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Single Ion Conductances in Non-aqueous Solvents[1,2]

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The conductance at 25° of tetrabutylammonium tetraphenylboride in propylene carbonate ($D = 65.1$) and in mixtures of nitrobenzene and carbon tetrachloride ($34.7 \geqslant D \geqslant 7.8$) has been measured. Since the two ions have very nearly the same volume, the single ion conductances in the above solvents can be obtained by taking one half the limiting equivalent conductances. The distance parameter a, which measures the center-to-center distance at cation–anion contact, was found to be 7.1 Å., as the average of three independent methods of calculation: (1) from limiting conductance, (2) from the limiting curvature of the phoreograms and (3) from the association constants.

With the exception of ammonia, methanol and ethanol, single ion conductances are not available for non-aqueous electrolytic systems in general, because reversible electrodes, essential for the determination of transport numbers, have not yet been found for such systems. If, however, we have the limiting conductance of a 1–1 salt whose ions are identical (except for charge), single ion conductances can be obtained simply by setting $\lambda^+_0 = \lambda^-_0 = \Lambda_0/2$. Fowler and Kraus[4] made this assumption for the ions of tetrabutylammonium triphenylborofluoride and of tetrabutylammonium triphenylborohydroxide and found limiting conductances of 52.4 and 52.3 respectively in ethylene dichloride; values are not known for other solvents. These salts are, however, not readily obtainable, and furthermore models suggest that the (unsymmetrical) anion has a somewhat smaller volume than the cation. Tetrabutylammonium tetraphenylboride,[5,6] on the other hand, is easily made by metathesis from sodium tetraphenylboride and tetrabutylammonium bromide and much more nearly approximates the requirement of equal size of cation and anion to permit assuming equality of transport numbers. In this paper are presented conductance data for tetrabutylammonium tetraphenylboride in propylene carbonate[7] ($D = 65.1$) and in mixtures of nitrobenzene and carbon tetrachloride covering the dielectric constant range $34.69 \geqslant D \geqslant 7.79$.

In addition to providing a determination of the single ion conductances of the tetrabutylammonium ion and of the tetraphenylboride ion in nitrobenzene–carbon tetrachloride mixtures, a result of theoretical significance was also derived from the data. It was found that the distance parameters obtained from electrostatic sources (curvature of the phoreogram and from the dependence of association constant on dielectric constant) and from hydrodynamic sources (limiting conductance) agreed well with each other. This suggests, at least for the case of equal ions, large compared to solvent molecules, that the conductance function is essentially a one parameter equation: $\Lambda = \Lambda(c, \Lambda_0)$.

Experimental

Tetrabutylammonium tetraphenylboride was prepared as described by Accasina, Petrucci and Fuoss.[6] Propylene carbonate (Jefferson Chemical Company) was fractionally distilled; the middle cut, boiling at 117° (17.5 mm.), was used for the conductance work. The solvent conductance was about 2×10^{-7}; viscosity at 25°, 0.02553; density at 25°, 1.1987. Nitrobenzene was purified as recommended

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[1] Office of Naval Research Project NR 051-002; Technical Report No. 61. This paper may be reproduced in whole or in part for any purpose of the United States Government.

[2] Presented at the International Symposium on Electrolytes, Congresso della Società Italiana per il Progresso delle Scienze, Trieste, 4-9 June, 1959.

[3] This paper is abstracted from a thesis presented by Ernest Hirsch to the Graduate School of Yale University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, June, 1959.

[4] D. L. Fowler and C. A. Kraus, THIS JOURNAL, **62**, 2237 (1940).

[5] R. M. Fuoss, J. B. Berkowitz, E. Hirsch and S. Petrucci, *Proc. Nat. Acad. Sci.* (*U. S. A.*), **44**, 27 (1958).

[6] F. Accascina, S. Petrucci and R. M. Fuoss, THIS JOURNAL, **81**, 1301 (1959).

[7] P. L. Kronick and R. M. Fuoss, *ibid.*, **77**, 6114 (1955).

by Witschonke and Kraus[8]; solvent conductance, about 5×10^{-9}. Carbon tetrachloride was distilled from activated aluminum oxide. Solvent mixtures were made up by weight. Their properties are summarized in Table I; these values were interpolated from those determined by Sadek.[9] In the last column of Table I are given also the values of concentration corresponding to $\kappa a = 0.2$, with $\mathring{a} = 7$; these values were never exceeded in our experiments and therefore the results can be treated by the electrostatic theory.[10] The cell used for the dilute solutions had a constant equal to 0.022191 as determined by comparison with a cell (k = 2.6268) calibrated using Shedlovsky's[11] data for potassium chloride solutions. The bridge already has been described.[12]

TABLE I

PROPERTIES OF SOLVENT MIXTURES (NITROBENZENE-CARBON TETRACHLORIDE)

No.	Wt. % CCl_4	ρ	D	$100\ \eta$	$10^3\ c$ (0.2)
1	0.00	1.1981	34.69	1.839	3.34
2	23.86	1.2749	26.52	1.570	2.55
3	24.07	1.2756	26.45	1.568	2.55
4	43.71	1.3455	19.95	1.361	1.92
5	64.83	1.4286	12.99	1.160	1.25
6	70.96	1.4532	11.00	1.107	1.06
7	80.95	1.4971	7.79	1.024	0.75

A summary of the experimental data[3] is given in Table II, where Λ is equivalent conductance and c is concentration in equivalents per liter. The mixtures are identified by the code numbers of Table I; "$C_5H_6O_3$" refers to the solutions in propylene carbonate.

TABLE II

CONDUCTANCE OF TETRABUTYLAMMONIUM TETRAPHENYLBORIDE

$10^4 c$	Λ
$PhNO_2$	
3.422	21.196
4.576	21.053
6.293	20.836
7.285	20.754
8.962	20.579
9.671	20.505
12.664	20.290
14.138	20.198
No. 2	
0.4398	24.559
0.7474	24.382
1.0897	24.215
1.7040	23.989
2.4262	23.773
No. 3	
3.405	23.596
5.974	23.133
10.332	22.532
20.615	21.614
No. 4	
0.4878	26.748
0.9123	26.399
1.4701	26.074
1.9758	25.800
No. 5	
0.4619	28.725
0.8602	27.802
1.2957	26.980
1.8917	26.134
2.4599	25.501
No. 6	
0.9028	26.921
1.5523	25.427
2.6976	23.647
6.2584	20.620
No. 7	
0.2919	23.205
0.7271	19.057
1.2316	16.618
1.8376	14.846
2.3782	13.759
$C_5H_6O_3$	
1.9212	16.760
2.8752	16.665
4.6913	16.536
10.426	16.259
16.326	16.050
21.493	15.882
38.141	15.531
38.722	15.479

Discussion[13]

Before considering the experimental results in detail, the basic equations to be used in their analysis will be reviewed briefly. The general conductance equation[10] for 1–1 electrolytes at concentrations at which κa does not exceed 0.2 and for solvents in which higher clusters than pairs do not form is

$$\Lambda = \Lambda_0 - Sc^{1/2}\gamma^{1/2} + Ec\gamma \log c\gamma + Jc\gamma - F\Lambda_0 c - K_A c\gamma f^2 \Lambda \quad (1)$$

which, when ion pair formation is negligible ($K_A \approx 0$, $\gamma \approx 1$), reduces to

$$\Lambda = \Lambda_0 - Sc^{1/2} + Ec \log c + Jc - F\Lambda_0 c \quad (2)$$

Here S and E are theoretically predictable constants (given a preliminary value of Λ_0), F is determinable from viscosity measurements and Λ_0, J and K_A are, from the mathematical point of view, arbitrary constants to be computed from the given conductance data. It is therefore convenient to segregate the "known" terms of (1) or (2) and to define a new practical dependent variable Λ' which will be used in place of the observed conductance in the numerical calculations: for the case of negligible association, we set

$$\Lambda' \equiv \Lambda + Sc^{1/2} - Ec \log c \quad (3)$$

Comparison with (2) shows that

$$\Lambda' = \Lambda_0 + Jc - F\Lambda_0 c \quad (4)$$

The variable Λ' thus collects the known terms in the observed conductance and reduces the unknown terms to a simple linear function of concentration. Consequently we see that the quantity of real interest (as far as determining J is concerned) is the *difference* between the observed conductance Λ and a reference quantity L which is defined as

$$L \equiv \Lambda_0 - Sc^{1/2} + Ec \log c \quad (5)$$

because

$$\Lambda - L = \Lambda' - \Lambda_0 = (J - F\Lambda_0)c \equiv Hc \quad (6)$$

and hence the ion size, *via* $J = J(a)$, is determinable from H if F is known. Stated in another way, if molecular parameters are the goal of the measurements, it is not the total conductance which is to be considered but rather the distance between the conventional $\Lambda - c^{1/2}$ curve and the reference curve 5, because this distance is a measure of H. The reference L is the Onsager tangent, corrected by the known transcendental term $Ec \log c$. By focussing attention on the *difference* between the observed conductance and a theoretically predictable reference curve, rather than on the *total* conductance, the current theory of electrolytic conductance automatically calls for high precision in the data.

At 25°, the coefficient E is given by the equation

$$E = (1.122 \times 10^3/\eta D^2)[(227.7\Lambda_0\eta/D) - 1] \quad (7)$$

It obviously decreases when the dielectric constant becomes large and when the Walden product is small; the reference curve 5 will coincide with the Onsager tangent in the special case

$$227.7\Lambda_0\eta = D \quad (8)$$

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(8) C. R. Witschonke and C. A. Kraus, THIS JOURNAL, **69**, 2472 (1947).

(9) H. Sadek and R. M. Fuoss, *ibid.*, **76**, 5905 (1954).

(10) R. M. Fuoss, *ibid.*, **81**, 2659 (1959).

(11) T. Shedlovsky, A. S. Brown and D. A. MacInnes, *Trans. Electrochem. Soc.*, **66**, 165 (1934).

(12) H. Eisenberg and R. M. Fuoss, THIS JOURNAL, **75**, 2914 (1953).

(13) The symbols used in subsequent equations are defined in ref. 10. See also "Electrolytic Conductance," by R. M. Fuoss and F. Accascina, Interscience Publishers, Inc., New York, N. Y., 1959.

for which $E = 0$ and will of course lie near it when (8) is approximately satisfied.

We now consider the data for $Bu_4N \cdot BPh_4$ in propylene carbonate. The phoreogram (upper curve of Fig. 1) is anabatic, as might be expected, due to the high dielectric constant of the solvent and the large size of the ions. We shall therefore use (2), the limiting form of the conductance equation for negligible association. The Walden product is small, and E is only 5.51; hence the reference curve L (dashed curve in Fig. 1) almost coincides with the limiting tangent and the difference $(\Lambda - L)$ is quite small. In order to determine Λ_0, Λ' is plotted against c (bottom plot of Fig. 1; note expanded scale). The points can be approximated by a straight line which extrapolates to $\Lambda_0 = 17.144 \pm 0.012$. The slope is $H = 41 \pm 7$, if the extreme values are taken. (The difference between Λ_0 and Λ' at the highest concentration is only 0.164 and $H = \Delta\Lambda'/\Delta c$ is therefore very sensitive to experimental error.) In order to separate H into its components, a value of F is required; from viscosity measurements,[5] $F = 2.0$ and a plot of

$$\Lambda'_\eta \equiv \Lambda' + F\Lambda_0 c = \Lambda_0 + Jc \qquad (9)$$

evaluates $J = 75$ from the slope. (Here Λ'_η is a convenient variable because it includes all the known contributions to Λ and segregates the terms involving the unknowns, Λ_0 and J.) This in turn gives $å = 5.1 \pm 0.5$. Since J is fairly small, its value is quite sensitive to the viscosity coefficient: for $F = 1.5$, 2.0 and 2.5, $J = 67$, 75 and 85 respectively. The corresponding values of $å$ are 4.5, 5.1 and 5.7. The value $F = 2.0$ corresponds to a hydrodynamic radius $R = 5.4$, and $å = 2R = 10.8$. Considering this value, $å$ from J seems to be too small; even a slight amount of association, however, would add a term $K_A\Lambda_0$ to the apparent value of J and raise the value of $å$. Final decision on the ion size for this system must therefore be made on the basis of measurements in mixtures of propylene carbonate with solvents of lower dielectric constant.

In nitrobenzene, $Bu_4N \cdot BPh_4$ likewise gives an anabatic phoreogram. In the case of nitrobenzene, however, data are also available for mixtures of lower dielectric constant, and therefore a more detailed analysis can be made. For the mixtures in the higher range of dielectric constant, the $\Lambda' - c$ plots are linear, and extrapolation to $c = 0$ evaluates the limiting conductances. Now both the ions are large compared to the molecules of the solvent mixture (volume ratio approximately 27:1) and therefore the system $Bu_4N \cdot B\ Ph_4$–$PhNO_2$–CCl_4 should be a fair approximation to the idealized model used in classical hydrodynamics, namely, a sphere in a continuum. Then the Walden product $\Lambda_0\eta$ should be constant, but inspection of the values in Table III shows that the product varies systematically with solvent composition. The variation appears to be too large to ascribe merely to mechanical inadequacies of the model, and we are therefore led to consider a non-hydrodynamic origin for the variation.

If we assume that $\lambda^+_0(Bu_4N^+) = \lambda^-_0(BPh_4^-)$, the apparent hydrodynamic radius R can be computed by the Stokes formula

$$10^8 R = 0.8194/\lambda_0\eta \qquad (10)$$

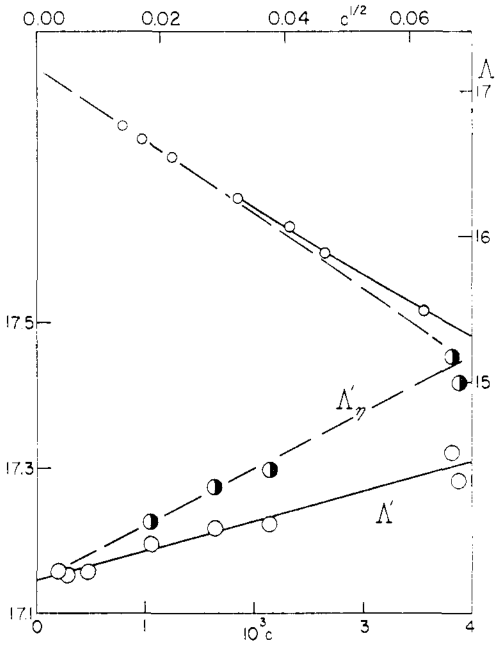

Fig. 1.—Conductance of $Bu_4N \cdot BPh_4$ in propylene carbonate.

If we consider the electrostatic braking force which solvent dipoles exert on a moving ion,[14] we expect that this radius will depend on the dipole content of the solvent. The dependence can be represented empirically[15] by the equation

$$RD = s + R_\infty D \qquad (11)$$

which has been shown to reproduce experimental data for a number of systems; furthermore, the sum $(R^+_\infty + R^-_\infty)$ was found to be equal to a, the electrostatic center-to-center distance between two ions at contact (evaluated either from J or K_A). Using the above method of calculation, we find $å = 7.1$ for $Bu_4N \cdot BPh_4$ in $PhNO_2$–CCl_4 mixtures from the limiting conductances obtained by the $\Lambda' - c$ extrapolations (the latter modified to allow for association, of course). This information considerably simplifies further analysis of our data, because the three parameter (Λ_0, a, K_A) equation

$$\Lambda' = \Lambda_0 + J(a)c\gamma - K_A c\gamma f^2 \Lambda \qquad (12)$$

then simplifies to a one parameter equation, by the symbolical sequence

$$\Lambda_0 \longrightarrow a \longrightarrow J, K_A;\ \Lambda_0 \longrightarrow S, E;\ \Lambda, c, \Lambda_0 \longrightarrow \Lambda'$$

and hence

$$\Lambda = \Lambda(c, \Lambda_0) \qquad (13)$$

One of the purposes of this paper in fact is to test the hypothesis implied in (13).

In the case of the $PhNO_2$–CCl_4 mixtures, association is not negligible, and hence the general equation 1 must be used. For this case, the auxiliary variable Λ'_η is defined as

$$\Lambda'_\eta \equiv \Lambda + Sc^{1/2}\gamma^{1/2} - Ec\gamma \log c\gamma + F\Lambda_0 c \qquad (14)$$

For the mixtures with dielectric constant greater than 20, the approximation $\gamma = 1$ can safely be made in (14); for lower dielectric constants, we ob-

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(14) F. Accascina, A. D'Aprano and R. M. Fuoss, THIS JOURNAL, **81**, 1058 (1959).

(15) R. M. Fuoss, *Proc. Nat. Acad. Sci.*, **45**, 807 (1959).

tained γ from the Fuoss–Kraus[16] function

$$\gamma = \Lambda/\Lambda_0 F(z) \qquad (15)$$

where $F(z)$ has been tabulated[17] as a function of

$$z = (S/\Lambda_0^{3/2})(c\Lambda)^{1/2} \qquad (16)$$

For F (in the term $F\Lambda_0 c$), we used the value 2.0, as in the propylene carbonate calculation, because F appears to be substantially independent[5] of the solvent. Then Λ'_η was plotted against c and extrapolated to $c = 0$ in order to determine the preliminary values of Λ_0 which were used to construct the $RD - D$ plots (11). Then using $\mathring{a} = 7.1$, as found by the method of reference 15, the term $Jc\gamma$ can be computed. Now all the terms of (1) are known, except the limiting conductance and the association term in K_A. This suggests defining another new variable Λ_K as

$$\Lambda_K \equiv \Lambda'_\eta - Jc\gamma \qquad (17)$$

where Λ'_η is defined by (14). Then by comparison with (1), we see that

$$\Lambda_K = \Lambda_0 - K_A c\gamma f^2\Lambda \qquad (18)$$

and Λ_K becomes a linear function of the variable

$$Z \equiv c\gamma f^2\Lambda \qquad (19)$$

where the activity coefficient is assumed to be given by the Debye–Hückel equation

$$-\log f = \beta'' c^{1/2}\gamma^{1/2}/(1 + \kappa a) \qquad (20)$$

and κ is the Debye–Hückel parameter calculated on the basis of the actual ionic concentration $c\gamma$. The $\Lambda_K - c\gamma f^2\Lambda$ plots were linear within the experimental error. From their slopes, we obtained the association constants for systems 1–5; the corresponding values of log K_A are given in Table III. It must be emphasized that the precision in K_A is low when association is slight; it is determined essentially by the difference between Λ_K at the highest concentration in a given run and the value of Λ_0. For systems 1–5, these differences are respectively 0.140, 0.029, 0.43, 0.065 and 1.58 Λ-units. Hence the K_A-values for systems 2 and 4 are probably only established to order of magnitude; these were two runs deliberately made at extreme dilutions.

For system 6, with $D = 11.00$, a variant of the $y - x$ method[10] was used. Since we assume that J is known (from Λ_0, *via* R_∞), a new variable v is defined by

$$v \equiv y - J = (\Lambda - \Lambda_{0t})/c\gamma \qquad (21)$$

where Λ_{0t} is the trial value of Λ_0. When the correct value of Λ_0 is found, (21) gives a straight line through the origin

$$v = -K_A x \qquad (22)$$

where $x = f^2\Lambda$ as before. In Fig. 2, the upper plot shows the data for system 6; using $\Lambda_0 = 31.3$ linearizes the function v and from the slope, $K_A = 970$. This method of determining K_A has one practical advantage: the $y - x$ method permits in principle evaluation of both J and K_A, but when K_A is large, J becomes uncertain because it is the difference between two much larger quantities. We prefer to obtain a value of J from the limiting conductance and then allow K_A to absorb any deviations due to as yet unknown terms in the conductance equation; since we are primarily interested in the logarithm of K_A, we are thus shifting the inadequacies of the present theory to the least sensitive function. Finally, for system 7, with $D = 7.79$, association is so marked that the curvature of the $v - x$ plot becomes insensitive to the trial value of Λ_0. But fortunately, with decreasing dielectric constant, the sum ($Jc\gamma + Ec\gamma \log c\gamma$) becomes negligibly small compared to the other terms,[18] and the conductance equation 1 reduces to the Fuoss–Kraus equation

$$\Lambda = \gamma(\Lambda_0 - Sc^{1/2}\gamma^{1/2}) \qquad (23)$$

which then can be applied to the data in the usual way. The lower plot of Fig. 2 shows $F(z)/\Lambda$ *vs.* $c\Lambda f^2/F(z)$ for this system. From the slope and intercept we find $K_A = 2.01 \times 10^4$ and $\Lambda_0 = 32.5$. The limiting conductances and association constants are summarized in Table III.

TABLE III

PROPERTIES OF $Bu_4N{\cdot}BPh_4$ IN $PhNO_2$–CCl_4 MIXTURES

No.	Λ_0	$\Lambda_0\eta$	$R^\pm$	δR	log K_A
1	22.34	0.4108	3.89	+0.08	0.67
2	25.16	.3950	4.15	− .06	0.76
3	25.35	.3975	4.12	− .04	1.15
4	27.69	.3769	4.35	− .11	1.11
5	30.91	.3586	4.57	− .01	2.72
6	31.3	.3465	4.73	+ .00	3.00
7	32.5	.3328	4.92	+ .26	4.30

As remarked above, our preliminary extrapolations gave $\mathring{a} = 7.1$ from the limiting conductances; this value was used to compute $J(a)$ and then the final extrapolations were made. The top line of Fig. 3 is a plot of RD against D, where R was calculated by means of the Stokes formula 10. The RMS equation for the line gives

$$R = 3.626 + 12.16/D \qquad (24)$$

(Since $R^+ = R^-$ by assumption, the identifying superscripts are omitted.) The deviations δR between the observed values (from $\Lambda_0\eta/2$) and the values calculated by means of (24) are given in the fifth column of Table III. The variance is 0.08; while the deviations appear to be systematic, the value $R = 3.63$ probably can be considered reliable to several per cent. for the purpose of calculating $J(a)$. Our calculations were made with the preliminary value $\mathring{a} = 7.1$; it was not considered necessary to recycle with the value 2(3.63) = 7.26.

The lower line of Fig. 3 is a plot of log K_A against $1/D$. It will be recalled that the point at lowest dielectric constant (largest D^{-1}) was obtained by neglecting the higher terms ($Jc\gamma + Ec\gamma \log c\gamma$). The next two points depend only slightly on the value of a, while the cluster of four points at high dielectric constant are extremely sensitive to the choice of a because the opposing terms Jc and $K_A cf^2 \cdot \Lambda$ are of the same order of magnitude. The collection of points can be approximated quite well by a linear function; from the slope, we derive $\mathring{a} = 7.00$, using the relation

$$\log K_A = \text{const.} + e^2/aDkT \qquad (25)$$

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(16) R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 476 (1933); R. M. Fuoss, *Chem. Revs.*, **17**, 27 (1935).

(17) R. M. Fuoss, *ibid.*, **57**, 488 (1935).

(18) H. Sadek and R. M. Fuoss, *ibid.*, **81**, 4507 (1959).

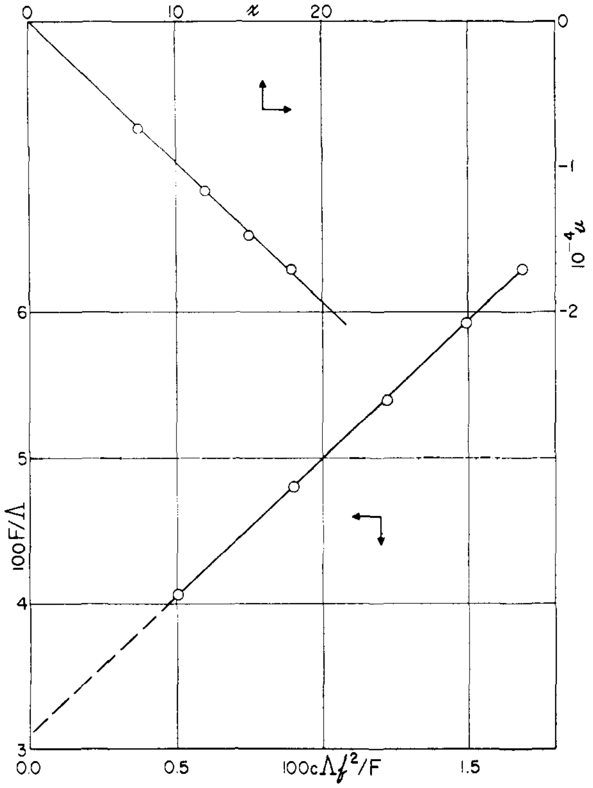

Fig. 2.—Determination of K_A: upper plot, system 6 by $v - x$ method; lower plot, system 7 by Fuoss–Kraus method.

The simplest form[19] of (25) is

$$K_A = 4\pi N a^3 e^b/3000 \qquad (26)$$

where N is Avogadro's number and b is the Bjerrum parameter $e^2/aDkT$. The constant in (25) is -0.21, according to Fig. 3; substitution in (26) gives $\mathring{a} = 6.25$, in fair agreement with the value from the slope and also with the value 7.26 obtained from the limiting conductances. The agreement can, of course, be made exact by inserting a factor exp $(-E_s/kT)$ in (26) to allow for solvent–solute interaction, as suggested by Gilkerson.[20] Using $\mathring{a} = 7.00$ in

$$K_A = (4\pi N a^3 e^b/3000)\exp(-E_s/kT) \qquad (27)$$

we find $E_s/kT = 1.4$ which is a reasonable magnitude for the interaction term. Once enough systems have been studied, a correlation may well appear between E_s and the constant s of equation 11, because both have by hypothesis the same physical origin.

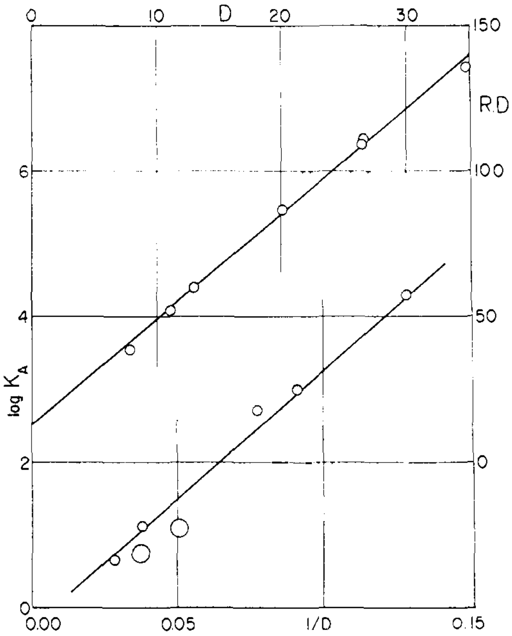

Fig. 3.—Upper plot, test of equation 9; lower plot, dependence of association on dielectric constant.

A parameter of dimensions length necessarily appears in any theoretical treatment of electrolytic properties which is based on a model more elaborate than the ultimate in simplicity, that of point charges. As a first step toward closer resemblance between theoretical model and physical system, spheres of diameter a in a continuum are the obvious choice. It has been shown that this model successfully accounts for the curvature observed in conductance curves of systems of high dielectric constant through the term Jc, whose coefficient is an explicit function $J(a)$ of the distance parameter a. Let us designate by a_J the value of a obtained from the curvature. The limiting conductance Λ_0 can be expressed in terms of the ionic radii R^+_∞ and R^-_∞ by means of an electrostatic correction to Stokes hydrodynamics; designate the sum of these hydrodynamic radii by a_Λ. When the dielectric constant decreases sufficiently, ionic association becomes measurable; from the slope of the plot log $K_A - D^{-1}$, another experimental value a_K of the distance parameter can be obtained. The results presented in this paper show that $a_J = 7.1$, $a_\Lambda = 7.26$ and $a_K = 7.00$ are identical within the limits of experimental determination for the system $Bu_4N\cdot BPh_4$–$PhNO_2$–CCl_4. If this result should turn out to be general, it is clear that analysis of conductance data will be simplified considerably. Investigation of other systems is therefore in progress.

NEW HAVEN, CONN.

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(19) R. M. Fuoss, THIS JOURNAL, **80**, 5059 (1958).

(20) W. R. Gilkerson, *J. Chem. Phys.*, **25**, 1199 (1956).