[CONTRIBUTION FROM THE UNIVERSITY OF ALEXANDRIA AND YALE UNIVERSITY[1]]

Electrolyte–Solvent Interaction. VII. The Conductance of Tetrabutylammonium Bromide in Mixed Solvents[2]

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Conductance data for tetrabutylammonium bromide in the mixed solvent systems MeOH–CCl_4, EtOH–CCl_4, $PhNO_2$–CCl_4 and MeOH–$PhNO_2$ have been analyzed by methods based on the electrostatic theory of conductance.[4] For the first three systems, plots of the logarithm of association constant against reciprocal dielectric constant are linear and parallel; hence the same center-to-center distance ($\mathring{a} = 5.45$) describes the salt in these solvents. The different values of the intercepts at $1/D = 0$ show that the energy of interaction between solute and solvent is specific for a given ion-polar solvent pair, as expected. Furthermore, the sums of the hydrodynamic radii, calculated from the limiting conductances by an electrostatic modification of Stokes law, are also the same in the various mixtures and equal the value of $\mathring{a}$ obtained from the association constants or those obtained from $J(a)$, the coefficient of the linear term from the relaxation field. Based on the latter observations, a simplified method is proposed for calculating Λ_0 and K_A (limiting conductance and association constant) for systems in which slight to moderate association ($K_A < 100$) occurs.

A general theory of the conductance of 1–1 salts, which takes into consideration both the decrease in mobility due to the long range interionic forces and the decrease in free ion population due to short range electrostatic attraction of oppositely charged ions, has been developed recently.[3,4] Furthermore, a correlation[5] has been found between ion sizes obtained from association constants (electrostatic origin) and from single ion conductances (hydrodynamic origin). The model used to represent the electrolytic system was in both cases the conventional spheres-in-continuum. The cation of tetrabutylammonium bromide has tetrahedral symmetry (spherical on averaging over rotation), while the anion is spherical. The conductance of this salt has been measured in several solvent mixtures, representing a variety of types: methanol–carbon tetrachloride,[6] ethanol–carbon tetrachloride,[7] nitrobenzene–carbon tetrachloride[8] and nitrobenzene–methanol.[9] The first two mixtures contain a polar hydrogen-bonding solvent and a non-polar component; the third is likewise a polar non-polar mixture, but nitrobenzene. being aprotoic, is not a hydrogen bonding solvent. The fourth mixture, on the other hand, is a nearly isodielectric system, made up of two markedly different polar components. The sizes of the solvent molecules cover a fairly wide range with respect to the ions, and their shapes and charge distributions vary considerably. These systems therefore present an excellent opportunity to test the model and also to illustrate the methods of applying the theoretical analysis to conductance data.

Briefly summarized, the electrostatic theory is based on the hypothesis that the decrease of equivalent conductance of ionophores with increasing concentration is the observable consequence of the electrostatic forces between the ions. These forces decrease the mobility of the ions due to the effects of electrophoresis and relaxation[10] and also decrease the population of free ions by increasing the dwell time[11] of oppositely charged ions which come into contact ("ionic association"). The electrostatic theory is expressed mathematically by the equation[3,4,12,13]

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

where the symbols have the values given in ref. 13. Depending on the magnitude of the association constant K_A (*i.e.*, on the dielectric constant in last analysis), the equation can be approximated by various limiting forms, as will be shown in the application of the theory to the data of refs. 6–9.

The nitrobenzene–carbon tetrachloride data cover the dielectric constant range $15.7 \leqslant D \leqslant 34.7$, with association constants $2090 \geqslant K_A \geqslant 57$ (see Table I). In the mixture of lowest dielectric constant, the curvature of the y–x plot is not very sensitive to the trial value of Λ_0 used in the equation

$$y = (\Lambda'_\eta - \Lambda_0)/c\gamma \quad (2)$$

which is obtained from (1) by rearrangement; using Λ_0 (trial) = 38.6 gives a concave-up plot while Λ_0 (trial) = 39.0 gives one which is concave-down (Fig. 1). Using the intermediate value $\Lambda_0 = 38.8$ gives a linear plot, the slope of which evaluates $K_A = 2090$. From the equation

$$y = J - K_A x \quad (3)$$

the average value of J is found to be 0.70×10^4, whence $\mathring{a} \cong 7.5$. The association is so great that the value of J (and hence of $\mathring{a}$) becomes uncertain; for example, at the lowest concentration, $10^{-4} J = (4.19 - 3.48)$ and as the small difference between two much larger quantities, J becomes uncomfortably sensitive to small errors in conductance and especially to those in dielectric constant and viscosity. (The numerator of (2) contains the theoretical terms $Sc^{1/2}\gamma^{1/2}$ and $Ec\gamma \log c\gamma$ and both S and E depend on D and η.) The value $K_A = 2090$ agrees almost exactly with the value $K^{-1} = 2100$ calculated[8] for this system by the modified

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(2) Presented at the International Symposium on Electrolytes sponsored by the Società Italiana per il Progresso delle Scienze, at Trieste, 4–10 June, 1959.

(3) R. M. Fuoss, THIS JOURNAL, **80**, 3163 (1958).

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

(5) R. M. Fuoss, *Proc. Natl. Acad. Sci.*, **45**, 807 (1959).

(6) H. Sadek and R. M. Fuoss, THIS JOURNAL, **76**, 5897 (1954).

(7) H. Sadek and R. M. Fuoss, *ibid.*, **76**, 5902 (1954).

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

(9) H. Sadek and R. M. Fuoss, *ibid.*, **72**, 301 (1950).

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

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

(12) R. M. Fuoss, *ibid.*, **79**, 3301 (1957).

(13) R. M. Fuoss and F. Accascina, "La Conducibilità Elettrolitica," Edizioni dell' Ateneo, Rome, 1959; English edition, Interscience Publishers, Inc., New York, N. Y., 1959.

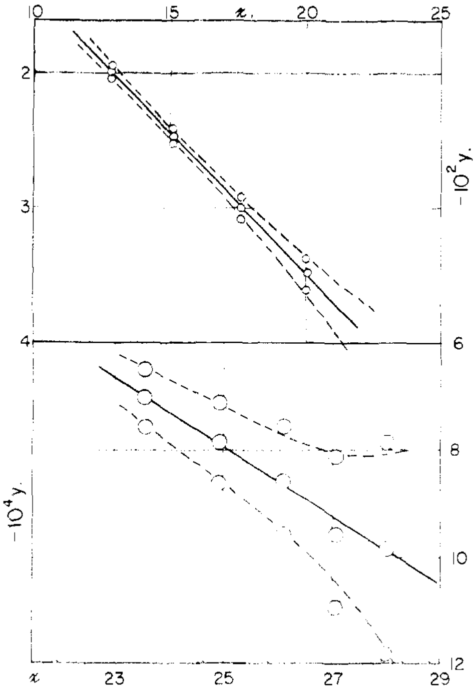

Fig. 1.—Application of y–x method to Bu_4NBr in $PhNO_2$–CCl_4 (D = 15.7), top curves; in $PhNO_2$ (D = 34.7), bottom curves.

Ostwald dilution law[14] which neglects both the term in J as well as the $c \log c$ term, because, as we shall see shortly, these two terms oppose each other, and their difference becomes negligible compared to the association term when the latter is large. As the dielectric constant increases, the y–x plot becomes increasingly sensitive to the trial value of Λ_0 and simultaneously becomes more nearly horizontal as K_A decreases. The lower curves in Fig. 1 correspond to Λ_0 = 33.25, 33.30 and 33.35 for nitrobenzene. The sensitivity to experimental error is also much increased; an error of 0.1% (= 0.0 3Λ-unit) at the lowest concentration ($c = 2.574 \times 10^{-4}$) now corresponds to an uncertainty of 115 in y where $980 \geq y \geq 705$ in the concentration range shown in Fig. 1.

When association is so slight that the y-x method becomes unreliable, either because the plot is too nearly horizontal or because the experimental error becomes too large, one of two other methods can be used, as shown in Fig. 2 for nitrobenzene. If K_A is known (for example, by extrapolation of a $\log K_A - D^{-1}$ plot), Λ_J is plotted against $c\gamma$, where

$$\Lambda_J = \Lambda'_\eta + K_A c\gamma f^2 \Lambda_\eta \quad (4)$$

$$= \Lambda_0 + Jc\gamma \quad (4')$$

The slope evaluates J and hence $å$, while the intercept gives Λ_0. On the other hand, if J is known, Λ_K defined by

$$\Lambda_K = \Lambda'_\eta - Jc\gamma \quad (5)$$

$$= \Lambda_0 - K_A c\gamma f^2 \Lambda_\eta = \Lambda_0 - K_A X \quad (5')$$

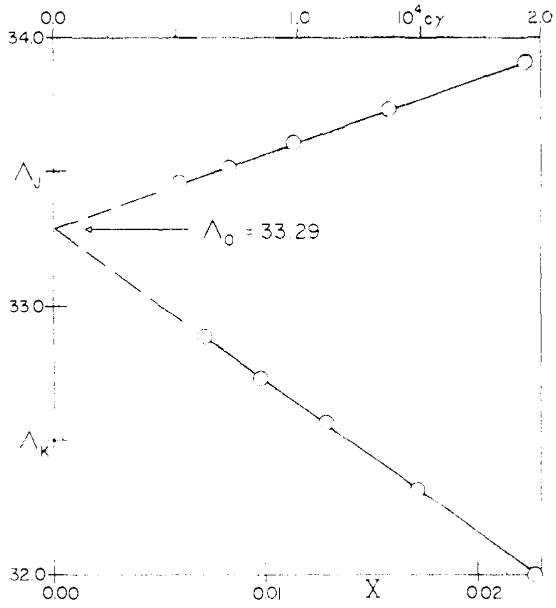

Fig. 2.—Application of equations 4 and 5 to Bu_4NBr in nitrobenzene.

is plotted against X in order to determine K_A and Λ_0 as slope and intercept, respectively. In Fig. 2, Λ_J was calculated for the nitrobenzene data, using K_A = 57, the value obtained from the slope of the y–x plot; from the figure, Λ_0 = 33.29 and $J = 640 \rightarrow å = 6.6$. Using $å$ = 6.6, Λ_K was calculated; from this plot, Λ_0 = 33.29 and K_A = 57. The intersection of both plots at Λ_0 = 33.29 at c = 0 confirms the self-consistency of the methods.

The conductance data in the nitrobenzene–carbon tetrachloride mixtures serve to illustrate the transition from the case of moderate to pronounced association and also to show the shift in control from long range to short range interionic forces as the dielectric constant is decreased. Symbolically the conductance equation may be written (if we neglect the small viscosity term $\Lambda_0 Fc$)

$$\Lambda = \Lambda_0 - \Delta_S - \Delta_E + \Delta_J - \Delta_K \quad (6)$$

where Δ_S is the decrease in conductance due to the limiting Onsager terms, Δ_E is the decrease due to the transcendental terms of order $c \log c$ from the relaxation field, Δ_J is the increase due to linear terms from the same source and Δ_K is the decrease due to ionic association. In nitrobenzene (D = 34.69), association is slight ($K \approx 60$), and at $c = 10^{-3}$, decreases conductance by about 4%. The long range term Δ_S is nearly twice this value at the same concentration but as concentration decreases (*cf.* Fig. 3, lower plots), the role of Δ_K rapidly becomes less important than that of Δ_S. Both Δ_E and Δ_J are smaller than Δ_K, and since they appear in (1) with opposite signs, it is only their difference which is observed. If both were neglected, a fairly satisfactory value of K_A could still have been obtained for this system by the modified Ostwald dilution law.[14] However, in higher ranges of dielectric constant, Δ_K would successively become of the order of Δ_E and Δ_J and then of the order of their difference, and finally negligible even

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[14] R. M. Fuoss, *Chem. Revs.*, **17**, 27 (1935); T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938); R. M. Fuoss and T. Shedlovsky, THIS JOURNAL, **71**, 1496 (1949).

compared to the difference. On the other hand, as dielectric constant is decreased, Δ_K rapidly becomes larger and dominates Δ_S, except at extreme dilutions. For example, for $D = 15.69$, $K_A \approx 2000$ (upper plots of Fig. 3; note change in ordinate scale!), association decreases conductance by about 33% from Λ_0 at a concentration of 10^{-3} N, while Δ_S is about 13%. Compared to nitrobenzene, both Δ_K and Δ_S have increased numerically very much, but Δ_K has increased at a far more rapid rate, because K depends exponentially on D^{-1} while S has only an algebraic rate of change with dielectric constant. We note also that Δ_E and Δ_J have increased relative to Δ_S; the former have leading terms in D^{-3}, while the electrophoresis term (the largest part of Δ_S) varies only as $D^{-1/2}$. The difference between Δ_E and Δ_J is now so small with respect to Δ_K that a completely satisfactory value of K_A could have been obtained by simultaneous neglect of *both* of these higher terms. If plots similar to Fig. 3 are constructed for all of the systems between nitrobenzene and the one with lowest dielectric constant, a smooth transition from a classical "strong" electrolyte to a "weak" one is observed: all the Δ-terms increase numerically, but Δ_K crosses Δ_S and as already mentioned, finishes by controlling the course of the conductance–concentration curve in the usual working range of concentration. (Eventually, of course, at sufficiently low dielectric constants, the effects of association higher than pairwise must be included in the analysis.)[15]

The figure also shows another interesting feature of the conductance function: over a range of concentration (5:1) which is completely adequate for determination of the constants Λ_0, K_A and J, the logarithm of concentration changes so slowly that the $E c \gamma \log c\gamma$ term closely simulates linearity. This behavior explains, of course, why earlier conductance equations of the form

$$\Lambda = \Lambda_0 - Sc^{1/2} + Bc + O(c^{3/2}) \qquad (7)$$

succeeded in fitting conductance data over moderate ranges of concentration; it is only at extreme dilutions that the approaching singularity in the slope of $c \log c$ at $c = 0$ makes itself visible. Hence functions of the form (7) may be used only for interpolation; they cannot extrapolate correctly to $c = 0$.

The constants for the other systems mentioned in the introduction are summarized in Table I. The ethanol–carbon tetrachloride system is light-sensitive, hydrogen chloride being formed on standing. Consequently the data are less precise than for the other systems and the points on the y–x plots scatter so badly that no independent conclusions can be drawn. By using the round value $\mathring{a} = 6.0$, however, based on the results for the other systems, values of Λ_K could be obtained which extrapolate to values of Λ_0 which are probably accurate to ± 0.05, and the slopes of the Λ_K–X plots permit estimates of the corresponding values of K_A. The methanol–carbon tetrachloride systems are completely stable, but association is so slight that the y–x method may only be used in the two mixtures of lowest dielectric constants, which give $\mathring{a} = 5.7$ and 6.0 from the corresponding J values. For the other five mixtures, the Λ_K method was used. Figure 4 shows a plot of log K_A against reciprocal dielectric constant for the three systems $PhNO_2$–CCl_4, EtOH–CCl_4 and MeOH–CCl_4. For the first, a straight line interpolates the data very well; from the slope, we obtain $\mathring{a} = 5.45$, a value somewhat smaller than those obtained from the values of J derived from the y–x plots. Lines parallel to this can be drawn through the EtOH–CCl_4 and the MeOH–CCl_4 and the MeOH–CCl_4 points; in other words, within the precision of the measurements, the same value of $\mathring{a}$ describes all three systems.

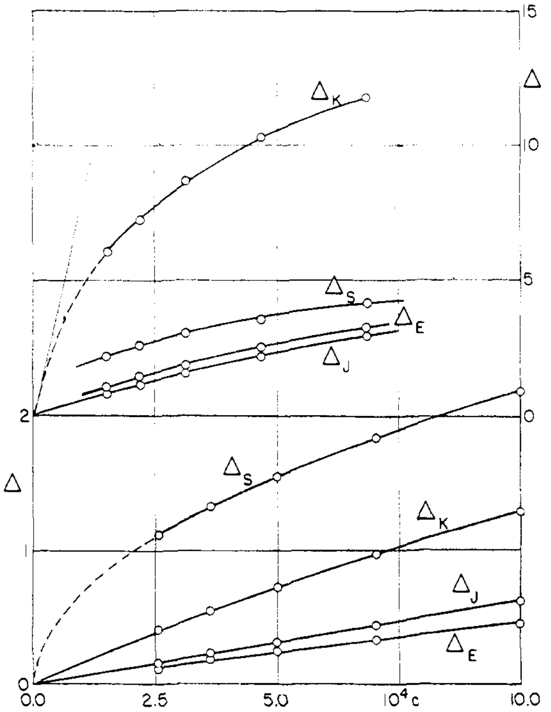

Fig. 3.—Dependence on dielectric constant of the various terms in the conductance equation: top curves, $D = 15.7$; bottom curves, $D = 34.7$.

One of the most interesting results of the experiments can be seen in Fig. 4: for the *same* dielectric constant, *different* values of association constant are found, even assuming the distance a to be the same for all three systems shown. Consequently the simple equation[11]

$$K_A = (4\,\pi\,La^3/3000)\exp(e^2/aDkT) \qquad (8)$$

does not suffice to describe association. Equation 8 was, as stated above, derived using a continuum to represent the solvent. Clearly, an additional effect must be involved, which is specific for a given ion–solvent system. Interaction between ions and solvent dipoles, as postulated in the first paper of this series,[9] should be considered in the next approximation. If we write, in accordance with Gilkerson's suggestion[16]

$$K_A = (4\pi La^3/3000)\exp[(e^2/aD - E_s)/kT] \qquad (9)$$

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(15) Ref. 13, Chapter XVIII.

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

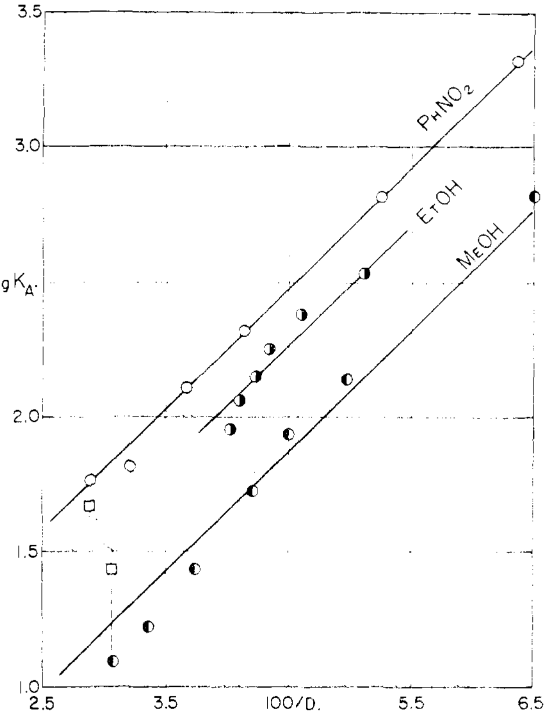

Fig. 4.—Dependence of association constant K_A on dielectric constant

and use $\mathring{a}$ = 5.45, these various values of E_s/kT are found from the lines of Fig. 4: PhNO$_2$–CCl$_4$, −2.0; EtOH–CCl$_4$, −1.5; MeOH–CCl$_4$, −0.6. These values appear to be of a reasonable order of magnitude but, until a wide variety of ions have been studied, there seems to be little point in speculating about their relative values. That conductance measurements will serve as a useful tool for exploring short range molecular interaction in liquid systems is, however, clearly demonstrated by these preliminary results.

The system PhNO$_2$–MeOH presents an interesting situation. Visible association, as already noted, occurs for tetrabutylammonium bromide in both solvents.[17] If we assume $\mathring{a}$ = 6.0 and calculate Λ_K, the Λ_K–X plots for Bu$_4$NBr in either MeOH or PhNO$_2$ have a slight negative slope. The two systems nearest the pure solvents (94.55 and 1.98% MeOH) also show a (still smaller) negative slope, indicating some association. But between 95% and 2% MeOH, the Λ_K–X plots are *horizontal*, indicating a negligible degree of association, despite the fact that the dielectric constant is nearly the same for these mixtures. We originally suggested[9] solvation by methanol as an explanation for the peculiar behavior, but this would require a larger ion size in the mixtures than in pure nitrobenzene; as we shall see shortly, this hypothesis is contradicted by the size of the ions calculated from the single ion mobilities. We can now only make the obvious statement that further work is needed on mixtures of polar solvents, before a rationalization of the results in terms of molecular parameters may be attempted.

TABLE I

DERIVED CONSTANTS FOR TETRABUTYLAMMONIUM BROMIDE IN MIXED SOLVENTS

D	K_A	$\mathring{a}$	Λ_0	$\Lambda_0\eta$	Method
		PnNO$_2$–CCl$_4$			
34.69	57	6.6	33.29	0.6122	Λ_K, Λ_J
31.13	65	6.6	33.96	.5865	y–x, Λ_J
27.20	130	6.35	35.27	.5633	y–x, Λ_J
24.23	210	6.10	36.14	.5374	y–x, Λ_J
19.07	655	6.30	37.78	.5063	y–x, Λ_J
15.69	2090	(7.5)	38.80	.4800	y–x, γ
		EtOH–CCl$_4$			
24.91	90	(6.0)	43.35	0.4784	Λ_K
24.40	115	(6.0)	43.20	.4787	Λ_K
23.68	145	(6.0)	43.95	.4878	Λ_K
23.05	180	(6.0)	42.75	.4745	Λ_K
21.77	240	(6.0)	41.90	.4638	Λ_K
19.59	(300)	..	...	....	Est.
		MeOH–CCl$_4$			
32.63	12.4	(6.0)	96.30	0.5244	Λ_K
29.74	16.4	(6.0)	88.44	.5212	Λ_K
26.72	27	(6.0)	81.42	.5169	Λ_K
23.80	53	(6.0)	74.95	.5068	Λ_K
22.23	85	(6.0)	72.75	.5073	Λ_K
20.13	140	5.7	68.75	.4992	y–x, Λ_K
15.31	655	6.0	58.55	.4603	y–x, γ
		MeOH–PhNO$_2$			
32.63	27	(6.0)	96.65	0.5277	Λ_K
32.44	..	(6.0)	93.70	.5287	Λ_K
31.78	..	(6.0)	83.95	.5271	Λ_K
31.56	..	(6.0)	74.35	.5288	Λ_K
31.69	..	(6.0)	64.10	.5363	Λ_K
32.05	..	(6.0)	52.40	.5427	Λ_K
32.32	..	(6.0)	46.80	.5432	Λ_K
32.99	..	(6.0)	38.40	.5437	Λ_K
33.91	..	(6.0)	33.05	.5611	Λ_K
34.82	47	(6.0)	33.05	.6148	Λ_K

Finally, we consider the dependence of equivalent conductance on the composition of the solvent. In the systems PhNO$_2$–CCl$_4$ and EtOH–CCl$_4$, the viscosity decreases as the CCl$_4$-content increases, while in the system MeOH–CCl$_4$, it increases. The Walden product $\Lambda_0\eta_0$ decreases in all three systems as the CCl$_4$–content increases; that is, there appears to be a correlation between the Walden product and the dielectric constant, rather than between $\Lambda_0\eta_0$ and the viscosity. This parallel, which has been observed in a variety of other systems, suggested[5] that Stokes law, when applied to electrolytic solutions, requires a correction of electrostatic nature. The classical Stokes radius

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[17] See squares in Fig. 4; the discrepancy between the 1950 and the 1954 data possibly is due to traces of impurities in one of the solvents. When association is as slight as it is here, extreme care must be taken in the experimental work. This was not fully realized when the experiments were made, because the theory was not then complete, and the sensitivity of the derived constants to experimental error was not yet understood. The early goal was a precision of 0.1%; it is now clear that a precision of 0.01% in conductance must be attained if reasonable precision in $\mathring{a}$ and K_A is desired. The source of this increased demand on the experimental technique lies in the mathematical form of equation 1 which essentially is a statement of the limiting *curvature* (second derivative) of the conductance curve, while the earlier theory only stated the limiting *slope* (first derivative).

R^+ for a cation is given by

$$R^+ = Fe/1800\pi\lambda^+{}_0\eta_0 = 0.8194 \times 10^{-8}/\lambda^+{}_0\eta_0 \quad (10)$$

Assuming a dipole relaxation term in local viscosity due to the work done in rotating dipoles in the path of the moving ion, it has been found that the Stokes equation becomes

$$R^+ = R^+{}_\infty + s/D + O(1/D^2) \quad (11)$$

where s is a constant for a given system ion–solvent and $R^+{}_\infty$ is the hydrodynamic radius of the cation in a hypothetical solvent of infinite dielectric constant, *i.e.*, the radius of the sphere hydrodynamically equivalent to the ion if the Stokes model were valid, and hydrodynamic friction were the only force to be overcome by the external field in order to produce ionic migration.

The conductance $\lambda^-{}_0$ of the bromide ion in methanol at 25° has been determined[18]: from this value, $\lambda^-{}_0 = 56.55$, and $\Lambda_0 = 96.30$ for tetrabutylammonium bromide in methanol the transport number of the bromide ion is 0.5871. If now the assumption is made that the transport number is independent of composition in mixtures of methanol and carbon tetrachloride, values of the products $\lambda^+{}_0\eta_0$ and $\lambda^-{}_0\eta_0$ for Bu_4N^+ and Br^- can be calculated for these mixtures from the observed values of $\Delta_0\eta_0$. These values are summarized in Table II. A test of equation 11 is shown in Fig. 5, where R^+D and R^-D are plotted against D; the plots are linear and can be reproduced by the equations $R^+ = 3.35 + 14/D$ and $R^- = 2.40 + 8/D$ as shown by the values of R^+ (calcd.) and R^- (calcd.) given in the last two columns of Table II. To state the results in words, the two ions of Bu_4NBr behave like Stokes spheres of radii 3.35 and 2.40 Å. radius in a medium whose relative viscosity is given by

$$\eta_r = \eta/\eta_0 = 1 + s/D \quad (12)$$

where s is a constant characteristic both of the ion and of the solvent. The explanation of the failure of Walden's rule then lies in the fact that $s \neq 0$. The data for the ethanol–carbon tetrachloride systems were analyzed in a similar fashion, assuming that the transport number of the bromide ion of Bu_4NBr in ethanol is the same as in methanol. The points (*cf.* Fig. 5) scatter somewhat more than the MeOH–CCl_4 points and cover a narrower range of dielectric constant; nevertheless, the linear trend is clear. The values of $R_{\pm\infty}$ are about the same as in MeOH–CCl_4, but the interaction coefficients $s_\pm$ are somewhat larger.

TABLE II

HYDRODYNAMIC RADII OF Bu_4NBr IN MeOH–CCl_4

D	$\lambda_0{}^+\eta_0$	$\lambda_0{}^-\eta_0$	R^+	R^-	R^+ (calcd.)	R^- (calcd.)
32.63	0.2165	0.3079	3.78	2.66	3.78	2.65
29.74	.2153	.3061	3.81	2.68	3.82	2.67
26.72	.2134	.3035	3.84	2.70	3.87	2.70
23.80	.2093	.2975	3.91	2.75	3.94	2.74
22.23	.2095	.2978	3.91	2.75	3.98	2.76
20.13	.2061	.2931	3.98	2.80	4.05	2.80
15.31	.1902	.2704	4.31	3.03	4.26	2.92

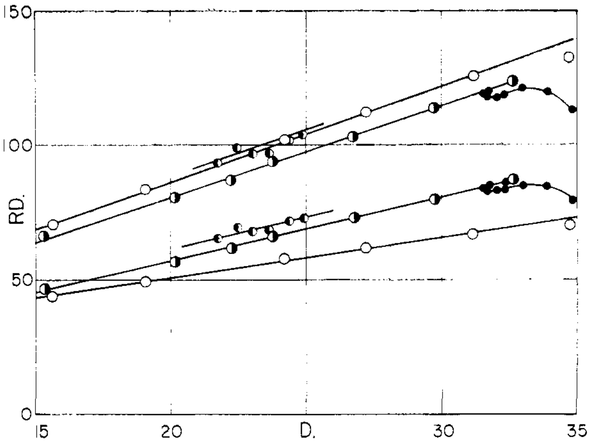

Fig. 5.—Dependence of classical Stokes radius on dielectric constant: ◐, EtOH–CCl_4; ○, $PhNO_2$–CCl_4, ◑, MeOH–CCl_4, ●, MeOH–$PhNO_2$.

For the nitrobenzene–carbon tetrachloride systems, no transference data are available. The conductance of tetrabutylammonium tetraphenylboride[19,20] has, however, been measured in these systems, and since models show that the two ions of this salt are practically identical in volume, we may safely assume that the transport numbers of both ions are one half. It is then possible to calculate R^+ and R^- for tetrabutylammonium bromide in these mixtures; the corresponding *RD–D* plots are also shown in Fig. 5. Again, straight lines are obtained, giving $R^+ = 3.55 + 17/D$ and $R^- = 1.34 + 24/D$. For the polar-polar mixture $PhNO_2$–MeOH, the situation is, as might be expected, somewhat more complicated (black points in Fig. 5). The dielectric constant goes through a minimum; the *RD–D* curve correspondingly is double-valued. The points lie quite close to the MeOH–CCl_4 line in the methanol-rich end of the curve, from 100% MeOH to 75% MeOH. Then the points begin to drop a little but still stay close to the MeOH–CCl_4 line up to 8% MeOH–92% $PhNO_2$. The last two points (2% and 0% MeOH) drop quite rapidly. This behavior of the hydrodynamic radius is as puzzling as was the peculiar behavior of the association constants in these mixtures; the need for further measurements of higher precision on a variety of salts in polar-polar mixtures is again demonstrated.

If we consider the two systems in which the best results were obtained (MeOH–CCl_4 and $PhNO_2$–CCl_4), the following satisfactory agreement is found for the center-to-center distance of the ions of Bu_4NBr: In MeOH–CCl_4, $(R^+{}_\infty + R^-{}_\infty) = 5.75$; $\mathring{a}$ from $J(a) = 5.7 - 6.0$; $\mathring{a}$ from the slope of the log $K_A - D^{-1}$ plot, 5.45. In $PhNO_2$–CCl_4, $(R^+{}_\infty + R^-{}_\infty) = 4.90$; $\mathring{a}$ from $J(a) = 6.1 - 6.6$; $\mathring{a}$ from slope = 5.45. From the data of Mercier

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[18] R. E. Jervis, D. R. Muir, J. P. Butler and A. R. Gordon, THIS JOURNAL, **75**, 2855 (1953).

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

[20] E. Hirsch, Dissertation, Yale University, June, 1959.

and Kraus[21] for the same salt in dioxane–water mixtures, $(R^+_\infty + R^-_\infty) = 5.55$ while $\mathring{a}$ from $J(a) = 5.0 - 5.4$ and $\mathring{a}$ from slope $= 4.94$. The agreement between the values of ion size for tetrabutylammonium bromide calculated by three different methods (from Λ_0, from J and from K_A) in three quite different solvent systems substantiates the theory used in the derivation of the conductance equation and also the model on which it is based. Furthermore, the parameter a now begins to acquire reality as a physical constant characteristic of a given solute, independent of the solvent.

The availability of a-values from Λ_0, if confirmed by future work, is especially important in the analysis of conductance data. It will be recalled that it is difficult to determine both J and K_A when association is slight, because then the conductance equation reduces effectively to

$$\Lambda = \Lambda_0 - Sc^{1/2} + Ec \log c + (J - K_A\Lambda_0)c \quad (13)$$

and the data therefore yield only Λ_0 and the difference $(J - K_A\Lambda_0)$. If $\mathring{a}$ can be determined from Λ_0, $J(a)$ is known and hence K_A; in other words, the Λ_K method becomes the one to use for the case of moderate to slight association. At the other extreme, when association is marked, K_A can be determined to good precision by the y–x method, but the value of J becomes uncertain, because it then is the difference between two much larger quantities, $y(0)$ and $K_A\Lambda_0$. By evaluating $J(a)$ from Λ_0 *via* a, the $Jc\gamma$ term can now be included in the known part of the extrapolation function. The stage thus appears to be set for an investigation of electrolyte–solvent interaction *via* conductance measurements; previously, these finer details were obscured by uncertainty in the calculation of the dominant parameters Λ_0 and K_A.

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