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Evaluation of Single Ion Conductivities in Acetonitrile, Nitromethane, and Nitrobenzene Using Tetraisoamylammonium Tetraisoamylboride as Reference Electrolyte

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The ions of tetraisoamylammonium tetraisoamylboride are large and symmetrical with a well-shielded single charge, and therefore should be relatively immune to specific solvation effects. In addition, the cation and anion have virtually the same crystallographic size, and therefore should have nearly the same mobility in solution. The results of high-precision conductivity measurements of this and other appropriate salts in acetonitrile and nitromethane are reported. Scales of single ion conductivities are derived for those two solvents and indirectly also for nitrobenzene. The scale for nitromethane could be checked against one derived from directly measured transference numbers. Although the formidable difficulties encountered in the purification of nitromethane made the comparison inconclusive, the evidence indicates that the use of the new reference electrolyte leads to single ion conductivities that may be accurate to within $\pm 0.1\%$.

Introduction

Although the original conception of the role of the solvent as a passive medium for chemical reactions long since has been abandoned, present knowledge about ion-solvent interactions still is embarrassingly incomplete. It is becoming increasingly clear that one of the obstacles that stand in the way of improved understanding of such processes is the general lack of exact knowledge about single ion mobilities in nonaqueous

solvents. The direct method for the evaluation of single ion mobilities from conductivities of electrolytes, which involves measurement of transference numbers, presents serious experimental difficulties in the majority of nonaqueous solvents. The only solvents other than water for which high-precision transference numbers have been reported are methanol,³ ethanol,⁴ and nitromethane.⁵ Indeed, Robinson and Stokes in 1955 commented that "Gordon's data on solutions in pure methanol form the sole oasis of exact knowledge in a desert of ignorance."⁶

For several other solvents, approximate values of single ion conductivities have been estimated on the basis of certain assumptions concerning the effective size of the ions of particular reference electrolytes. Walden's rule has been used extensively for this purpose, but the limitations of that approach have been demonstrated conclusively.^{7,8} From a more promising point of departure, Kraus and his co-workers assumed that in all solvents tetrabutylammonium and triphenylfluoroboride ions will have equal mobilities, since these ions have approximately equal size and (low) charge density and are reasonably symmetrical, with the result that specific solvation effects should be rela-

(3) J. A. Davies, R. L. Kay, and A. R. Gordon, *J. Chem. Phys.*, **19**, 749 (1951).

(4) J. R. Graham and A. R. Gordon, *J. Am. Chem. Soc.*, **79**, 2350 (1957).

(5) S. Blum and H. I. Schiff, *J. Phys. Chem.*, **67**, 1220 (1963).

(6) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London, 1955, p. 125.

(7) C. A. Kraus, *Ann. N. Y. Acad. Sci.*, **51**, 789 (1949).

(8) M. A. Coplan and R. M. Fuoss, *J. Phys. Chem.*, **68**, 1181 (1964); also earlier papers by Fuoss, *et al.*

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(2) From the Ph.D. thesis of his author, University of Pittsburgh, 1964.

tively unimportant. Fuoss made a further improvement by substituting tetraphenylboride as the anion and estimated that single ion mobilities calculated on this basis should be accurate to within a few per cent.

Recently we have synthesized a new reference electrolyte, tetraisoamylammonium tetraisoamylboride, and have presented evidence that this salt should be a more satisfactory reference electrolyte than tetrabutylammonium tetraphenylboride, the anion of which may not be ideally free from attack by specific solvation.⁹ In the present communication we present the results of high-precision conductance measurements with the new reference electrolyte and other appropriate salts in acetonitrile and nitromethane as solvents. A scale of single ion conductivities is given for acetonitrile, and values for nitromethane are compared with those obtained from the direct transference number measurements of Blum and Schiff. In addition, a scale for nitrobenzene is derived indirectly. It is concluded that the new reference electrolyte provides single ion conductivities that may be accurate to within $\pm 0.1\%$.

Experimental

Purification of Solvents. Acetonitrile. Matheson Coleman and Bell practical grade acetonitrile was purified by a procedure described elsewhere,¹⁰ with the addition of a final step which involved fractional distillation under nitrogen from calcium hydride through a 4-ft. Stedman column. The take-off was controlled by a needle valve incorporated into the distillation head. The conductivity of the distillate was monitored periodically by means of a small conductance cell attached to the receiver. Collection of the distillate was deferred until its conductivity had dropped to 5×10^{-8} ohm⁻¹ cm.⁻¹ and was terminated as soon as the conductivity had increased to the same value. The product was stored in a vessel from which it could be dispensed in a closed system by applying nitrogen pressure and had the following properties: water content, below 1 mM (lower limit of detection by Karl Fischer reagent); conductivity, 2 to 4×10^{-8} ohm⁻¹ cm.⁻¹; viscosity, 3.448 mp.; density, 0.77670 g. ml.⁻¹. For further details, see ref. 2.

Nitromethane. It is known that industrial nitromethane may contain water, methanol, ethanol, formaldehyde, acetaldehyde, higher nitroalkanes, and possibly other impurities as well. Its purification presents formidable difficulties. The procedure used in the very careful work of Schiff, *et al.*,¹¹ was modified slightly in order to remove water more effectively and involved treatment of Eastman Spectrograde nitromethane (d 1.1240 g. ml.⁻¹) by four fractional vacuum distillations from Drierite, as well as six fractional freezing steps.¹² Density measurements after each step indicated that freezing provided more effective purification than distillation and that after three freezings the density no longer changed appreciably. Schiff, *et al.*,¹¹ after a thorough study, concluded that density is an important criterion of purity for nitro-

methane and that an impure sample generally has a lower density than the pure solvent. Even after our ten purification steps, we were unable to reach a density as high as that reported by Schiff, *et al.* In Table I the properties of nitromethane purified by five

Table I. Properties of Five Preparations of Nitromethane

Purification	d , g. ml. ⁻¹	η , mp.	K_0 , ohm ⁻¹ cm. ⁻¹
<i>a</i>	1.1251	6.275	10^{-7}
<i>b</i>	1.13064	6.08	
Ref. 11	1.13124	<i>c</i>	$5-10 \times 10^{-9}$
Ref. 8	1.1230-1.1246	6.210-6.218	$2-6 \times 10^{-8}$
This work	1.12795	6.118	$7-8 \times 10^{-9}$

^a R. M. Fuoss and R. C. Miller, *J. Am. Chem. Soc.*, **75**, 3076 (1953). ^b C. J. Thompson, H. J. Coleman, and R. V. Helm, *ibid.*, **76**, 3445 (1954). ^c Value of 6.27 assumed (see ref. 11 for origin of this value).

different groups are compared. The considerable fluctuations stress the need for further study of purification methods for nitromethane, as well as the caution which must be exercised in interpreting results obtained in this solvent. It is to be noted that nitroethane, 1-nitropropane, and 2-nitropropane all have much lower densities (and higher viscosities) than the range of values reported for nitromethane. However, gas chromatographic analysis indicated the presence of small amounts of two lower-boiling impurities in our solvent, which were not water, methanol, ethanol, formaldehyde, or acetaldehyde, and remained unknown.¹³ Fortunately, the relatively ideal ions studied in this work are not likely to undergo specific reactions, as will be evident from the comparisons below of their properties in a variety of solvents. However, it remained necessary to correct for the viscosity difference between our solvent and that of Schiff, *et al.*

Purification of Salts. Tetraisoamylammonium tetraisoamylboride, (i-Am)₄NB(i-Am)₄, the reference electrolyte, was synthesized as we have described elsewhere⁹; information about the properties of tetraalkylboride compounds was given by Damico.¹⁴

Tetrabutylammonium tetraphenylboride, Bu₄NBPh₄, was prepared as described elsewhere.¹⁵

Tetraisoamylammonium tetraphenylboride was prepared by adding slowly a methanolic solution of recrystallized sodium tetraphenylboride (Fisher) to a methanolic solution of tetraisoamylammonium iodide, prepared as described in ref. 9. The precipitate was recrystallized five times from a 1:5 acetone-water mixture and dried *in vacuo* for 8 hr. at 70°.

Tetraisoamylammonium perchlorate and tetrabutylammonium perchlorate were prepared in a manner analogous to that given for tetraethylammonium perchlorate.¹⁶ The products were recrystallized five times from a 1:5 acetone-water mixture and dried *in vacuo* for 8 hr. at 70° and 6 hr. at 60°, respectively.

Tetrabutylammonium bromide (Eastman White Label) was dissolved in ethanol, and the solution was puri-

(9) J. F. Coetzee and G. P. Cunningham, *J. Am. Chem. Soc.*, **86**, 3403 (1964).

(10) J. F. Coetzee, G. P. Cunningham, D. K. McGuire, and G. R. Padmanabhan, *Anal. Chem.*, **34**, 1139 (1962).

(11) A. K. R. Unni, L. Elias, and H. I. Schiff, *J. Phys. Chem.*, **67**, 1216 (1963).

(12) The exact sequence of steps and other details are given in ref. 2.

(13) For further details, see ref. 2 and compare ref. 8.

(14) R. Damico, *J. Org. Chem.*, **29**, 1971 (1964).

(15) F. Accascina, F. Petrucci, and R. M. Fuoss, *J. Am. Chem. Soc.*, **81**, 3101 (1959).

(16) I. M. Kolthoff and J. F. Coetzee, *ibid.*, **79**, 870 (1957).

fied by extracting with five 50-ml. portions of ether. After evaporation of the ethanol the salt was recrystallized five times from a 1:10 acetone-ether mixture and dried *in vacuo* for 12 hr. at 80°.

Instrumentation. High-precision conductivity, density, and viscosity measurements were carried out at the Mellon Institute, Pittsburgh, Pa., using the equipment of Dr. Robert L. Kay. The conductance bridge and cells and a special salt dispensing device, operating in a closed system, are described in detail elsewhere.^{2,17} Conductance measurements were carried out in a 110-gal. oil bath, constructed of insulated stainless steel, at 25 ± 0.002°. The electrodes were platinized to a light gray color. Two cells were used with cell constants of 1.2227 ± 0.0001 and 1.12060 ± 0.0001 cm.⁻¹.

Density measurements were carried out in pycnometers which were constructed by sealing a 10/30 standard taper, 1.5-mm. capillary bore, male joint to the top of a 25-ml. erlenmeyer flask (heavy-wall type). An etch mark was placed on the capillary by means of hydrofluoric acid. A cap was constructed from a 10/30 standard taper female joint. The pycnometers were calibrated using conductivity water. The capillaries of the pycnometers were calibrated by measuring the distance from the etch mark with a traveling microscope. The pycnometers were immersed in a water bath (not oil), which was controlled at 25 ± 0.003° by a Bayley Instrument Co. precision temperature controller, Model 102, and were viewed by means of a traveling microscope focused through the glass wall of the bath. The pycnometers were filled with a 20-ml. syringe, and the unfilled portions of the capillaries were dried with lens paper. Each density determination was made twice using different pycnometers. By this technique, densities could be determined to better than 1 part in 20,000.

Viscosity measurements were made with a Cannon-Ubbelohde dilution viscometer, Model CUCU-25, which was calibrated with conductivity water and had a flow time of 548.5 ± 0.1 sec. A "water check" was made before the viscosity of any other solvent was determined. The flow times of the solvents were reproducible to within 0.1 sec.

Results

The results of conductivity measurements of solutions of the reference electrolyte, $(i\text{-Am})_4\text{NB}(i\text{-Am})_4$, and other appropriate salts in acetonitrile and nitromethane as solvents are given in Table II. The data were analyzed on an IBM 7070 computer using the improved Fortran program of Kay¹⁷ for the solution of the Fuoss-Onsager equation,¹⁸ both for nonassociated electrolytes

$$\Lambda = \Lambda_0 - SC^{1/2} + EC \log C + JC \quad (1)$$

as well as for associated electrolytes

$$\Lambda = \Lambda_0 - S(C\gamma)^{1/2} + EC\gamma \log C\gamma + JC\gamma - K_A\Lambda_0 f^2 C\gamma \quad (2)$$

It was found that none of the electrolytes was associated in either solvent. In Table III are given the unweighted values obtained for Λ_0 and a , as well as the standard

(17) J. L. Hawes and R. L. Kay, *J. Phys. Chem.*, in press.

(18) R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience Publishers, Inc., New York, N. Y., 1959.

deviations of Λ , Λ_0 , and a . The data proved to be sufficiently precise to give virtually the same results whether Λ was weighted by C or not. Table III also lists values of the constants S , E , and J of eq. 1, as well as the dependence of J on a .

Table II. Conductivity of Salts in Acetonitrile (AN) and Nitromethane (NM)

10°C	Λ	10°C	Λ
$(i\text{-Am})_4\text{NB}(i\text{-Am})_4$ in AN (3.40×10^{-8}) ^a		$(i\text{-Am})_4\text{NB}(i\text{-Am})_4$ in NM (6.34×10^{-9}) ^a	
3.8830	108.34	4.0895	61.01
7.8262	106.05	7.3649	59.92
11.9695	104.26	10.7816	59.07
16.5932	102.66	14.4861	58.28
20.4198	101.54	17.3601	57.75
24.3690	100.52	21.0466	57.13
28.5513	99.55	24.2414	56.64
$(i\text{-Am})_4\text{NB}(\text{Ph})_4$ in AN (4.71×10^{-8}) ^a		$(i\text{-Am})_4\text{NB}(\text{Ph})_4$ in NM (7.02×10^{-9}) ^a	
4.3311	108.47	5.3456	60.70
9.1077	105.87	7.7425	59.94
14.0565	103.93	10.1099	59.35
18.9806	102.38	12.3575	58.85
24.5119	100.93	14.8229	58.37
30.2451	99.63	17.7519	57.87
35.5560	98.56		
Bu_4NBPh_4 in AN (3.82×10^{-8}) ^a		Bu_4NBPh_4 in NM (5.96×10^{-9}) ^a	
4.0601	113.30	3.6074	63.84
8.9688	110.49	7.2231	62.62
14.5417	108.08	10.9886	61.65
18.6479	106.89	15.2219	60.78
24.0956	105.38	19.4361	60.03
28.5365	104.31	24.3963	59.23
33.3689	103.27	28.8044	58.70
Bu_4NBr in NM (5.58×10^{-9}) ^a			
4.4946	92.23		
11.6474	89.85		
16.5303	88.67		
21.9011	87.61		
27.4056	86.68		
32.9465	85.86		
37.9371	85.18		
47.4226	84.04		
$(i\text{-Am})_4\text{NClO}_4$ in AN (5.13×10^{-8}) ^a		Bu_4NClO_4 in AN (4.08×10^{-8}) ^a	
3.8847	153.56	4.4497	157.42
8.5398	150.32	10.0615	153.69
12.6720	148.19	15.5460	151.07
16.3550	146.61	21.0287	148.96
20.9685	144.91	26.9113	147.00
25.1932	143.54	36.3877	144.46
29.7417	142.22	40.5818	143.45
34.4024	141.03		

^a K_0 value in parentheses.

Table IV gives the scale of single ion conductivities obtained by assuming that in acetonitrile $(i\text{-Am})_4\text{N}^+$ and $(i\text{-Am})_4\text{B}^-$ ions have equal limiting mobilities. Only high-precision conductance data are included. For cations, the new scale is 0.41 unit (*ca.* 0.5 to 1% for the ions listed) higher than the 1964 scale (based on $(i\text{-Am})_3\text{BuNBPh}_4$) and 2.02 units (*ca.* 2 to 4%) higher than the 1960 scale (based on Bu_4NBPh_4). For anions, the new scale is lower by the same amounts.

Table III. Calculated Parameters of the Fuoss–Onsager Equation for Acetonitrile (AN) and Nitromethane (NM)

Salt	Solvent	$\sigma\Delta$	Λ_0	a	S	E	J^a	$\partial J/\partial a^a$
$(i\text{-Am})_4\text{NB}(i\text{-Am})_4$	AN	0.04	114.48 ± 0.04	4.83 ± 0.07	315.3	163.1	1643.2	273.5
	NM	0.04	64.58 ± 0.03	4.72 ± 0.08	178.0	92.7	914.4	155.4
$(i\text{-Am})_4\text{NBPh}_4$	AN	0.05	114.96 ± 0.04	4.74 ± 0.07	315.6	164.3	1624.6	275.2
	NM	0.008	64.65 ± 0.01	5.22 ± 0.05	178.1	92.9	992.3	153.1
Bu_4NBPh_4	AN	0.06	119.65 ± 0.05	4.55 ± 0.08	319.1	175.4	1624.5	286.3
	NM	0.05	67.26 ± 0.04	4.85 ± 0.08	180.0	99.1	966.3	159.8
Bu_4NBr	NM	0.05	96.67 ± 0.05	4.25 ± 0.08	201.8	169.4	1192.8	222.8
$(i\text{-Am})_4\text{NClO}_4$	AN	0.02	160.62 ± 0.02	3.79 ± 0.02	349.3	272.8	1813.2	383.9
Bu_4NClO_4	AN	0.02	165.06 ± 0.01	3.57 ± 0.01	352.6	283.3	1771.6	400.6

^a NO viscosity correction applied.

Table IV. Single Ion Conductivities in Acetonitrile Based on Tetraisoamylammonium Tetraisoamylboride as Reference Electrolyte

Ion	λ_0	Ion	λ_0
Me_4N^+	94.55 ^a	PCP^- ^c	84.52 ^d
Et_4N^+	85.05 ^a	HCAP^- ^e	71.30 ^d
Pr_4N^+	70.64 ^a	Pi^-	77.32 ^f
Bu_4N^+	61.93	Br^-	100.05 ^f
$(i\text{-Am})_4\text{BuN}^+$	58.54 ^b	I^-	102.03 ^f
$(i\text{-Am})_4\text{N}^+$	57.24	ClO_4^-	103.38
$(i\text{-Am})_4\text{B}^-$	57.24	PF_6^-	102.8 ^g
Ph_4B^-	57.72		

^a D. S. Berns and R. M. Fuoss, *J. Am. Chem. Soc.*, **82**, 5585 (1960). ^b T. L. Fabry and R. M. Fuoss, *J. Phys. Chem.*, **68**, 907 (1964). ^c 1,1,2,3,3-Pentacyanopropenide. ^d J. E. Lind, Jr., and R. M. Fuoss, *J. Am. Chem. Soc.*, **83**, 1828 (1961). ^e 1,1,2,4,5,5-Hexacyano-3-azapentadienide. ^f Private communication from R. L. Kay and D. F. Evans, Mellon Institute; based on conductivities of Bu_4N^+ salts. ^g J. Eliassaf, R. M. Fuoss, and J. E. Lind, Jr., *J. Phys. Chem.*, **67**, 1941 (1963).

Discussion

Single Ion Conductivities in Acetonitrile and Nitromethane. Final proof of the accuracy of the new scale of single ion conductivities given in Table IV requires the direct measurement of transference numbers.¹⁹ Until such measurements can be carried out in a sufficiently precise manner, an indication of the reliability of $(i\text{-Am})_4\text{NB}(i\text{-Am})_4$ as a reference electrolyte can be obtained from the data for nitromethane as solvent using the conductivities listed in Table III and the transference numbers of Blum and Schiff for the ions of Bu_4NBr .⁵ Unfortunately, this test is not as conclusive as might have been wished because of the difference in properties between our solvent and that of Blum and Schiff, as discussed above, but at present there is no other choice.²⁰ Fortunately, for the relatively ideal ions of Table III a simple viscosity correction may be adequate to bring our results and those of Blum and Schiff on a common basis (note the constancy of the Stokes radii in acetonitrile and nitromethane, Table VII). By correcting our Λ_0 values for $(i\text{-Am})_4\text{NB}(i\text{-Am})_4$, $(i\text{-Am})_4\text{NBPh}_4$, and Bu_4NBPh_4 from Table

(19) We are engaged in such a program for acetonitrile, acetone, and other nonhydrogen-bonding solvents.

(20) The solubility of $(i\text{-Am})_4\text{NB}(i\text{-Am})_4$ in water, methanol, and ethanol, for which transference numbers are available, is too low for reliable, direct conductivity measurements. Indirect evaluation of ion mobilities in alcohols by using alkali metal tetraisoamylborides may be possible, but salts of this type are not ideally stable.¹⁴ The low solubility of tetraalkylammonium tetraphenylborides and tetraisoamylborides in hydroxylic solvents contrasts sharply with the high solubility of these salts in acetonitrile, nitromethane, and acetone. It is possible that in strongly structured solvents the interaction between these relatively ideal ions and the solvent is too weak to allow appreciable dissolution.

III by multiplying by the viscosity ratio from Table I, $6.118/6.27 = 0.976$, we derive a value for Bu_4N^+ (34.1) which agrees exactly with that of Kay, Blum, and Schiff (34.06).²¹ A list of single ion conductivities for nitromethane as solvent is given in Table V. In view of the varying viscosities of the nitromethane used in other studies, only values derived from our measurements and those of Kay, Blum, and Schiff are included. As for acetonitrile as solvent, the use of Bu_4NBPh_4 as reference electrolyte in nitromethane leads to single ion conductivities for cations which are lower (by 1.25 units, or again *ca.* 2 to 4%) and for anions which are higher by the same amount.

Table V. Single Ion Conductivities in Nitromethane Based on Transference Numbers

Cation	λ_0	Anion	λ_0
Me_4N^+	54.51 ^{a,b}	$(i\text{-Am})_4\text{B}^-$	31.51 ^c
Et_4N^+	47.65 ^{a,b}	Ph_4B^-	31.57 ^c
Pr_4N^+	39.20 ^{a,b}	Br^-	62.91 ^{a,d}
Bu_4N^+	34.06 ^{a,b}	Cl^-	62.51 ^{a,d}
$(i\text{-Am})_4\text{N}^+$	31.51 ^c		

^a Ref. 21. ^b Transference number for bromide salt used. ^c This study; see Table III. ^d Transference number for tetrabutylammonium salt used.

Single Ion Conductivities in Nitrobenzene. Although only a few salts in nitrobenzene have been treated by the Fuoss–Onsager equation,²² there nevertheless exists an abundance of older but precise conductivity data for this solvent.^{23,24} It should be borne in mind that retreatment of these older data by the Fuoss–Onsager equation may alter the Λ_0 values slightly.

We made no measurements in nitrobenzene, but it nevertheless is possible to derive a scale of single ion conductivities based indirectly on $(i\text{-Am})_4\text{NB}(i\text{-Am})_4$ as reference electrolyte. In both acetonitrile and nitromethane (Table III) the following relationship holds.

$$\frac{\Lambda_0[\text{Bu}_4\text{NBPh}_4]}{\Lambda_0[(i\text{-Am})_4\text{NB}(i\text{-Am})_4]} = 1.043 \quad (3)$$

It seems permissible to assume that the same relationship holds for nitrobenzene, which has nearly the same dielectric constant as nitromethane and acetonitrile (see below, discussion on Walden products and Stokes radii). From the Λ_0 value reported by Hirsch and

(21) R. L. Kay, S. C. Blum, and H. I. Schiff, *J. Phys. Chem.*, **67**, 1223 (1963).

(22) E. Hirsch and R. M. Fuoss, *J. Am. Chem. Soc.*, **82**, 1018 (1960).

(23) C. R. Witschonke and C. A. Kraus, *ibid.*, **69**, 2472 (1947).

(24) E. G. Taylor and C. A. Kraus, *ibid.*, **69**, 1731 (1947).

Fuoss²² for Bu₄NBPh₄ (22.34), we base our scale of single ion conductivities in nitrobenzene on the following values.

$$\lambda_0[(i\text{-Am})_4\text{N}^+] = \lambda_0[(i\text{-Am})_4\text{B}^-] = \frac{1}{2} \frac{22.34}{1.043} = 10.70 \quad (4)$$

In addition, in both acetonitrile and nitromethane (Tables IV and V) it was found that

$$\lambda_0[\text{Bu}_4\text{N}^+]/\lambda_0[(i\text{-Am})_4\text{N}^+] = 1.08 \quad (5)$$

and

$$\lambda_0[\text{Ph}_4\text{B}^-]/\lambda_0[(i\text{-Am})_4\text{B}^-] = 1.01 \quad (6)$$

Again assuming that the same relationships apply in nitrobenzene, we derive from eq. 4, 5, and 6 that in nitrobenzene the single ion conductivities of Bu₄N⁺ and Ph₄B⁻ are 11.55 and 10.79, respectively. Single ion conductivities based on this indirect scale are presented in Table VI. Even more than for acetonitrile, verification of this scale must await the precise measurement of transference numbers.

Table VI. Single Ion Conductivities in Nitrobenzene Based Indirectly on Tetraisoamylammonium Tetraisoamylboride as Reference Electrolyte

Cation	λ_0	Ref.	Anion	λ_0	Ref.
NH ₄ ⁺	18.12	23	Cl ⁻	22.68	23
BuNH ₃ ⁺	16.69	23	Br ⁻	21.93	23
Bu ₂ NH ₂ ⁺	14.13	23	I ⁻	21.25	22
Bu ₃ NH ⁺	12.57	23	NO ₃ ⁻	22.79	22
Me ₂ NH ⁺	18.5	24	AcO ⁻	23.95	23
Me ₃ EtN ⁺	17.0	24	Pi ⁻	16.28	22
Me ₃ PhN ⁺	15.3	24	F ₄ B ⁻	22.41	23
Me ₄ N ⁺	17.0	24	Ph ₃ FB ⁻	11.8	24
Et ₄ N ⁺	16.1	24	Ph ₄ B ⁻	10.79	22
Pr ₄ N ⁺	13.2	24	ClO ₄ ⁻	17.7	23
Bu ₄ N ⁺	11.55	22			
Na ⁺	16.02	23			
K ⁺	17.53	23			

Walden Products and Stokes Radii. It is obvious that for ions which experience specific solvation (short-range) effects, the Walden product, $\lambda_0\eta_0$, generally will vary in different solvents. However, in solvents of different dielectric constant, the Walden product may vary even in the absence of specific solvation effects. Fuoss^{25,26} has accounted satisfactorily for such variations observed in mixtures of polar with nonpolar solvents (e.g., acetonitrile with carbon tetrachloride) by considering the additional frictional force produced as a result of the dielectric relaxation induced by ionic motion in a polar medium. The subject has been treated theoretically by Boyd and more recently by Zwanzig.²⁷ On this basis, if R_∞ represents the "hydrodynamic" radius of an ion in a hypothetically ideal solvent of infinite dielectric constant, and R the Stokes radius in a real solvent of dielectric constant D , which is related to the ionic conductivity

$$R \text{ (in } \text{\AA}.) = \frac{0.8194|Z|}{\lambda_0\eta_0} \quad (7)$$

(25) R. M. Fuoss, *Proc. Natl. Acad. Sci. U. S. A.*, **45**, 807 (1959).
 (26) D. S. Berns and R. M. Fuoss, *J. Am. Chem. Soc.*, **83**, 1321 (1961).
 (27) R. Zwanzig, *J. Chem. Phys.*, **38**, 1603, 1605 (1963).

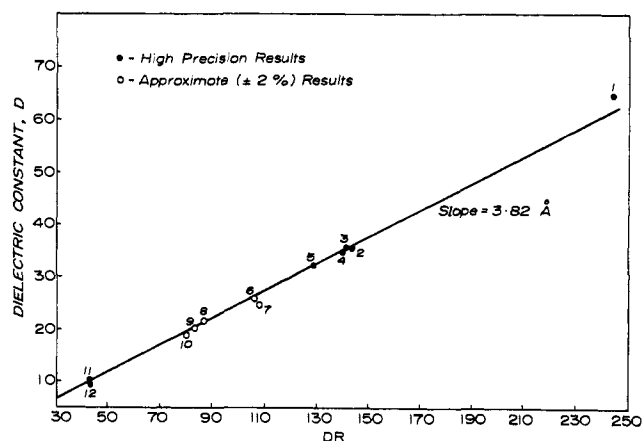


Figure 1. Dependence of average Stokes radius of Bu₄NBPh₄ on dielectric constant (references given in parentheses): solvent 1, propylene carbonate (28); 2, acetonitrile (this work); 3, nitromethane (this work); 4, nitrobenzene (28); 5, methanol (8); 6, propionitrile (29); 7, benzonitrile (29); 8, acetone (29); 9, isobutyronitrile (29); 10, phenylacetonitrile (29); 11, 1,2-dichloroethane (30); 12, *o*-dichlorobenzene (30).

then the following relationship applies

$$RD = B + DR_\infty \quad (8)$$

where B is a constant. In a classical series of studies on ion-solvent interactions, Fuoss and his co-workers found that eq. 8 generally holds well for mixtures of carbon tetrachloride with methanol, ethanol, acetonitrile, and nitrobenzene, but, as expected, less well in mixtures of polar solvents in which specific solvation effects vary appreciably.⁸

Figure 1 represents the dependence of the average Stokes radius of the ions of Bu₄NBPh₄ on the dielectric constant of the solvent in twelve pure solvents.²⁸⁻³⁰

Table VII. Some Ionic Radii in Acetonitrile (AN), Nitromethane (NM), Nitrobenzene (NB), and Water

Ion	Effective crystallographic radii		Stokes radii (R) ^a			
	Models ^b	Calcd.	AN	NM	NB	W
Me ₄ N ⁺	3.2	3.47 ^c	2.51	2.40	2.62	2.05
Et ₄ N ⁺	4.0	4.00 ^c	2.79	2.74	2.77	2.82
Pr ₄ N ⁺	4.6	4.52 ^c	3.36	3.33	3.37	3.93
Bu ₄ N ⁺	5.0	4.94 ^c	3.83	3.85	3.85	4.73
(<i>i</i> -Am) ₄ N ⁺	5.4		4.15	4.16	4.17	
(<i>i</i> -Am) ₄ B ⁻	5.4		4.15	4.16	4.17	
Ph ₄ B ⁻	4.8	4.04 ^d	4.11	4.14	4.12	
Pi ⁻			3.07		2.73	3.03
ClO ₄ ⁻			2.29		2.51	1.37
I ⁻		2.16 ^e	2.33		2.10	1.20
Br ⁻		1.95 ^e	2.37	2.09	2.03	1.18
Cl ⁻		1.81 ^e		2.08	1.97	1.21

^a Viscosity values: AN, 3.448; NM, 6.27; NB, 18.39²²; W, 8.903 mp. ^b Estimated from Fisher-Taylor-Hirschfelder models. ^c Reference 6, 2nd Ed., 1959, p. 127. ^d E. Grunwald in "Electrolytes," B. Pesce, Ed., Pergamon Press, New York, N. Y., 1962, p. 74. ^e L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p. 514.

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Apart from the fact that the high-precision value for propylene carbonate and the relatively low-precision value for benzonitrile deviate from linearity, an average value for R_{∞} of 3.82 Å. adequately accounts for the results. This value is a little above the range of 3.35 to 3.70 Å. found by Fuoss, *et al.*, for Bu_4NBPh_4 in polar-nonpolar solvent mixtures. Obviously the ions of this electrolyte are reasonably ideal.

The relative ideality of a number of ions in acetonitrile, nitromethane, and nitrobenzene is illustrated by the Stokes radii listed in Table VII. These three solvents have similar dielectric constants (36.0, 35.9, and 34.7, respectively), so that the frictional force experienced by a moving ion owing to dielectric relaxation should be similar in these solvents. Hence, those ions which do not experience specific solvation effects should have constant Walden products and Stokes radii in these solvents. That this is the case for $(i\text{-Am})_4\text{B}^-$ and Ph_4B^- , as well as for quaternary ammonium ions

larger than Me_4N^+ , is shown in Table VII. It should be noted that the difference in Walden products previously obtained for Ph_4B^- in acetonitrile (0.199) and nitromethane (0.203) on the basis of an earlier scale of single ion conductivities⁸ virtually disappears on our scale. However, for the majority of anions considerable variations occur in different solvents, as is well known. Finally, for the series of quaternary ammonium ions, the Stokes radii in water increase more rapidly and finally approach the effective crystallographic radii more closely than they do in the three nonaqueous solvents.

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Hydrogen Bonding and the *ortho* Effect in Acetonitrile. Reaction of *ortho*-Substituted Benzoic Acids with Amines

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*In acetonitrile, which has little capacity to solvate anions, the effect of ortho substitution by hydroxyl or nitro groups on the properties of benzoic acids and phenols is more marked than in water. In order to obtain information about the ortho effect and other structural factors in acetonitrile, we have titrated conductometrically *n*-butyl-, dibutyl-, and tributylamine with benzoic, salicylic, and 2,6-dihydroxybenzoic acids, as well as aniline with picric acid. The titration curves are quite different from those in water, and several equilibria must be considered. The necessary single ion conductivities were evaluated, and all titration curves, except those of benzoic acid, could be interpreted quantitatively.*

Introduction

It is well known that the simple electronic theory of organic chemistry has been of limited success in predicting the influence of *ortho* substituents on the strength of benzoic acids and phenols. The problem is a complex one, because in addition to factors such as inductive, field, resonance, and steric effects, several implications of hydrogen bonding must be considered, including solvation and intramolecular (chelation) effects, as well as intermolecular association (dimerization in the case of carboxylic acids). Consequently, it is to be expected that the so-called *ortho* effect may vary markedly in different solvents. Nevertheless little systematic information is available for solvents other

than water, with the notable exception of the thorough study of Davis and Hetzer in benzene as solvent.³

Acetonitrile is a logical choice for studies that are intended to provide improved resolution of the factors mentioned above. Its dielectric constant is sufficiently high (36.0) to allow precise and technically simple conductometry and potentiometry, yet it is more inert than hydroxylic solvents in that it solvates the majority of cations and particularly anions much more weakly. One consequence of this weak solvation is that in the presence of their conjugate acids, certain anions derive stability by resorting to hydrogen bonding ("homoconjugation") with the acid to produce the species $(\text{A} \cdots \text{HA})^-$,⁴ while ammonium ions form corresponding complexes such as $(\text{BH} \cdots \text{B})^+$.⁵ These homoconjugated complexes are sufficiently stable to produce striking differences between acid-base reactions in acetonitrile and in water.

A second consequence of the weak solvation of anions by acetonitrile is that one would expect a clearer picture in acetonitrile than in water of the extent to which different *ortho*-substituted benzoate and phenolate ions are stabilized by intramolecular hydrogen bonding. Considerable information about such stabilization and also other factors of interest can be obtained by following the reaction of these acids with appropriate bases conductometrically, as described in

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