[CONTRIBUTION NO. 1431 FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY AND THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Ionic Association. II. Several Salts in Dioxane–Water Mixtures

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RECEIVED MARCH 1, 1957

A new method of mathematical analysis is applied to conductance data for several salts in dioxane–water mixtures. It is shown that the association constant A is a simple function $A_0 \exp(e^2/aDkT)$ of the dielectric constant of the solvent mixture, unless a dipole is present in one of the ions (*e.g.*, the bromate ion), when an additional ion–dipole free energy appears in the exponent. Data for quaternary ammonium salts show the presence of a previously unsuspected linear term in conductance, which is due to the viscosity increase produced by bulky ions. Consequently solution viscosity rather than solvent viscosity should be used in treating conductance. Finally, it is concluded that the Bjerrum theory of ion association and the Fuoss–Shedlovsky extrapolations should both be replaced by the methods used in the present analysis.

In the preceding paper,[1] it was shown that association constants may be derived from conductance data, even when the fraction of ions associated to pairs is small. A fundamental prerequisite is that the data be of high precision ($\pm$ 0.02% at least); at a concentration of 0.005 N, for example, an association constant $A = 5$ corresponds to only about 2.5% association. A further prerequisite is that data be available over a range of values of dielectric constant; the range must be wide enough to include solvent mixtures in which the association constant has a value of at least 10. The reason for the latter requirement is simply that association gives a leading term of order concentration in the conductance equation, and there are also present linear terms from long range ionic interaction. When A is small, the difference of the interaction term $J_1(a)$ and $A\Lambda_0$ can be determined but the quantity cannot be resolved into its components. When one (or both) of the ions is bulky compared to the solvent molecules, an additional linear term ($5\Lambda_0\delta c/2$) also appears, which can only be separated from the coefficient of the linear term if A and $\mathring{a}$ are independently known. From the data in solvents of low dielectric constant, the ion size a can be determined; given the ion size, A can be calculated for the solvents of higher dielectric constant, within the validity of the assumption that the parameter a is independent of composition. Recent work by Kraus[2] and co-workers satisfy the criteria described above. (There are many data of high precision in the literature for aqueous solutions, but they cannot be examined for ionic association because, if association occurs for say the alkali halides in water, it is so slight that it is undetectable by our present analysis; a small A would be absorbed in $J_1(a)$, and merely appear as a slightly different value of ion size from the one which should have been found.) In this paper, we shall present an analysis of several cases where the method is applicable. They will serve to show that conductance can become a considerably more powerful research tool than has previously been realized, in that it can serve to evaluate parameters characteristic of ions in addition to the limiting conductance.

Sodium Bromate.[2]—The conductance of this salt has been measured in water–dioxane mixtures covering the range $78.48 \geqslant D \geqslant 31.53$. When treated by the method appropriate for unassociated electrolytes,[3] the data give linear Λ''' *vs.* c plots and extrapolate to an unambiguous value of Λ_0, but the value of a required to make the Λ''' *vs.* c plot horizontal is only 3.00 Å., which seems unrealistically small. Hence, despite the fact that the conductance curve lies above the Onsager tangent, we are led to suspect ion association. In 55% dioxane, the phoreogram is catabatic, clearly indicating association. On the basis of the Bjerrum theory, it would be possible to have ion association at low dielectric constants, with an abrupt cessation of pairing above a critical value of the dielectric constant.[4] But this critical value is merely the consequence of a device used by Bjerrum to avoid divergence of an integral and corresponds to no physical reality; it seems more reasonable to assume that, as the dielectric constant is raised, the fraction of solute present as ion pairs gradually decreases at a given stoichiometric concentration, but never completely vanishes. Indeed, as already has been pointed out,[1] just as soon as a non-zero ion size is introduced into the model, the existence of ion pairs is tacitly admitted, because a non-zero size can only make itself visible experimentally by the effects of actual contacts of ions, and for the duration of the contact, neither ion can be considered to be "free" in any of the senses implied by that adjective. Availability of data for a salt over a range of dielectric constant in which the phoreogram starts below the Onsager tangent and crosses it as dielectric constant increases provides an ideal means of testing the above hypotheses.

For the four mixtures of lower dielectric constant, the functions y and x defined by equations 21 and 22 of the preceding paper were computed; the corresponding plots are shown in Fig. 1. For the 55 and 50% mixtures, the calculation was made to second approximation, as described in the previous paper. It should be emphasized that y is extremely sensitive to experimental error at low concentrations, because it contains in the numerator a *difference* which approaches zero as c approaches zero, while the denominator is proportional to c itself. For example, at 5×10^{-4} N in the 55% mixture, an error of only 0.020 Λ-unit in Λ makes an error of 10% in y. Hence relatively more weight is given to the points at higher concentrations; the latter must, of course, satisfy the condition $\kappa a < 0.20$, in order to permit application of the model

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[1] R. M. Fuoss, THIS JOURNAL, **79**, 3301 (1957).

[2] R. W. Martel and C. A. Kraus, *Proc. Nat. Acad. Sci.*, **41**, 9 (1955).

[3] R. M. Fuoss and L. Onsager, *J. Phys. Chem.*, **61**, 668 (1957).

[4] R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 1019 (1933).

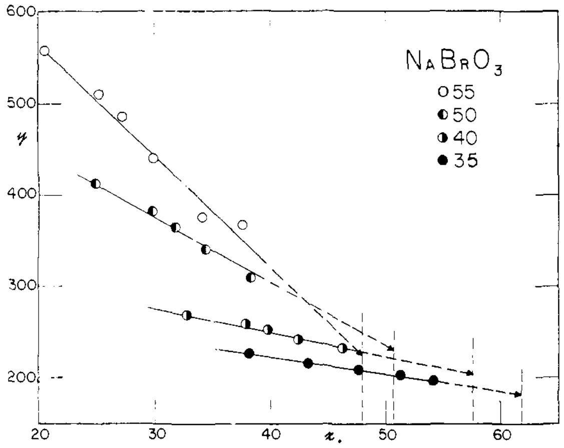

Fig. 1.—Extrapolation plots for sodium bromate in low range of dielectric constants.

and method.) Within experimental error, the plots are linear; the slopes determine the association constants A immediately. Extrapolation to $x = \Lambda_0$ gives the ordinate

$$y(0) = J_1(a) - A\Lambda_0$$

from which $J_1(a)$ is evaluated, because the product $A\Lambda_0$ is now known. Then from a plot of $J_1(a)$ against a, the value of a is determined. The results of these calculations are shown in the last four lines of Table I; it will be noted that the parameter a remains substantially constant.

TABLE I

SODIUM BROMATE IN DIOXANE–WATER MIXTURES AT 25°

% Dioxane	D	A	$J_1(a)$	$\mathring{a}$	λ_0
0	78.48	0.50	191	(4.00)	105.75_5
10	70.33	0.68	202	(4.00)	90.41_5
20	61.86	0.90	225	(4.00)	77.31_5
30	53.28	1.33	272	(4.00)	66.47
35	48.91	2.10	307	3.96	61.78_5
40	44.54	2.73	360	3.94	57.66
50	35.85	6.87	570	4.03	50.74
55	31.53	11.8	790	4.17	47.92

At dioxane contents of less than 35% ($D > 50$), the y *vs.* x plots are so nearly horizontal that no reliable value of the slope (and hence of A) could be obtained; that is, the (nearly) constant ordinate evaluates the quantity $(J_1 - A\Lambda_0)$ but separation of the terms is no longer possible. We therefore assumed that a remained constant at 4.00, and computed Λ''', using $a = 4.00$ to evaluate J_1 and J_2, and plotted Λ''' against $z = c\Lambda f^2/(1 - \alpha c^{1/2})$; according to equation 30, the plot should be

$$\Lambda''' = \Lambda_0 - Az$$

linear with slope A and intercept Λ_0. The graphs are shown in Fig. 2, where for compactness in presentation, the ordinate scales are shifted vertically by arbitrary amounts. The values of Λ_0 are indicated by the arrows. The unit of the vertical scale is shown by indicating 0.10 Λ-unit between the vertical lines at the lower left; this distance corresponds to about 0.10% for the aqueous system and 0.15% for the 30% mixture. The points lie on the lines within 0.01%. The numerical results are summarized in the upper half of Table I.

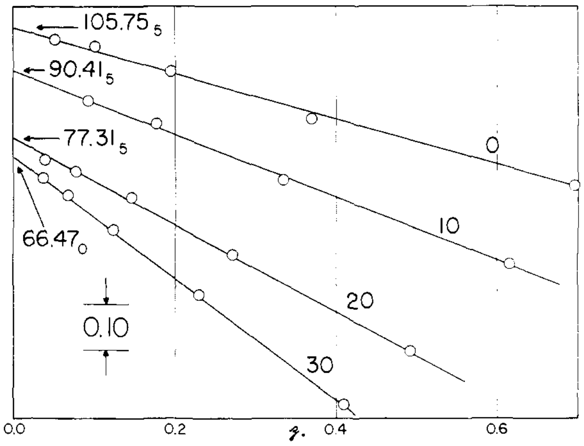

Fig. 2.—Extrapolation plots for sodium bromate in high range of dielectric constants.

The A column of Table I thus contains two sets of values: four values directly determined as slopes of the y–x plots where a was simultaneously evaluated with A and Λ_0, and four values from the slopes of the Λ''' *vs.* z plots, whose construction required an *a priori* value of a. For the latter, we used the average of the first four values; the self-consistency of the ensemble of values of the constants is tested in Fig. 3, where log A is plotted against the reciprocal of the dielectric constant. Both sets of points line on the same graph, which moreover is linear. If a were not a constant, the lowest points in Fig. 3 obviously could not lie on a prolongation of the line through the top four, except by an amazing compensation.

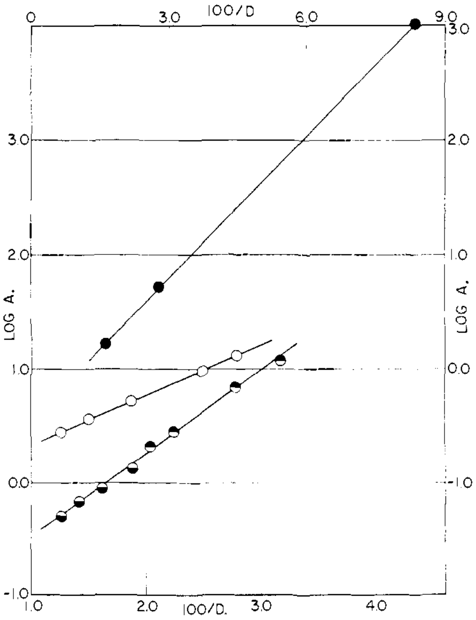

Fig. 3.—Dependence of association on dielectric constant: ○, tetrabutylammonium iodide, from y *vs.* x plots; ◓, sodium bromate, from y *vs.* x plots; ◒, sodium bromate, from Λ''' *vs.* z plots; coördinates left and below. ●, tetraisoamylammonium nitrate, from y *vs.* x plots; coördinates, right and above.

The linearity of the log A *vs.* D^{-1} plot suggests that A has the simple form

$$A = A_0 \exp(u/kT)$$

where μ is an electrostatic free energy. But if we assume that u is simply a charge–charge energy e^2/aD, the slope of the line in Fig. 3 gives $\mathring{a} = 3.30$ instead of 4.00, the electrostatic center-to-center distance found from the y *vs.* x analysis. The discrepancy can be removed, quickly however, if we recall that the bromate ion contains a dipole, because it has a pyrimidal structure with Br^{++} at the apex and three O^- ions at the base in one of its canonical forms.[5] The energy u therefore is the sum

$$u = (e^2/aD) + (\mu e/d^2D)$$

where μ is the dipole strength and d is the distance from the center of the cation to the electrostatic center of the dipole. For $10^8d = 2.00$, $10^{18}u = 1.03$ and for $10^8d = 4.00$, $10^{18}\mu = 4.10$, if we set $\mathring{a} = 4.00$ above. These values lie in an entirely reasonable range.

This result naturally suggests a conductimetric study of a variety of other ions; nitrates, for example, should give the same value of a from the y *vs.* x plot and the log A *vs.* D^{-1} plot, because the nitrate ion is electrically symmetrical.[5] Chlorates, on the other hand, should have a steeper log A *vs.* D^{-1} plot than corresponds to the a determined from the y *vs.* x plot. Conversely, conductance data should be helpful in determining previously unknown structures.

Tetrabutylammonium Iodide.[2]—The conductance was measured in water and in four dioxane–water mixtures, covering the range $35.85 \leqslant D \leqslant 78.48$. As is shown in Fig. 4, the y *vs.* x plots are linear; the slopes give the association constants. The latter are plotted as the open circles on Fig. 3. From the slope of the log A *vs.* D^{-1} line, we obtain $\mathring{a} = 5.55$ as the nitrogen–iodine center-to-center distance in the ion paris. It will be noted that the Bu_4NI line is less steep in Fig. 3 than the one for $NaBrO_3$; the difference is due first to the smaller size of the sodium ion and second to the reinforcement of charge–charge attraction by the charge–dipole interaction already discussed.

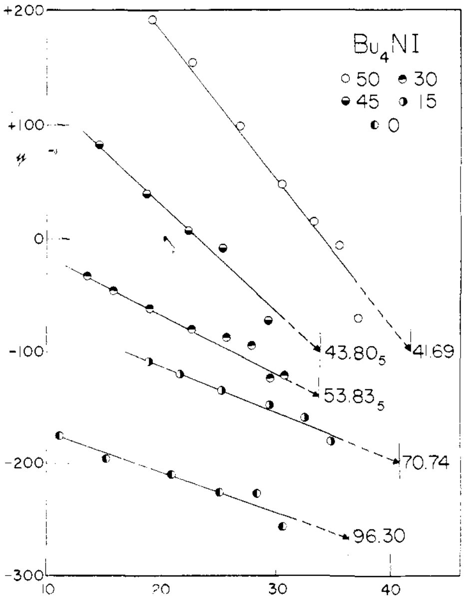

Fig. 4.—Extrapolation plots for tetrabutylammonium iodide. Abscissa scales: 50%, as shown; 45%, $(x - 10)$; 30%, $(x - 20)$; 15%, $(x - 30)$; 0%, $(x - 60)$.

If now values of $J_1(a)$ are calculated by adding $A\Lambda_0$ to the ordinate $y(0)$ obtained by extrapolating the y *vs.* x plots of Fig. 4 to $x = \Lambda_0$, absurdly small (1.5–3.5) and variable values of the parameter $\mathring{a}$ result from the values of $J_1(a)$ so obtained. This is in marked contrast to the case of sodium bromate, where it was shown that the $\mathring{a}$ value from the slope of the log A *vs.* D^{-1} plot was consistent with the values obtained from the y *vs.* x intercepts, *i.e.*, remained constant over the entire range of solvents investigated. Clearly, an effect is appearing in Bu_4NBr which is absent (or at least negligible) in the case of $NaBrO_3$. The outstanding physical difference between the two salts is the disparity in size of the cations; the tetrabutylammonium ion, according to molecular models, should exclude a spherical volume $7–8 \times 10^{-8}$ cm. in radius, while the sodium ion is about the same size as a water molecule. Using equation 34 of the preceding paper in the form

$$5\Lambda_0\delta/2 = J_1(a) - y(0) - A\Lambda_0$$

and using $\mathring{a} = 5.55$ to evaluate $J_1(a)$, the values of δ obtained are shown in the fifth column of Table II. The next column gives the corresponding values of the hydrodynamic radius R, calculated as

$$R = 7.32\delta^{1/3} \times 10^{-8}$$

The resulting quantity is reasonably constant and agrees remarkably well with the value expected on the basis of the model, assuming the Einstein formula to give the viscosity contribution due to the large cations. It should be mentioned that earlier work on the viscosity of bolaform electrolytes[6] shows that the Einstein limit of 5/2 for the ratio of specific viscosity to volume fraction is approached as these ions approach spherical shape. Introduction of the $(5\delta c/2)$ term into the conductance equation is thus not completely an *ad hoc* hypothesis. The fact that the viscosity term leads to reasonable R values argues for its reality; granting this, the long debated question of solution viscosity *versus* solvent viscosity as the pertinent variable in conductance theory appears to have found its answer.

TABLE II

TETRABUTYLAMMONIUM IODIDE IN DIOXANE–WATER MIXTURES AT 25°

% Dioxane	D	A	$J_1(5.5)$	δ	$\mathring{R}$	Λ_0
0	78.48	2.73	245	0.98	7.3	96.30
15	66.10	3.65	253	1.03	7.3	70.74
30	53.28	5.1	303	1.30	8.0	53.83_5
45	40.20	9.5	476	1.46	8.3	43.80_5
50	35.85	13.0	604	1.56	8.5	41.69

Tetraisoamylammonium Nitrate.[2]—This salt was measured in 0, 10, 20, 30 and 50% dioxane, but

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[5] J. C. Slater, *Phys. Rev.*, **38**, 325 (1931).

[6] P. Goldberg and R. M. Fuoss, *Proc. Nat. Acad. Sci.*, **38**, 758 (1952).

only at 20 and 50% was the concentration range wide enough to permit a reliable determination of slope (A) and intercept ($J_1 - 5\Lambda_0\delta/2 - A\Lambda_0$). The span from D = 61.86 (20%) to D = 35.85 (50%) is rather narrow to use to evaluate $\mathring{a}$ from the slope of the log A *vs.* D^{-1} plot, but fortunately some older data on this salt in 79.8% dioxane are available[7]; the y *vs.* x plot (second approximation) is shown in Fig. 5. From the slope, we obtain A = 1050. This point, together with the points for the 20 and 50% mixtures, establish a satisfactory straight line (solid points, Fig. 3): $A = 0.354 \exp(96.1/D)$. Equating the exponent to $e^2/aDkT$, we find $\mathring{a}$ = 5.83. This equation was then used to evaluate A for the 0, 10 and 30% mixtures, and the corresponding values of J_1 and J_2 were computed, using $\mathring{a}$ = 5.83. Using these constants, the

$$\Lambda^{\mathrm{IV}} = \Lambda''' + Az$$

quantity was then computed; if the conductance obeys the equations derived in the previous paper, Λ^{IV} includes the effect of both ion association and ion atmosphere, leaving only the viscosity term to be evaluated. From equation 33, we have

$$\Lambda^{\mathrm{IV}} = \Lambda_0 - 5\Lambda_0\delta c/2$$

The corresponding plots are shown in Fig. 6; they are linear, well within the limit of experimental error, and δ is determined from the slopes. For the 20 and 50% mixtures, δ was determined from $y(0)$ as for tetrabutylammonium iodide, using $\mathring{a}$ = 5.83 to evaluate $J_1(a)$; for the 79.8% mixture, the ($J_1 - A\Lambda_0$) term is so large that it completely masks the $5\Lambda_0\delta/2$ term. From Fig. 5, $J_1(a) = 1.47 \times 10^4$; calculated for $\mathring{a}$ = 5.83, $J_1 = 1.20 \times 10^4$. Considering the sensitivity of $J(a)$ to a when b is large (low dielectric constant) and the uncertainty in determining J_1 from the graph when A is so large, we consider the agreement satisfactory. Other details of the calculation are summarized in Table III. Again, an entirely reasonable value of the hydrodynamic radius is found; since this constant in effect collects *all* of the residual uncertainties of the calculation in this particular example, we are inclined to place considerable confidence in both the data and the theoretical treatment, because such agreement among six sets of data has practically zero probability of being fortuitous.

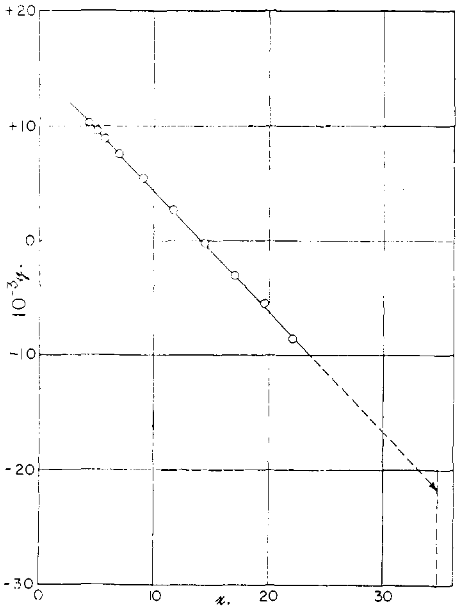

Fig. 5.—Extrapolation plot for tetraisoamylammonium nitrate in 79.8% dioxane.

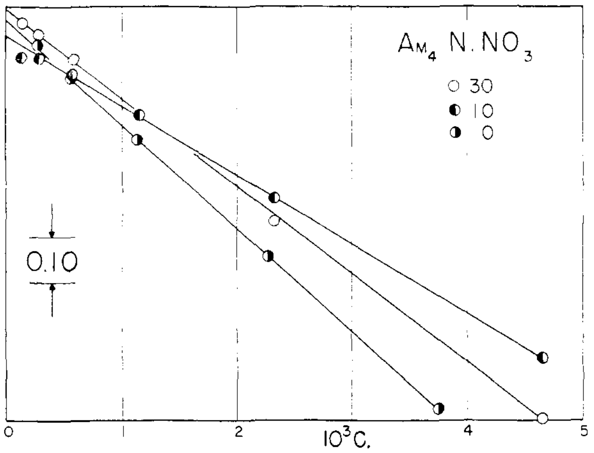

Fig. 6.—Extrapolation plots for tetraisoamylammonium nitrate in 0, 10 and 30% dioxane.

TABLE III

TETRAISOAMYLAMMONIUM NITRATE IN DIOXANE–WATER MIXTURES AT 25°

% Dioxane	D	A	$J_1(5.83)$	δ	$\mathring{R}$	Λ_0
0	78.48	(1.20)	248	1.02	7.3	89.27$_5$
10	70.33	(1.38)	252	1.04	7.4	74.84$_5$
20	61.86	1.67	274	1.17	7.7	63.13
30	53.28	(2.14)	320	1.13	7.6	54.04
50	35.85	5.2	643	1.53	8.4	42.57$_5$
80	12.01	1050	1.2×10^4	..	..	34.8

We finally remark that, since the a-value obtained from the slope of the line in Fig. 3 leads to a satisfactory value of R, the charge–charge energy is all that is required to account for the slope of the log A *vs.* D^{-1} plot; in other words, as expected, the nitrate ion shows no dipole.

Tetramethylammonium Picrate.[8]—This salt presents an unusually interesting case: it was measured in a series of mixtures including 70% dioxane. where the dielectric constant is only 19.07. The conductance curve lies a little below the Onsager tangent in the dioxane-rich systems, and one might be tempted to assume a small amount of ion association. When, however, the y *vs.* x plots are constructed, they are seen to be practically horizontal; in other words, within the experimental error, A is zero. The fact that no association due to Coulomb forces appears for this salt confirms the generally accepted picture of the picrate ion: the single negative charge is not localized at the phenolic oxygen but is distributed over the peripheral π-electron system of the whole molecule. Conse-

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[7] R. M. Fuoss, Thesis, Brown University, 1932; C. A. Kraus and R. M. Fuoss, THIS JOURNAL, **55**, 21 (1933).

[8] P. L. Mercier and C. A. Kraus, *Proc. Nat. Acad. Sci.*, **41**, 1033 (1955).

quently the electrostatic force field is so weak that thermally stable pairs with the cation cannot form. The only pairing possible is that due to chance collisions, which evidently do not reduce conductance appreciably.

TABLE IV

TETRAMETHYLAMMONIUM PICRATE IN DIOXANE–WATER MIXTURES AT 25°

% Dioxane	D	$J_1(a)$	$\mathring{a}$	Λ_0
55.0	31.53	848	7.35	33.33_5
60.0	27.21	1269	7.78	32.42_5
62.5	25.15	1533	7.85	32.12
65.0	23.14	1812	7.22	31.93_5
67.5	21.12	2290	7.08	31.77
70.0	19.07	3030	6.97	31.75

If the $A\Lambda_0$ term is negligibly small compared to the other terms, then

$$y(0) = J_1 - 5\Lambda_0\delta/2$$

and the problem is to separate the components. In the mixtures of higher dielectric constant, J_1 and the hydrodynamic terms are of comparable magnitude; as the dielectric constant decreases, J_1 increases rapidly while δ remains constant, according to our hypotheses. The data were therefore treated as follows. A series of a-values were chosen, and Λ''' was computed and plotted against concentration. If the association term is negligible

$$\Lambda''' = \Lambda_0 - 5\Lambda_0\delta c/2$$

Each value of a will obviously give a straight line with a different slope; from the slopes in the water-rich mixtures, $\delta(a)$ was thus determined. Plots of $\delta(a)$ against the selected a-values were then made for the systems with 0, 20, 35 and 45% dioxane. Ideally, these curves should have intersected at a single point, corresponding to the unique values of a and δ theoretically required to describe the system. Actually, the curves gave a cluster of intersections: the range of $\mathring{a}$-values was from 7.48 to 8.00 (average, 7.73) while the δ-values ran from 0.39 to 0.55, averaging to 0.48. Both values seem quite reasonable. If we assume that $\delta \sim (R_1^3 + R_2^3)$ and further assume equal radii for the two ions as a rough approximation, $\delta = 0.48$ leads to $R = 4.54$ for the equivalent hydrodynamic radius. Then, using $\delta = 0.48$ to calculate $5\Lambda_0\delta/2$ for the dioxane-rich systems, values of $J_1(a)$ were obtained from the (practically constant) values of $y(c) \approx y(0)$. The corresponding values of $\mathring{a}$ were then obtained by interpolation on J_1–a plots. The results are shown in Table IV; there is a slight systematic trend to lower values as D decreases, but the average of 7.38 is in excellent agreement with the values obtained as described above in the water-rich mixtures. The decrease in $\mathring{a}$ may foreshadow the onset of association, which must eventually occur in solvents of sufficiently low dielectric constant. But when J_1 is so large, a small Ax term is practically invisible.

Tetrabutylammonium Bromide.[8]—This salt was also measured over the range 0–70% dioxane. Even a rough estimate shows that its association at a given value of dielectric constant is *less* than that for the iodide; it was only possible to obtain reliable values of A from the slopes of the y–x plots in the mixtures containing 50% or more dioxane. These values gave a straight line on a log A *vs.* $1/D$ plot, which can be represented by the equation $A = 0.11 \exp(133/D)$; the corresponding $\mathring{a}$-value is 4.21. On the other hand, if we calculate $\mathring{a}$ from $J_1(\mathring{a})$ obtained from the intercepts $y(0)$, using $\delta = 0.535$ (see later), the values shown in Table V result. Unlike tetrabutylammonium iodide and tetraisoamylammonium nitrate, a different ion size is required to reproduce the experimental association constants on the one hand and the long range J_1-terms on the other. The former constant, which describes ion pairs in semi-permanent contact, is small and constant, while the latter, which describes contacts in which ions of opposite charge collide without forming a pair, is larger and increases with decreasing dielectric constant.

TABLE V

TETRABUTYLAMMONIUM BROMIDE IN DIOXANE–WATER MIXTURES AT 25°

% Dioxane	D	A	$y(0)$	Λ_0	$J_1(a)$	$\mathring{a}$
50	35.85	4.6	345	43.71	605	5.22
55	31.53	7.8	456	41.54	835	5.42
60	27.21	16.4	600	39.76	1305	6.24
65	23.14	37	615	38.32	2090	6.90
70	19.07	103	0	37.11	3870	8.12

When we compare tetrabutylammonium iodide and bromide, the following rationalization of the experimental results can be made. The small value of 4.21 seems reasonable for the N^+–Br distance in an ion pair. We note that the iodide is more highly associated than the bromide: for the former, $A = 0.78 \exp(101/D)$ while for the latter, $A = 0.11 \exp(133/D)$. The smaller exponent for the iodide corresponds of course to the greater size of the iodide ion compared to the bromide, but the large difference in coefficients A_0 requires comment. Part of A_0 is an entropy term $\exp(-\Delta S/R)$, but this should be practically the same for Bu_4NBr and Bu_4NI. Therefore the only explanation remaining is that the association constant of Bu_4NI contains an additional energy term $\exp(u/kT)$ which is independent of dielectric constant. The ratio 0.78/0.11 equals $e^{1.95}$, so an energy of about $2kT$ is required to stabilize iodide–N^+ pairs with respect to bromide–N^+ pairs. We suggest that this energy is the potential between the N^+ center and the dipole which it induces in the highly polarizable iodide ion, after coulomb forces have brought the pair to near contact (and withdrawn from the medium of dielectric constant D). The larger values of $\mathring{a}$ from J_1 then represent averages between contact diameters in stable pairs and diameters from collisions which do not lead to pair formation, *i.e.*, collisions with the periphery of the quaternary ion from which the bromide ion diffuses away again. In the case of the iodide ion, the additional induction force comes into play at contact and makes most collisions lead to pairs which later disassociate when they acquire sufficient thermal energy.

Another difference between bromide and iodide must be mentioned: the Walden product for the former drops sharply, starting at about 50% dioxane. This might mean some specific interaction between the bromide ion and dioxane which does not occur with the iodide (and picrate), and which increases the effective size of the free bromide ion. Until bromide–iodide comparisons are made in other solvent mixtures, however, further speculations seem pointless.

Before discussing the results in the mixtures of higher dielectric constant, we shall present some data on the viscosity of aqueous solutions of tetrabutylammonium bromide. We acknowledge with thanks measurements made by Dr. Joan B. Berkowitz, which supplement those in the literature.[6] The results are summarized in Table VI, where the first two columns give concentration in equivalents per liter and specific viscosity $\eta_{sp} = (\eta - \eta_0)/\eta_0$, respectively. As is well known, there is a square root term in the viscosity of electrolytic solutions in addition to the Einstein term $5\phi/2$ (and also higher terms than $c^{1/2}$ from long range forces, which we shall neglect here). For 1 − 1 salts

TABLE VI

VISCOSITY OF Bu_4NBr IN WATER AT 25°

c	η_{sp}	$S_\eta c^{1/2}$	η'_{sp}/c	R
0.290	0.430	0.0049	1.466	6.16
.204	.284	.0041	1.372	6.03
.144	.192	.0034	1.312	5.94
.0992	.130	.0029	1.280	5.89
.1064	.145	.0030	1.333	5.96
.1007	.131	.0029	1.272	5.88
.0635	.086	.0023	1.31	5.94
.0610	.081	.0022	1.30	5.91
.0321	.045	.0016	1.34	5.97
.0175	.026	.0012	1.43	6.10
			1.34	5.98

$$\eta/\eta_0 = 1 + S_\eta c^{1/2} + 5\phi/2$$

where

$$S_\eta = \frac{\beta^*\Lambda_0}{320\lambda_0{}^+\lambda_0{}^-}\left\{1 - 0.6863\left(\frac{\lambda_0{}^+ - \lambda_0{}^-)}{\Lambda_0}\right)^2\right\}$$

For Bu_4NBr in water, $S_\eta = 9.07 \times 10^{-3}$. The quantity η'_{sp} in the table is defined as

$$\eta'_{sp} = \eta_{sp} - S_\eta c^{1/2}$$

It serves to isolate the volume effect in which we are interested. It will be seen that $\eta'_{sp}/c = 5\,\phi/2c$ is quite constant; further, if we equate $\phi/c = \delta$ with $4\pi NR^3/3000$, we obtain the average value 5.98 Å. for the hydrodynamic radius of the tetrabutylammonium ion. Thus direct viscosity measurements confirm the hydrodynamic term whose presence was suggested first by the conductance data for tetrabutylammonium iodide. It should perhaps be mentioned that the Dole–Falkenhagen term $S_\eta c^{1/2}$ in the viscosity is to be omitted in the conductance equation, because it describes transfer of momenta over distances large compared to $(1/\kappa)$, *i. e.*, refers to bulk flow of the solution.

Finally, we consider tetrabutylammonium bromide in the range of higher dielectric constants. Here, association is so slight that the y *vs.* x method becomes far too sensitive to experimental error. The conductance equation was therefore rearranged to the form

$$\Lambda'' + J_2c^{3/2} = \Lambda_0 - y(0)c$$

where the approximations $\Lambda = \Lambda_0$ and $f^2 = 1$ are made in the ion association term. The quantity on the left was plotted against c, using $\mathring{a} = 5.5$ to evaluate J_2; straight lines were obtained, with slopes $y(0)$ given in Table VII.

TABLE VII

TETRABUTYLAMMONIUM BROMIDE IN WATER–DIOXANE MIXTURES AT 25°

% Dioxane	D	$y(0)$	Λ_0	A	$A\Lambda_0$	$J_1(5.5)$	$5\delta/2$
0	78.48	−28	97.47_5	0.62	61	248	(2.2)
10	70.33	8	80.80_5	0.76	62	255	(2.3)
20	61.86	110	67.57_5	1.00	68	273	1.40
30	53.28	163	57.26	1.38	79	319	1.34
35	48.91	185	53.08_5	1.78	95	357	1.45
40	44.54	235	49.44	2.24	110	415	1.42
45	40.20	272	46.30	3.16	146	498	1.73

The problem then is: given the sum $y(0) = J_1(a) - A\Lambda_0 - 5\Lambda_0\delta/2$; to evaluate the components. The plot of log A *vs.* $1/D$ from the dioxane-rich range was extrapolated linearly into the water-rich range to give the values of A shown in the table. Then the round value $\mathring{a} = 5.50$ was used to evaluate J_1; this value was chosen to be consistent with the value which $\mathring{a}$ from Table V appeared to be approaching in the mixtures of higher dielectric constant. We then were able to evaluate

$$5\Lambda_0\delta/2 = J_1(5.50) - A\Lambda_0 - y(0)$$

The results are given in the last column; if we disregard the first two values (where the uncertainty in the slopes of the Λ''–c plots is naturally very great and for which the longest log A *vs.* D^{-1} extrapolation was made), we obtain $5\delta/2 = 1.47 \pm 0.13$, to compare with the direct viscometric value of 1.34 ± 0.06 of Table VI.

Discussion.—If ion association depends on the parameter $b = e^2/aDkT$, then there are two ways of varying the extent of association of a given electrolyte: by varying the DT product by change of temperature, or by using solvent mixtures to change D. The latter is by far the more convenient method, and the constancy of the a-values reported here argues that it is an experimentally valid method. One might have some misapprehensions on the score of selective solvation, but when it is recalled that both solvents are usually present in tremendous molar excess over the electrolyte present in the range ($\kappa a < 0.2$) where the data are susceptible to the present analysis, constancy of solvation appears to be a safe assumption. Exceptions might be expected to appear only when one component of the mixed solvent is present at minute concentrations.

While we report here only four cases which show that the logarithm of the association constant is a simple linear function of reciprocal dielectric constant, we believe that the result is general. Seen in retrospect, it does seem logical that a thermodynamic approach[9] to the problem of ion pair formation should be preferable to a statistical one, because the former concerns itself only with reagents and products and the associated free energy difference and ignores mechanism. The Denison–Ramsey treatment has further advantages over the

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[9] J. T. Denison and J. B. Ramsey, THIS JOURNAL, **77**, 2615 (1955).

Bjerrum model which we have used for so long: (1), only ions in contact are counted as pairs; (2), no quibbles about an arbitrary limit of integration arise; and (3), association is not automatically excluded beyond a critical value of the parameter b.

Another former tool must, in our opinion, also be discarded as obsolete in the analysis of conductance data. Our earlier calculations[10] of limiting conductance and "dissociation" constants by various modifications of the Ostwald dilution law were subject to the recognized (but then unknown) hazard of error due to the inclusion in K of terms of higher order arising from long range interionic forces. In solvents of low dielectric constant, the association term is the controlling one, so the error there was not very large: for example, our early analysis[4] of the data for Am_4NNO_3 in 80% dioxane gave $K = 9.0 \times 10^{-4}$ which is in almost exact agreement with the value of A^{-1} given in Table III. These earlier methods may therefore still be used as a convenient approximation for $A \geqslant 100$. But in solvents where association is less marked, and especially when it is only moderate, then the earlier methods can only lead to erroneous results.

Our present point of view is that association can in principle and does in fact occur in any solvent. The extent to which the alkali halides, for example, associate in water is presumably small, but if the limit of A as D increases is not zero, then a non-zero concentration of ion pairs must be present at any non-zero concentration. We hasten to admit that the actual amount may be quite small. The device of mixed solvents offers an experimental approach to a quantitative answer to the question, of course.

It should be mentioned that the presence of a non-vanishing A will not change the value of Λ_0 found by the Λ'''–c extrapolation method,[3] but a small change in $\mathring{a}$ will result. Likewise, inclusion of the $5\Lambda_0\delta/2$ term for most simple inorganic salts will only change $\mathring{a}$ by a small amount; since $\delta \sim R^3$ and since the alkali ions certainly have radii not greater than half that of the tetrabutylammonium ion, the δ-term will be roughly an order of magnitude smaller for the alkalies than that for the quaternaries, *i.e.*, $5\Lambda_0\delta/2 \approx 0.25\Lambda_0$. Since $J_1(a)$ is several times Λ_0 in aqueous solutions, no drastic change in $\mathring{a}$ is to be expected from inclusion of the viscosity term. Self-consistency, however, requires that if one linear term is retained, all should be.

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(10) R. M. Fuoss and T. Shedlovsky, THIS JOURNAL, **71**, 1496 (1949).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Microwave Absorption and Molecular Structure in Liquids. XIX. The Effect of Internal Field upon Molecular Relaxation Times in Liquids[1]

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RECEIVED JANUARY 22, 1957

The effect of the internal field in a liquid upon the dielectric relaxation time of its molecules is examined by comparing the macroscopic relaxation time of a highly polar liquid with that of a liquid consisting of molecules of the same size and shape as those of the polar liquid, but with very small dipole moment. Alternatively, the comparison is made between the pure polar liquid and its dilute solutions in a non-polar solvent. After correction for viscosity differences in most cases, the assumption is made that the macroscopic relaxation time of the pure liquid of low polarity or of the dilute solutions of the polar liquid is equal to the molecular relaxation time of the highly polar liquid. The molecular relaxation times thus obtained are compared graphically with those calculated by means of the various available equations. It becomes evident that the relation of the molecular relaxation time to the macroscopic relaxation time is dependent not only upon the dielectric constant of the liquid, but also, to some extent, upon the molecular shape. Consequently, no equation thus far proposed for calculating the molecular relaxation time from the directly measured macroscopic relaxation time of a polar liquid is wholly adequate, but that proposed by Powles and obtained by O'Dwyer and Sack as a first approximation is the most nearly adequate.

It has been common practice in discussing the relations between dielectric relaxation and molecular size and shape and liquid viscosity to use as the basis of discussion the macroscopic relaxation time τ_M or the critical wave length, $\lambda_m = 6\pi \times 10^{10}\tau_M$, at which the measured dielectric loss is a maximum. This is certainly justified in the case of dilute solutions and, in the case of pure polar liquids, has been commonly considered preferable to the use of a molecular relaxation time calculated by means of the Debye theory based upon the Lorentz expression for the internal field of the liquid.

Calculation of Molecular Relaxation Times.—The macroscopic relaxation time may be written

$$\tau_M = \beta\tau_\mu \qquad (1)$$

where τ_M is the molecular relaxation time and β a factor correcting for the effect of internal field. From the original equations of Debye[3] based on the Lorentz internal field

$$\beta = \frac{\epsilon_0 + 2}{\epsilon_\infty + 2} = 1 + \frac{\epsilon_0 - \epsilon_\infty}{\epsilon_\infty + 2} \qquad (2)$$

where ϵ_0 is the static dielectric constant and ϵ_∞ is the optical or infinite frequency dielectric constant. Powles[4] has proposed an approximate expression for the internal field which gives

$$\beta = \frac{3\epsilon_0}{2\epsilon_0 + \epsilon_\infty} = 1 + x \qquad (3)$$

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(1) This research was supported in part by the United States Air Force through the Office of Scientific Research of the Air Research and Development Command. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

(2) Supported by a Grant-in-Aid to the Chemistry Department, Princeton University, from E. I. du Pont de Nemours and Company.

(3) P. Debye, "Polar Molecules," Chemical Catalog Co., New York, N. Y., 1929, Chap. V.

(4) J. G. Powles, *J. Chem. Phys.*, **21**, 633 (1953).