served from the X-ray and electron microscope studies. The $\delta$ value corresponded to a $p$ of only 8. By assuming a $\pm$ 15% error (about three times that for $\Theta$) the calculated $p$ varied from 5 to 20. Thus all one can say from the data is that the minor axis of the equivalent ellipsoid for TMV is probably around 180 Å. No attempt will be made to estimate the effective volume of the equivalent ellipsoid since the uncertainty involved is even greater than that for the length and thickness.

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# The Dependence of Ionic Mobility on the Dielectric Constant of the Solvent

BY DONALD S. BERNS[1] AND RAYMOND M. FUOSS

The conductance of tetrabutylammonium and of tetramethylammonium nitrates in acetonitrile–carbon tetrachloride mixtures was measured over the range $11 < D < 36$ at 25°. Using these data and previous results for the corresponding tetraphenylborides, a comparison was made between the directly observed limiting conductance of $Me_4N \cdot NO_3$ in the various mixtures, and the calculated values obtained by using data for the other three salts and a form of Walden's rule modified to account for electrostatic ion-solvent interaction. Agreement was within about 1%.

Knowledge of the limiting equivalent conductance $\Lambda_0$ is necessary for the calculation of the various coefficients which appear in the theoretical conductance equation. This information is readily available for solvents of dielectric constant greater than about 10, but as the dielectric constant decreases, only the quotient $K_A/\Lambda_0^2$ can be determined with any precision, regardless of how good the data are, due to the long extrapolation involved when the association constant $K_A$ becomes large. Until recently, the only means for estimating limiting conductances in solvents of lower dielectric constant was Walden's rule, which is known to vary systematically with solvent composition.[2] The use of tetrabutylammonium tetraphenylboride to determine single ion conductances in non-aqueous solvents[3] without recourse to transference data, when combined with the equation

$$R = R_\infty + s/D \qquad (1)$$

which relates the Stokes radius $R$ of an ion to the dielectric constant $D$ of the solvent,[4] permits in principle the evaluation of the limiting conductance $\Lambda_0$ of any electrolyte in any given solvent of known dielectric constant. The purpose of this paper is to present a test of this working hypothesis. By measuring the conductance of tetrabutylammonium nitrate in mixtures of acetonitrile and carbon tetrachloride and combining the results with previous data for tetrabutylammonium and tetramethylammonium tetraphenylborides in the same solvent system, the limiting conductance of tetramethylammonium nitrate in these mixtures can be predicted. Comparison of the calculated values with the experimentally determined conductances of tetramethylammonium nitrate shows agreement within about 1% over the approximate

range $11 \leqslant D \leqslant 36$, which is much better than could have been achieved by application of Walden's rule in its original form.

## Experimental

Tetramethylammonium nitrate was a sample prepared by Dr. O. V. Brody several years ago from tetramethylammonium bromide by passing a solution through a column packed with Amberlite XE75 (Cl) which had been charged with nitrate ion. The effluent (halogen free) was slightly yellow; it was decolorized with charcoal. The solution was evaporated to dryness under vacuum, and the residue was twice recrystallized from conductance grade methanol; density, 1.25 at 25°. Tetrabutylammonium nitrate was prepared from pure tetrabutylammonium bromide and silver nitrate solutions; after separation of silver bromide and vacuum evaporation of the water, the salt was recrystallized from benzene (15 g./100 ml.); m.p. 119°; density, 0.909 at 25°. Acetonitrile and carbon tetrachloride were purified as described in an earlier paper.[5] Solutions were made up by weight. Two conductance cells were used; they were calibrated using aqueous potassium chloride solutions[6] and have constants 0.073993 $\pm$ 0.000006 and 0.39099 $\pm$ 0.00004. All measurements were made at 25 $\pm$ 0.002°. Dielectric constants (1 megacycle), viscosities and densities were determined for all solvent mixtures used; the physical constants are summarized in Table I. The conductance data

### TABLE I
#### PROPERTIES OF SOLVENTS

| No. | CCl₄, wt. % | $D$ | 100 $\eta$ | $\rho$ |
|-----|------------|-------|-----------|--------|
| 1 | 0.00 | 36.01 | 3.449 | 0.7768 |
| 2 | 63.20 | 18.91 | 4.796 | 1.1478 |
| 3 | 63.85 | 18.45 | 4.822 | 1.1527 |
| 4 | 68.46 | 16.99 | 5.076 | 1.1944 |
| 5 | 68.71 | 17.02 | 5.078 | 1.1975 |
| 6 | 74.54 | 14.65 | 5.429 | 1.2547 |
| 7 | 75.81 | 13.93 | 5.551 | 1.2676 |
| 8 | 78.84 | 12.29 | 5.800 | 1.3000 |
| 9 | 80.80 | 11.35 | 5.961 | 1.3226 |

are summarized in Tables II and III where the solvents are identified by the code numbers of Table I.

(1) California Research Corporation Postdoctoral Fellow, Yale University, 1959–1960.

(2) H. Sadek and R. M. Fuoss, *J. Am. Chem. Soc.*, **72**, 301 (1950); **76**, 5897, 5902, 5905 (1954); **81**, 4507 (1959).

(3) R. M. Fuoss and E. Hirsch, *ibid.*, **82**, 1013 (1960).

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

(5) D. S. Berns and R. M. Fuoss, *J. Am. Chem. Soc.*, **82**, 5585 (1960).

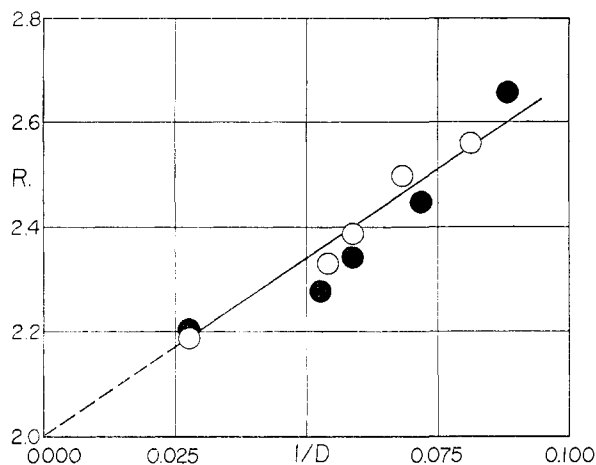(6) J. E. Lind, Jr., J. J. Zwolenik and R. M. Fuoss, *ibid.*, **81**, 1557 (1959).

Fig. 1.—Comparison of nitrate radii from $Bu_4N \cdot NO_3$ (O) and from $Me_4N \cdot NO_3$ (●).

## Discussion

The conductance data were analyzed by the IBM-650 Computer, using Kay's program[7] for the equation

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

in order to obtain numerical values for $\Lambda_0$, $a$ and $K_A$; these results are summarized in Table IV.

### TABLE II
#### CONDUCTANCE OF $Me_4N \cdot NO_3$ IN $CH_3CN-CCl_4$

| $10^4 c$ | $\Lambda$ | $10^4 c$ | $\Lambda$ |
|---|---|---|---|
| | No. 1 | | No. 4 |
| 20.073 | 177.62 | 10.002 | 81.82 |
| 15.393 | 180.69 | 7.730 | 86.41 |
| 11.585 | 183.55 | 5.8512 | 91.20 |
| 7.876 | 186.82 | 3.9472 | 97.55 |
| 4.4514 | 190.59 | 2.2086 | 105.71 |
| | No. 1 | | No. 7 |
| 16.506 | 179.79 | 7.078 | 57.73 |
| 13.114 | 182.25 | 5.680 | 61.34 |
| 6.675 | 187.97 | 4.2670 | 66.05 |
| 3.7066 | 191.50 | 2.9175 | 72.32 |
| | | 1.7680 | 80.31 |
| | No. 2 | | No. 9 |
| 12.390 | 95.55 | 5.820 | 37.00 |
| 9.450 | 100.30 | 4.3378 | 40.79 |
| 6.966 | 105.38 | 3.5218 | 43.64 |
| 4.4117 | 112.25 | 2.5582 | 48.19 |
| 2.2471 | 120.51 | 1.3913 | 57.29 |

(For solutions in acetonitrile, where association is slight, the $\Lambda_K$ method[8] was used.) Then using the previous[5] result

$$\lambda(Bu_4N^+) = 0.8194 \times 10^{-8}/\eta(3.842 + 5.07/D) \quad (3)$$

the conductances of the tetrabutylammonium ion was calculated for the various solvents of Table III and subtracted from the corresponding values of $\Lambda_0$ in order to obtain $\lambda_0(NO_3')$. These values (open circles in Fig. 1) can be represented by the equation

$$\lambda(NO_3') = 0.8194 \times 10^{-8}/\eta(2.00 + 6.83/D) \quad (4)$$

(7) R. L. Kay, *J. Am. Chem. Soc.*, **82**, 2099 (1960).
(8) R. M. Fuoss and F. Accascina, *Proc. Natl. Acad. Sci. U. S.*, **45**, 1383 (1959).

### TABLE III
#### CONDUCTANCE OF $Bu_4N \cdot NO_3$ IN $CH_3CN-CCl_4$

| $10^4 c$ | $\Lambda$ | $10^4 c$ | $\Lambda$ |
|---|---|---|---|
| | No. 1 | | No. 5 |
| 11.045 | 155.77 | 9.764 | 81.71 |
| 8.558 | 157.24 | 7.653 | 84.37 |
| 6.457 | 158.65 | 5.750 | 87.29 |
| 4.771 | 159.97 | 4.088 | 90.43 |
| 2.581 | 162.12 | 2.242 | 95.04 |
| | No. 1 | | No. 6 |
| 10.716 | 156.23 | 7.479 | 67.89 |
| 8.060 | 157.80 | 5.811 | 70.85 |
| 6.288 | 159.02 | 4.382 | 73.98 |
| 4.119 | 160.82 | 2.850 | 78.41 |
| 2.307 | 162.78 | 1.619 | 83.28 |
| | No. 3 | | No. 8 |
| 11.261 | 91.25 | 6.727 | 53.20 |
| 9.009 | 93.54 | 5.111 | 56.53 |
| 6.710 | 96.23 | 3.736 | 60.27 |
| 4.326 | 99.96 | 2.657 | 64.22 |
| 2.425 | 103.77 | 1.505 | 70.22 |

### TABLE IV
#### DERIVED CONSTANTS

| No. | $K_A$ | $Me_4N \cdot NO_3$ $d$ | $\lambda_0$ ($NO_3'$) | $\Lambda_0$ (obsd.) | $\Lambda_0$ (calcd.) |
|---|---|---|---|---|---|
| 1 | 23[a] | 4.64 | 107.6 | 200.5 | 201.6 |
| 2 | 465 | 5.93 | 75.0 | 137.6 | 135.1 |
| 4 | 840 | 5.39 | 68.9 | 127.2 | 125.6 |
| 7 | 2950 | 7.50 | 59.8 | 111.4 | 111.0 |
| 9 | 9600 | 8.31 | 51.7 | 98.0 | 99.1 |
| | | $Bu_4N \cdot NO_3$ | | | |
| 1 | 7[a] | 3.73 | 108.5 | 168.2 | ... |
| 3 | 130 | 5.85 | 72.9 | 114.1 | ... |
| 5 | 250 | 5.89 | 67.6 | 106.6 | ... |
| 6 | 665 | 6.77 | 60.4 | 96.5 | ... |
| 8 | 1670 | 7.14 | 55.1 | 88.4 | ... |

[a] From $\Lambda_K$ program.

Using (4) and the previous[5] result

$$\lambda(Me_4N^+) = 0.8194 \times 10^{-8}/\eta (2.37 + 6.87/D) \quad (5)$$

the limiting conductances for $Me_4N \cdot NO_3$, based on data from measurements on $Bu_4N \cdot BPh_4$, $Me_4N \cdot BPh_4$ and $Bu_4N \cdot NO_3$, could be calculated. These values (Table IV) agree within an average of about 1% with the values obtained directly from the measurements made on $Me_4N \cdot NO_3$. A graphical comparison is shown in Fig. 1 where $R^-$ for the nitrate ion, obtained from data on $Bu_4N \cdot NO_3$ and on $Me_4N \cdot NO_3$, using (3) and (5) respectively. is plotted against reciprocal dielectric constant. The scatter of the data in Fig. 1 shows that the average 1% discrepancy between calculated and observed values of $\Lambda_0$ for $Me_4N \cdot NO_3$ probably has its origin mostly in experimental errors rather than in inadequacy of the function 1 to represent the dependence of conductance on solvent. It must be remembered that the discrepancy includes not only the experimental errors in the conductance data themselves but also those in viscosity and dielectric constant, both directly (via $\eta$ and $D$ in the modified Walden equation) and indirectly (via the constants $S$ and $E$ of the extrapolation function).
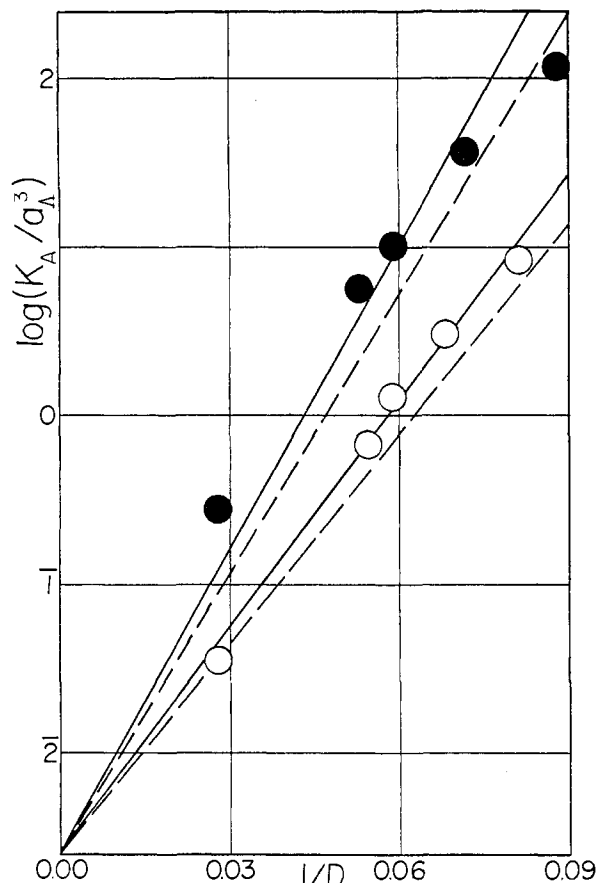
Fig. 2.—Test of equation 6.

A direct comparison, which eliminates discrepancies due to errors in $\eta$ and $D$, can be made by applying the Kohlrausch law to the results in pure aceto-nitrile; here we have

$\Lambda(Me_4N \cdot NO_3) = \Lambda_0(Me_4N \cdot BPh_4) + \Lambda(Bu_4N \cdot NO_3) -$

$\Lambda(Bu_4N \cdot BPh_4) = 152.27 + 168.18 - 119.48 = 200.97$

The directly observed value is 200.51; agreement is within 0.23%.

The association constants are shown in Fig. 2 where log $(K_A/a_A{}^3)$ is plotted against $1/D$; here $a_A$ is set equal to the sum $(R^+_\infty + R^-_\infty)$. The electrostatic theory[9] of association leads to the equation

(9) R. M. Fuoss, J. Am. Chem. Soc., 80, 5059 (1958).

$K_A = (4\pi Na^3/3000) \exp (e^2/aDkT)$          (6)

$= 2.523 \times 10^{-3} a^3 e^b$

If the data conform to (6), the points in Fig. 2 should lie on a straight line through the point $(0, - 2.60 = \log 2.523 \times 10^{-3})$. The data for $Bu_4N \cdot NO_3$ give a good straight line, from the slope of which we find $a_K = 5.43$. The data for $Me_4N \cdot NO_3$ scatter rather badly; the average line shown gives $a_K = 4.01$. The dotted lines in Fig. 2 are drawn with slopes corresponding to $a_A$, the contact distance obtained by summing the corresponding hydrodynamic radii. The two values agree within about 10% for both salts.
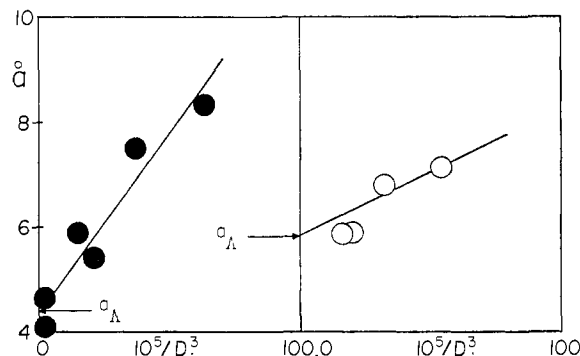


Fig. 3.—Dependence of calculated $a_J$ on dielectric constant.

A third source of values of $a$ is found in the coefficient $J(a)$ of (1). The values obtained by numerical analysis of the data are shown in Fig. 3; it will be noted that they depend systematically on the dielectric constant of the medium but approach the value $a_A$ or $a_K$ at infinite dielectric constant on a $D^{-3}$ scale. This is another[10] example of a varying contact distance calculated from experimental values of $J$. Recent theoretical work[11] shows that several of the approximations made in deriving[12] equation 2 discarded some linear terms in concentration which become increasingly visible as the dielectric constant decreases. As stated in an earlier paper,[10] we therefore attempt no ad hoc explanation of the variation of $a_J$ but reserve further comment until the theoretical work is completed. Meantime, we feel that $a_A$ or $a_K$ may be used with confidence as additive parameters, characteristic of the ions.

(10) E. Hirsch and R. M. Fuoss, ibid., 82, 1018 (1960).
(11) R. M. Fuoss, unpublished calculations.
(12) R. M. Fuoss and L. Onsager, J. Phys. Chem., 61, 668 (1957).