproduce the general course of the experimental values, particularly in the intermediate temperature range. Inspection of the curves shows that the terms involving the equilibrium constants change only slightly with temperature; the change of $d \ln \Lambda/dT$ with T is almost entirely controlled by the change of $d \ln \varphi/dT$. Since the latter curve is calculated by (5), it is possible that some of the systematic deviation arises from incorrect constants in this equation. Furthermore, a change of the product $\Lambda_0\eta$ with temperature would introduce another term in the temperature coefficient, which would correspond to a different change of $d \ln \Lambda/dT$ with increasing T than is given by Curve I.

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[19] Born, *Z. Physik*, **1**, 221 (1920); H. Schmick, *ibid.*, **24**, 56 (1924); R. H. Lattey, *Phil. Mag.*, **6**, 258 (1928).

Another feature of the observed values is reproduced by the calculated: the decrease of d ln Λ/dT with increasing concentration at a given temperature. At very low concentrations, where the curves are parallel, with a slope of minus $^1/_2$ on a log Λ–log c plot, the temperature coefficient is independent of concentration. But when the curves begin to flatten out toward the minimum, a decrease of the coefficient with increasing concentration appears. This is due to the shift of the minimum toward higher concentrations with increasing temperature, owing to increased dissociation of triple ions. The average differences between the observed temperature coefficients at 10^{-3} N and at 5×10^{-4} and 2×10^{-4} N are, respectively, 0.10 and 0.25%, while the calculated differences are 0.11 and 0.23% at 325° Abs. and 0.12 and 0.25% at 300°.

Using the average values of the parameters a and a_3 for tetra-n-butylammonium nitrate in anisole, together with various equations presented above, the conductance as a function of temperature may be calculated. The conductance minimum represents a characteristic point of the conductance curve; the influence of temperature on the location of the minimum is illustrated in Fig. 5, where Curve I is the calculated curve for the logarithm of the minimum equivalent conductance plotted against temperature and Curve II is the calculated curve for the logarithm of the corresponding concentration. The circles represent experimental values read directly from the curves of Fig. 2. Considering the simplicity of the assumed mechanism and the numerous assumptions and approximations made, not to mention possible experimental errors, the agreement between calculated and experimental values is quite as good as was to have been expected. For a temperature change of 128°, $\Lambda_{\text{min.}}$ varies approximately in the ratio 1:20 and $c_{\text{min.}}$ in the ratio 1–2; maximum deviations in $\Lambda_{\text{min.}}$ at the extreme temperatures amount to about 20% and maximum variations in $c_{\text{min.}}$ to about 10%.

Summary

1. The conductance of tetra-n-butylammonium nitrate and picrate in anisole, over the concentration range 0.00001 to 0.01 N and the temperature range −33 to +95.1°, are presented.

2. The experimental results at concentrations up to about 0.001 N are in numerical agreement with results calculated from previously derived equations which are based on the hypothesis of ion association.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Dissociation Constants of Organic Boric Acids

BY BERNARD BETTMAN, G. E. K. BRANCH AND DAVID L. YABROFF

In two previous papers[1] we reported the dissociation constants of the phenetyl, the chlorophenyl and some of the hydrocarbon boric acids. A discussion of the relative strengths of these acids based on resonance and negativity was given. The present paper is a continuation of this work and deals with the dissociation constants of some other substituted boric acids, all derived from phenylboric acid. With the exception of *o*-nitrophenylboric acid, all the results are in accord with the principles we have discussed in the previous articles. *o*-Nitrophenylboric acid is anomalously weak.

The dissociation constants were again obtained by measuring the P_H of a series of partially neutralized solutions with a hydrogen electrode. The constants we are using as a measure of acidic strength are actually a combination of activities and molalities, *i. e.*, $Ka = (H^+)\text{act.}\ (A^-)\ \text{mol.}/(HA)\ \text{mol.}$ We are again assuming that the measured P_H is equal to the negative logarithm of the hydrogen-ion activity in the alcohol solutions, as well as in aqueous solution. The constants were again calculated by means of the equation

$$Ka = \frac{(H^+)\text{act.}\ (Na^+ + H^+ - Kw/H^+)}{M - (Na^+ + H^+ - Kw/H^+)}$$

M represents the total molality of the boric acid in the form of both acid and salt. Kw was again taken as 5×10^{-15} for 25% alcohol ($N_{\text{alc.}} = 0.0910$) and as 1.5×10^{-15} for 50% alcohol ($N_{\text{alc.}} = 0.225$). No other corrections were used

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[1] (a) Branch, Yahroff and Bettman, THIS JOURNAL, **56**, 937 (1934); (b) Yabroff, Branch and Bettman, *ibid.*, **56**, 1850 (1934).