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Electrolyte–Solvent Interaction. IX. Tetra-alkylammonium Tetraphenylborides in Acetonitrile–Carbon Tetrachloride Mixtures at 25°

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The conductances of tetramethyl-, tetraethyl-, tetra-*n*-propyl- and tetra-*n*-butyl-ammonium tetraphenylborides have been measured at 25° in acetonitrile–carbon tetrachloride mixtures covering the range $10 < D < 36$ in dielectric constant. Limiting conductances and association constants follow the sequence expected from the structure of the salts. The apparent Stokes radius is linear in reciprocal dielectric constant; extrapolated values for the hydrodynamic radii of the above cations are 2.37, 2.75, 3.31 and 3.84. The center-to-center distance for anion and cation at contact in an ion pair, derived from the linear dependence of the logarithm of association constant on reciprocal dielectric constant, is 0.75 Å. (about 10%) larger than the sum of the hydrodynamic radii.

Reduction of conductance data to molecular parameters characteristic of solute and solvent requires among other things a knowledge of single ion conductances. It has been shown[2] recently that these can be obtained for non-aqueous systems from measurements of the conductance of tetrabutylammonium tetraphenylboride in a given solvent system by assuming that $\lambda_0(\mathrm{Bu_4N^+}) = \lambda_0(\mathrm{BPh_4^-}) = \Lambda_0/2$. The interpolation for limiting conductances in solvent mixtures by means of Walden's Rule $\Lambda_0\eta$ = const. is unreliable, however, since experiment shows that this product varies systematically with composition.[3] Study of Walden products for a number of systems showed[4] that the dielectric constant D of the solvent is the controlling independent variable and that single ion conductances are in fair agreement with the semi-empirical equation

$$\lambda_0\eta = (Fe/1800\pi)/(R_\infty + s/D) \qquad (1)$$

where η is solvent viscosity, the coefficient is 0.8194×10^{-8}, R_∞ is the hydrodynamic radius of the ion and s is a constant presumably characteristic of the ion-solvent interaction. The suggestion was made that s has its origin in a process which occurs in a mixed solvent having a polar component, due to the orientation and relaxation of dipoles in the solvent as the ion moves through it.

The purpose of this paper is to present a systematic study of eq. 1, using as test compounds the series of salts tetra-methyl, ethyl, *n*-propyl and *n*-butyl ammonium tetraphenylborides in the solvent system acetonitrile–carbon tetrachloride. This series gives a sequence of cations of increasing size; furthermore, all of them, as well as the anion, have volumes considerably larger than the volumes of the constituent molecules of the solvent. The data were found to conform to eq. 1. Furthermore, the hydrodynamic radii found ($\mathrm{Me_4N^+}$, 2.37; $\mathrm{Et_4N^+}$, 2.75; $\mathrm{Pr_4N^+}$, 3.31; $\mathrm{Bu_4N^+}$, 3.84) are in the sequence expected from structure and agree well with values derived by electrostatic theory from the association constants.[5]

Experimental

Materials.—Tetra-*n*-butylammonium tetraphenylboride $\mathrm{Bu_4NBPh_4}$ was prepared as before[6]; m.p., 233–235° (the "223°" in ref. 6 is a misprint); density, 1.023 at 25°. Tetra-*n*-propylammonium tetraphenylboride $\mathrm{Pr_4NBPh_4}$ was prepared from $\mathrm{Pr_4NI}$ and $\mathrm{NaBPh_4}$. After several recrystallizations from 2:1 acetone–water, the melting point was 205–207°, unchanged after one more recrystallization; density, 1.049 at 25°. Tetraethylammonium tetraphenylboride $\mathrm{Et_4NBPh_4}$ was prepared from $\mathrm{Et_4NBr}$ and $\mathrm{NaBPh_4}$ and recrystallized from 4:1 acetone–water. A crystal change appears at 260–265°; m.p., 350°; density, 1.069 at 25°. Tetramethylammonium tetraphenylboride was prepared from $\mathrm{Me_4NBr}$ and $\mathrm{NaBPh_4}$ and recrystallized from 2:1 acetone-water (200 cc./g.); m.p. > 350°; density, 1.084 at 25°.

Acetonitrile (Matheson) was kept over potassium hydroxide pellets (100 g./500 g. solvent) for 24 hr. and then over anhydrous sodium carbonate for several days. It was finally distilled from Drierite after several hours refluxing; after discarding a small forerun, the conductance remained constant at about 5×10^{-8} mho or less; b.p. 81.5° at 760 mm. Carbon tetrachloride was stored over barium oxide and distilled from activated alumina; b.p. 76.8° at 760 mm. Solvent mixtures were prepared by weight. Densities, viscosities and dielectric constants[7] (1 megacycle, General Radio 716 CS1 Bridge) were measured for each mixture used; these data are summarized in Table I which also gives code numbers for identification of the various mixtures. As a control on the purity of the salts, check conductance runs after several repeated recrystallizations were made in acetonitrile for each salt; in no case were discrepancies greater than 0.02% (the estimated precision) observed.

Salts were weighed on the microbalance (50–100 mg.) and added to solvent in the cell after the solvent conductance was determined. All solutions were made up by weight; volume concentrations c (eq./l.) were calculated from the known weights of materials and the densities of the solutions. The latter were obtained by measuring densities of solutions in the range of $2\text{–}5 \times 10^{-3}$ N and assuming that $\rho = \rho_0 + \alpha c$ where ρ_0 is solvent density, and α is a constant for a given salt and solvent mixture. If w g. of solute of molecular

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[1] California Research Corporation Postdoctoral Fellow, Yale University 1959–1960.

[2] R. M. Fuoss and E. Hirsch, THIS JOURNAL, **82**, 1013 (1960).

[3] H. Sadek and R. M. Fuoss, *ibid.*, **72**, 301, 5803 (corr.) (1950); **76**, 5897 (1954); **76**, 5902 (1954); **76**, 5905 (1954); **81**, 4507 (1959).

[4] R. M. Fuoss, *Proc. Natl. Acad. Sci. U. S.*, **45**, 807 (1959).

[5] E. Hirsch and R. M. Fuoss, THIS JOURNAL, **82**, 1018 (1960).

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

[7] The dielectric constants of systems 3, 4 and 5 of ref. 6 should be revised as follows: 27.20 for 40.23% $\mathrm{CCl_4}$, 22.00 for 55.25% and 14.40 for 74.89%.

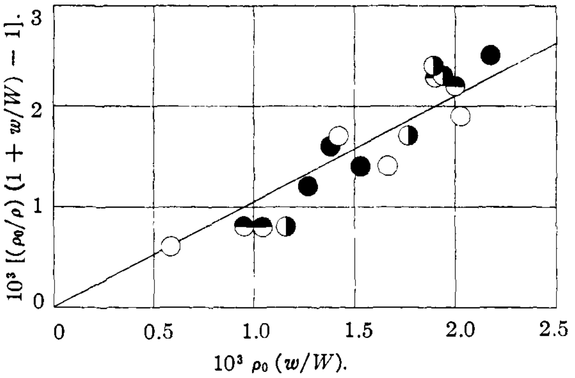

Fig. 1.—Determination of v_s from density data: ○, Me_4NBPh_4; ◑, Et_4NBPh_4; ⊖, Pr_4NBPh_4; ●, Bu_4NBPh_4.

weight M are dissolved in W g. of solvent of density $\rho_0 = 1/v_0$ to give $(w + W)$ g. of solution of density $\rho = 1/v$, and it is assumed that the specific volume v_s of the *dissolved* solute is independent of concentration, then from

$$v(w + W) = v_s w + v_0 W$$

it is easy to show that

$$\rho = \rho_0 + (M/1000)(1 - v_s/v_0)c$$

where

$$c = 1000\rho w/M(w + W)$$

By plotting $[(\rho_0/\rho)(1 + w/W) - 1]$ against $\rho_0 w/W$, v_s is determined as the slope of the line through the points and the origin, and then

$$\alpha = (1 - v_s/v_0)(M/1000)$$

where α may be positive or negative, depending on the relative values of v_s and v_0. The density data for all four of the salts can be summarized by the value $v_s = 1.06$, as shown in Fig. 1 where solvent densities cover the range 0.78–1.36 and w/W varies from 0.0007 to 0.0021. It will be noted that v_s is about 15% larger than the dry volumes of the crystalline salts and that the 5% difference in densities between the extremes Me_4NBPh_4 and Bu_4BPh_4 is imperceptible at these low concentrations. The equation $\rho = \rho_0 + \alpha c$, using $v_s = 1.06$, reproduces the observed densities to better than 0.01%.

TABLE I

PROPERTIES OF SOLVENT MIXTURES (ACETONITRILE–CARBON TETRACHLORIDE)

No.	Wt. % CCl_4	D	ρ	$100\ \eta$
1	0.00	36.01	0.7768	0.3449
2	28.66	30.62	0.9097	.3802
3	54.84	22.32	1.0793	.4449
4	60.15	20.60	1.1210	.4658
5	60.61	19.87	1.1252	.4676
6	62.47	19.46	1.1410	.4768
7	67.74	17.45	1.1876	.5020
8	68.06	17.18	1.1910	.5042
9	68.69	17.05	1.1967	.5107
10	70.81	16.13	1.2174	.5200
11	75.22	14.21	1.2619	.5502
12	75.97	13.92	1.2695	.5561
13	77.73	13.06	1.2884	.5698
14	78.77	12.31	1.3000	.5792
15	79.65	12.14	1.3095	.5863
16	80.68	11.16	1.3258	.5992
17	82.72	10.68	1.3449	.6145
18	84.27	9.80	1.3633	.6301

Cells used had constants equal to 1.06830 ± 0.00024 (standard, calibrated with KCl by the LZF method[8] to the Jones and Bradshaw point[9]) and 0.142098 ± 0.000020 (by comparison with the standard). Measurements were all made at 25 ± 0.002°, using a Shedlovsky[10] bridge with a calibrated Leeds and Northrop decade box in the known arm. The data are summarized in Tables II–V.

TABLE II

CONDUCTANCE OF Me_4NPh_4B IN CH_3CN-CCl_4 MIXTURES AT 25°

$10^4 c$	Λ	$10^4 c$	Λ	$10^4 c$	Λ
No. 1		No. 3		No. 13	
6.2569	143.64	8.1123	102.19	8.6685	60.12
4.9123	144.59	6.3266	103.60	6.9386	62.10
3.6592	145.62	4.6010	105.19	5.3309	64.38
2.4743	146.81	3.0707	106.93	3.7196	67.34
1.4209	148.09	1.7434	108.94	2.1601	71.28
No. 1		No. 7		No. 17	
10.3079	141.51	6.8124	84.87	6.0170	46.57
8.1980	142.59	5.2678	86.53	4.7641	48.77
6.0939	143.85	3.9102	88.30	3.7972	50.90
4.1286	145.34	2.5107	90.53	2.6804	54.10
2.0826	147.30	1.5317	92.56	1.5299	58.90

TABLE III

CONDUCTANCE OF Et_4NPh_4B IN CH_3CN-CCl_4 MIXTURES AT 25°

$10^4 c$	Λ	$10^4 c$	Λ	$10^4 c$	Λ
No. 1		No. 4		No. 11	
14.0136	130.63	10.1896	89.13	9.2780	64.76
8.6159	133.11	7.8836	90.67	7.2174	66.73
6.4489	134.36	5.8284	92.31	5.3598	68.94
4.3738	135.78	3.9937	94.12	3.5925	71.65
2.2095	137.72	2.4114	96.09	2.0332	75.07
No. 2		No. 9		No. 15	
8.8750	117.63	11.7671	76.04	9.1371	53.47
7.0887	118.74	8.9259	77.94	6.8476	55.92
5.3756	119.87	5.1009	81.38	5.3366	58.12
3.7857	121.16	4.1412	82.53	3.6277	61.03
		2.4433	85.02	2.0337	65.12

TABLE IV

CONDUCTANCE OF Pr_4NPh_4B IN CH_3CN-CCl_4 MIXTURES AT 25°

$10^4 c$	Λ	$10^4 c$	Λ	$10^4 c$	Λ
No. 1		No. 6		No. 14	
10.9717	118.04	10.2439	78.07	8.6932	53.17
8.2757	119.20	8.0037	79.41	6.8989	54.80
5.8928	120.63	3.9367	82.86	5.0312	56.91
3.9043	122.01	2.2243	84.83	3.3700	59.41
2.1320	123.59			1.9087	62.48
No. 1		No. 10		No. 18	
9.4486	118.83	11.0478	66.07	6.4290	40.47
7.2967	119.91	8.6411	67.60	5.0539	42.29
5.5479	120.94	6.4687	69.27	3.7091	44.62
3.7657	122.20	4.2563	71.45	2.5619	47.34
2.0964	123.72	2.4508	73.87	1.5423	50.80

Discussion

The data of Tables II–V were analyzed by the IBM-650 computer, using Kay's program[11] (with slight modification) for the equation[12]

$$\Lambda = \Lambda_0 - Sc^{1/2}\gamma^{1/2} + Ec\gamma \log c\gamma + Jc\gamma + J_2(c\gamma)^{3/2} - F\Lambda c - K_A c\gamma f^2\Lambda \quad (2)$$

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[8] J. E. Lind, Jr., J. J. Zwolenik and R. M. Fuoss, THIS JOURNAL, **81**, 1557 (1959).

[9] G. Jones and B. C. Bradshaw, *ibid.*, **55**, 1780 (1933).

[10] T. Shedlovsky, *ibid.*, **52**, 1793 (1930); H. Eisenberg and R. M Fuoss, *ibid.*, **75**, 2914 (1953).

[11] R. L. Kay, *ibid.*, **82**, 2099 (1960). We are indebted to Professor Kay for use of the program before its publication and for many helpful discussions.

[12] R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience Publishers, Inc., New York, N. Y., 1959. Symbols used in this paper are defined in Chapters 15 and 17.

TABLE V

CONDUCTANCE OF Bu_4NPh_4B IN CH_3CN–CCl_4 MIXTURES AT 25°

$10^4 c$	Λ	$10^4 c$	Λ	$10^4 c$	Λ
No. 1		No. 5		No. 12	
16.0902	107.59	9.7081	73.37	7.0327	56.17
9.1684	110.30	7.6241	74.52	5.4431	57.61
6.1596	111.89	5.7048	75.78	4.0635	59.17
3.1150	113.95	3.8144	77.33	2.6842	61.13
2.7764	114.25	2.1505	79.16	1.5191	63.37
No. 1		No. 8		No. 16	
12.1003	108.99	8.2582	66.26	5.6492	47.63
9.5708	110.05	6.5722	67.42	4.4807	49.12
6.7915	111.48	4.9163	68.77	3.3693	50.86
4.6413	112.80	3.3977	70.28	2.4125	52.77
2.3533	114.59	1.8704	72.34	1.3090	55.83

(It will be noted that the J_2 term, with

$$J_2 = (2^{1/2}/24)(\kappa a/c^{1/2})^3(1.0776b^2 - 2b - 1)\Lambda_0 - \beta\kappa^2a^2/c \quad (3)$$

is retained in (2), although it has been neglected in a number of recent publications from this Laboratory. This term is indeed small, but its retention has been found[13] to reduce a spurious systematic change of ion size with solvent composition.) The derived constants, Λ_0 and K_A, for the systems studied are summarized in Table VI, together with the values of a_J, the ion size derived from J.

In the case of the solvents of high dielectric constant, association was slight, so the limiting form of (2) corresponding to $K_A = 0$, $\gamma = 1$ was used in these cases in order to obtain preliminary values of Λ_0. Also, for these systems, where (2) gave a K_A value of dubious precision while the limiting form for no association gave too small an a-value (*via J*), a different procedure[14] was adopted. Using preliminary values for Λ_0 obtained from (2) or its limiting form, Λ_K can be computed, where

$$\Lambda_K \equiv \Lambda + Sc^{1/2} - Ec \log c + F\Lambda c - Jc - J_2c^{3/2} \quad (4)$$

provided a value of a (which evaluates J and J_2) is known. Then a plot of Λ_K, which is also given by

$$\Lambda_K = \Lambda_0 - K_A c f^2 \Lambda \quad (5)$$

for cases where association is slight, against $cf^2\Lambda$ evaluates Λ_0 and K_A. In (4), we set $a = a_\Lambda$, where a_Λ is the sum of the radii obtained by applying (1) to the preliminary values of Λ_0.

The final plots of $R = 0.8194 \times 10^{-8}/\lambda_0\eta$ against reciprocal dielectric constant are shown in Fig. 2 where the various circles represent the observed points and the solid lines are drawn with the constants obtained from a least square treatment of a $R\ D - D$ plot. (This method of evaluating the constants puts more weight on the data at high dielectric constant, where the precision of extrapolation for Λ_0 is higher.) In Table VI is shown a comparison of observed[15] values of Λ_0 with the values obtained by taking appropriate sums from

$$\lambda_0(Bu_4N^+) = \lambda_0(BPh_4^-) \quad (6)$$

$$= 0.8194 \times 10^{-8}/\eta\ (3.842 + 5.07/D) \quad (7)$$

$$\lambda_0(Pr_4N^+) = 0.8194 \times 10^{-8}/\eta\ (3.313 + 4.80/D) \quad (8)$$

$$\lambda_0(Et_4N^+) = 0.8194 \times 10^{-8}/\eta(2.748 + 4.20/D) \quad (9)$$

$$\lambda_0(Me_4N^+) = 0.8194 \times 10^{-}/{}^{8}\eta(2.366 + 6.87/D) \quad (10)$$

The value of R_∞ for the Me_4N^+ ion (2.37 Å.) agrees fairly well with a molecular model, but the increments $\Delta R_\infty = 0.38, 0.56, 0.53$ between successive members of the series are less than that corresponding to one methylene group. The flexibility of the alkyl chains in the R_4N^+ ions would, of course, lead to an equivalent hydrodynamic sphere whose radius is less than the length of an extended chain. Data for the Bu_4N^+ ion are now available[4] in five solvent systems; the corresponding values of R^+_∞ are 3.84 in MeCN-CCl_4, 3.55 in $PhNO_2$-CCl_4, 3.35 in MeOH-CCl_4, 3.53 in EtOH-CCl_4 and 4.46 in dioxane-water. Except for the last system, R^+_∞ appears to be substantially independent of the solvent. Further work on a wider variety of systems is needed, of course, but it now seems justifiable to hope that R_∞ will turn out to be a constant characteristic of a given ion in aprotonic solvents, from which many solution properties then can be predicted theoretically with good precision.

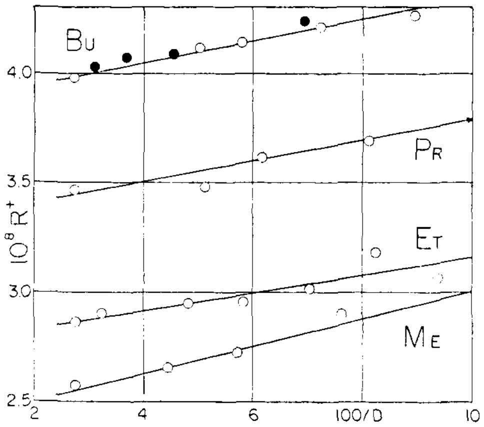

Fig. 2.—Dependence of apparent Stokes radii on dielectric constant.

Equations 7–10 evidently permit the calculation of the limiting conductances of the four salts in any mixture of MeCN and CCl_4 with $D \geqslant 10$ and represent the best available means of extrapolating into the region of still lower dielectric constants where direct determination from $\Lambda - c$ data is impossible. The average variation over the 21 systems of Table VI for [Λ_0 (calcd.) − Λ_0 (obsd.)] is 0.46%; if the three cases (marked with an asterisk) in which the variation exceeds statistical expectation are excluded, the variation over the remaining 18 systems is 0.3 %. (It should be mentioned that the precision of the $\Lambda - c$ data in a given solvent is of the order of 0.02%; the above variation of 0.3% represents the over-all consistency of all the data for a given salt in the different solvent mixtures.)

The coefficient J, which is essentially a measure of the curvature of the phoreograms, in principle permits evaluation of the center-to-center distance a_J of anion and cation at contact. As a quantity obtained from a second derivative, however, its precision is of course much less than that of a from Λ_0. The values of a_J are summarized in Table VI. The uncertainty in the numerical values is reflected

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[13] John E. Lind, Jr., Dissertation, Yale University, 1960.

[14] R. M. Fuoss and F. Accascina, *Proc. Natl. Acad. Sci. U. S.*, **45**, 1383 (1959).

[15] The Petrucci points[6] for Bu_4NBPh_4 in Fig. 2 (solid circles) are plotted using the corrected dielectric constants.[7]

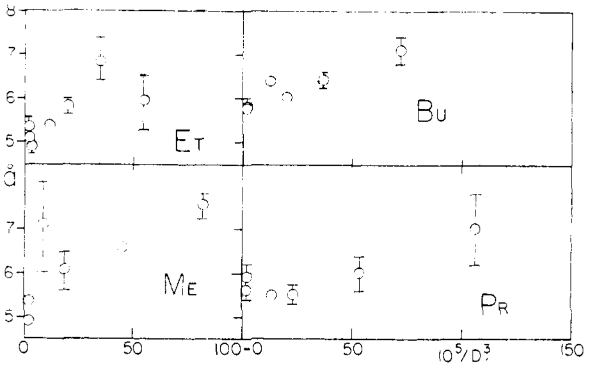

Fig. 3.—Dependence of a_J on dielectric constant.

in the following facts: (1) the values change only slightly from Me_4NBPh_4 to Bu_4NBPh_4; (2) they are smaller than the corresponding a_A values and also smaller than the values estimated from models; and (3) they vary systematically with solvent, as shown in Fig. 3 where a_J is plotted against D^{-3} for the four salts. The last item appears to be especially significant; it suggests that there are still some small unknown linear terms in the Λ-c function which are now being absorbed in J. A study[13] of the conductance equation shows that terms linear in c which are still missing from the theoretical equation probably would vary as D^{-3} or D^{-4}. Hence our present opinion is that no attempt should be made to "explain" the trend of a_J by an *ad hoc* hypothesis such as solvation. It is at least gratifying that the values of a_J turn out to be within an Å.-unit or so of the expected values. More weight must be given to ion sizes determined from Λ_0 by (1) or from the association constant (as will be presented below).

Table VI

Derived Constants

No.	D	a_J	K_A	Λ_0(obsd.)	Λ_0(calcd.)
		Me_4NBPh_4			
1	36.01	5.1	3	152.27	152.58
3	22.32	7.1	20	114.85	114.16
7	17.45	6.1	62	99.31	99.67
13	13.06	6.6	328	83.60	82.72
17	10.68	7.6	1110	74.39	75.20*
		Et_4NBPh_4			
1	36.01	5.2	4	142.77	142.60
2	30.62	4.9	8	128.08	128.49
4	20.60	5.4	21	102.95	102.64
9	17.05	5.8	60	93.18	92.36
11	14.21	6.9	184	84.91	84.41
15	12.14	5.9	408	76.72	77.99*
		Pr_4NBPh_4			
1	36.01	5.8	4	128.36	128.59
6	19.46	5.5	31	91.29	90.17
10	16.13	5.5	70	81.55	81.56
14	12.31	6.0	235	71.62	71.46
18	9.80	7.0	880	63.10	64.02*
		Bu_4NBPh_4			
1	36.01	5.8	6	119.48	119.31
5	19.87	6.4	21	85.03	85.54
8	17.18	6.0	45	78.37	78.57
12	13.92	6.4	133	70.04	70.06
16	11.16	7.1	365	64.18	63.93

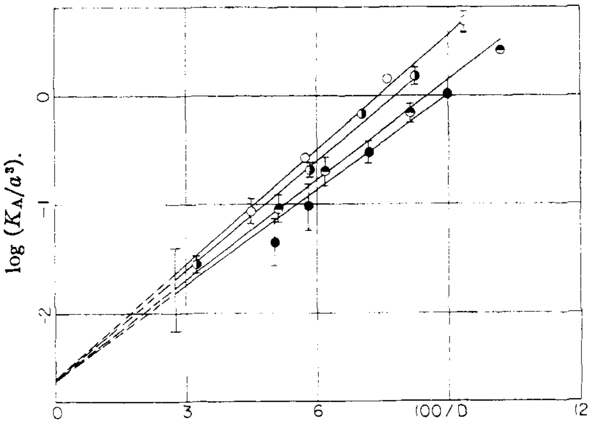

Fig. 4.—Test of equation 11; dependence of association constant on ion size and dielectric constant, same code as Fig. 1.

In acetonitrile, with a dielectric constant of 36, ion association is almost negligible due to the large size of the ions. Consequently the computer finds it difficult to separate the $Jc\gamma$ and $K_Af^2\Lambda c\gamma$ terms, both of which are to first approximation linear in c. In the mixtures of lower dielectric constants, where $f^2\Lambda$ becomes significantly different from Λ_0, reliable values of both J and K_A can be obtained by equation 2. As mentioned above, we simplified the analysis of the data by using a_A to compute J and J_2 and extrapolated by means of equation 5 in order to obtain the final values of Λ_0 and K_A. Theoretically[16]

$$K_A = (4\pi Na^3/3000)e^b \qquad (11)$$

(where $b = e^2/aDkT$) for systems in which ion-solvent interaction is small; for the R_4NBPh_4 salts under consideration here (11) evidently is an adequate approximation, as shown in Fig. 4 where log (K_A/a^3) is plotted against $1/D$. The four straight lines as drawn originate at log $(4\pi N/3000)$, showing that the Gilkerson[17] term exp $(-E_s/kT)$ is unity within the experimental error. From the slopes of the lines, we evaluate a_K values as follows: Me_4NBPh_4, 6.96; Et_4NBPh_4, 7.30; Pr_4NBPh_4, 7.95; Bu_4NBPH_4, 8.36. These are in the expected sequence and like the a_A values (Me_4NBPh_4, 6.21; Et_4NBPh_4, 6.59; Pr_4NBPh_4, 7.15; Bu_4NBPh_4, 7.68) give center-to-center distances somewhat smaller than dimensions from models. The difference between a_K and a_A is practically constant (average, 0.75); agreement within 10% of values obtained from two completely independent sources ($\Lambda_0 \rightarrow a_A$, hydrostatic; $K_A \rightarrow a_K$, electrostatic) supports the hypothesis that the a values are additive molecular parameters characteristic of the ions and not merely numbers obtained by curve-fitting. As already mentioned, the a_J values are less reliable than a_A or a_K, but comparison of the latter with Fig. 3 shows that even the a_J values are at least reasonable in magnitude. For quantitative arguments, however, the values of a from Λ_0 and/or K_A naturally are preferable, because they are defined to a much better precision.

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(16) R. M. Fuoss, This Journal, **80**, 5059 (1958).

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