$$c\psi(d) = \frac{0.00810c - 0.003903c^{3/2}}{0.99704 + 0.00810c - 0.00260c^{3/2}} \quad (4)$$

The mobility term was computed by substituting the values: $D = 78.54$,[8] $\eta_0 = 8.949 \times 10^{-3}$,[9] $T = 298.16$, $\lambda_1^0 = 61.92$ and $\lambda_2^0 = 71.44$ in equation (2). The values of the limiting conductances of the silver and nitrate ions were those obtained by MacInnes, Shedlovsky and Longsworth.[10] The equation for the mobility term reduces to the numerical form

$$(\overline{\mathfrak{M}}/c) \times 10^{20} = 35.6512 - \frac{0.08241\sqrt{c}}{1 + 0.995\sqrt{c}} + 18.959c\phi(0.995\sqrt{c}) \quad (5)$$

The third column in Table I contains the results computed by equations (1), (3), (4) and (5). With the exception of the result at the lowest concentration, the agreement of the observed results with theory is remarkably good.

A more detailed description of the calculation is illustrated in Fig. 1. In this figure, the upper (solid) curve represents the calculation by the complete theory and the lower (solid) curve the result obtained by the limiting law of the theory[6] which for silver nitrate becomes

$$\mathfrak{D} \times 10^5 = 1.7675 - 1.040\sqrt{c} \quad (6)$$

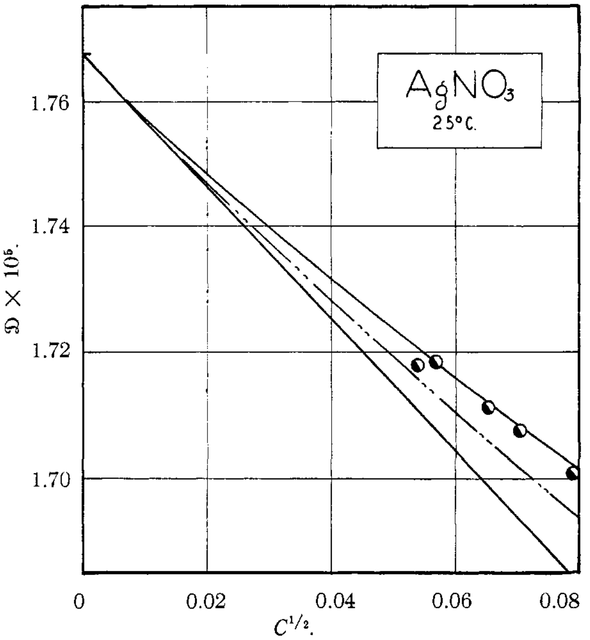

Fig. 1.—Upper curve represents complete theory. Lower curve represents the limiting law (Eq. 6). The intermediate curve was obtained by assuming constancy of $(\overline{\mathfrak{M}}/c)$.

The plot which lies between these results is obtained when $(\mathfrak{M}/C \times 10^{20})$ is constant and equal to its value at zero concentration. The difference between the center and top curve represents the calculated effect of electrophoresis. There seems to be little doubt from the positions of the circles representing the experimental results that the mobility term is required for the calculation.

NEW HAVEN, CONN. RECEIVED FEBRUARY 26, 1951

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[8] Ref. 6, p. 118.

[9] Ref. 6, p. 128.

[10] MacInnes, Shedlovsky and Longsworth, THIS JOURNAL, **54**, 2758 (1932).

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. LII. Conductance of Some Salts of Acetone

BY MAURICE J. MCDOWELL[1] AND CHARLES A. KRAUS

To fill some gaps in the list of ion conductances in acetone, the conductances of a number of salts were determined in this solvent. Thus, the conductances of the ammonium, the tetramethyl-, tetrapropyl- and tetraamylammonium ions have been determined. The conductances of octadecyltributyl- and dioctadecyldibutylammonium ions have been determined as also has been that of the chloride ion. Dissociation constants have been evaluated on the basis of the Fuoss analysis. Some comparisons are made of dissociation constants and ion conductances in different solvents.

I. Introduction

Reynolds and Kraus[2] have measured the conductance of a number of salts in acetone at 25°. For purposes of intercomparison of ion conductances and dissociation constants of electrolytes in different solvents, the earlier measurements in acetone leave a number of gaps which the present investigation is intended to fill. In particular, the conductances of several symmetrical quaternary ammonium salts have been measured so as to provide data on the conductances of the quaternary ammonium ions from tetramethyl- to tetra-*n*-amyl, inclusive. The conductances of the octadecyltributyl- and the dioctadecyldibutylammonium ions have been determined. The conductances of the chloride and the ammonium ions have likewise been evaluated.

II. Experimental

1. Apparatus, Procedure and Materials.—The electrical measuring apparatus and the thermostat were the same as those of Reynolds.[2] The temperature was controlled at 25 ± 0.002°.

With the exception of tetrabutylammonium chloride, with which the dilution method was employed, all measurements were carried out according to the procedure described by Daggett, Bair and Kraus[3] for aqueous solutions. The conductance cell of the erlenmeyer type had a capacity of approximately 1 liter. Salt samples were weighed out on a microbalance in quartz cups. Since acetone is insensitive to carbon dioxide, samples were introduced into the cell as it rested in the thermostat. The cell was provided with a magnetic stirrer.

Acetone[4] was purified according to the method of Rey-

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[1] Ethyl Corporation Fellow (1947–1948); University Fellow (1948–1949); Metcalf Fellow (1949–1950) in Brown University.

[2] M. B. Reynolds and C. A. Kraus, THIS JOURNAL, **70**, 1709 (1948).

[3] H. M. Daggett, E. J. Bair and C. A. Kraus, *ibid.*, **73**, 799 (1951).

[4] This material was kindly furnished by the Tennessee Eastman Company of Kingsport, Tennessee.

nolds.[2] The solvent conductance varied between 1–4 × 10^{-9} and the maximum correction for solvent conductance in the most dilute solution was 0.2%.

The following salts were prepared by conventional methods and purified by recrystallization from suitable solvents; tetramethylammonium picrate, m.p. 318–320°; tetra-*n*-propylammonium iodide, m.p. 293°; tetra-*n*-amylammonium bromide, m.p. 100°; octadecyltri-*n*-butylammonium iodide, m.p. 101–102°; dioctadecyldi-*n*-butylammonium iodide, m.p. 107°. Ammonium picrate was recrystallized repeatedly from alcohol and acetone.

2. Results.—In Table I are presented conductance values for the salts at the concentrations indicated. Concentrations are expressed in moles of salt per liter of solution assuming the density of the solution to be that of the solvent. In making buoyancy corrections, the density of the organic salts has been assumed to be 1.5. In making computations, the density of acetone has been taken to be 0.7845, the dielectric constant, 20.47 and the viscosity 3.040 × 10^{-3} poise.[2]

TABLE I

CONDUCTANCE OF SOME SALTS IN ACETONE AT 25°

$C \times 10^4$	Λ	$C \times 10^4$	Λ
A. Ammonium picrate		B. Tetramethylammonium picrate	
0.44390	170.016	0.6538	176.95
0.83417	164.354	1.3292	173.86
1.7149	154.784	2.9794	168.57
3.0237	144.452	4.6256	164.65
5.2188	132.389	6.2838	161.44
C. Tetra-*n*-propylammonium iodide		D. Tetra-*n*-amylammonium bromide	
0.4105	184.945	0.29802	169.90
0.80496	182.129	0.72344	166.66
1.5752	177.832	1.3930	162.71
3.1535	171.286	2.7820	156.48
5.0574	165.321	5.6153	147.64
E. Octadecyltributylammonium iodide		F. Dioctadecyldibutylammonium iodide	
0.10815	161.12	0.13042	154.66
.23874	160.00	.26540	153.55
.43455	158.49	.54327	151.67
.66288	157.04	1.2474	148.24
1.0712	154.91	1.9566	145.51
		G. Tetra-*n*-butylammonium chloride[a]	
		1.9789	154.79
		1.0084	160.25
		0.55310	164.19
		.23774	167.63
		.13683	169.40

[a] Measurements by Mr. Edward Baker of this Laboratory.

III. Discussion

The results of Table I have been analyzed by the method of Fuoss and values of Λ_0 and K have been derived. In Table II, values of Λ_0 are recorded in column 2, ion conductances in columns 3 and 4 and dissociation constants in the last column.

1. Dissociation Constants.—The dissociation constants of the salts measured are in accord with those found earlier by Reynolds[2] for similar salts. The large value of the constants for the substituted ammonium picrates is rather striking. Thus, the constant for tetramethylammonium picrate is 11.2 × 10^{-3}; that of the tetrabutyl salt is 22.3 × 10^{-3}. For tetrabutylammonium chloride, the constant is 2.28 × 10^{-3} and for tetraamylammonium bromide it is 4.25 × 10^{-3}. For ammonium picrate, however, the constant is only 1.11 × 10^{-3}, one-tenth that of the corresponding methyl derivative. In this connection, it is of interest to note that in nitrobenzene[5] the constants of ammonium and of tetramethylammonium picrate are, respectively, 1.46 × 10^{-4} and 400 × 10^{-4}, while, in pyridine,[6] the constants are 2.8 × 10^{-4} and 6.7 × 10^{-4}. The variation in the ratio of the dissociation constants of these two salts in different solvents is due, in the main, to the weaker interaction of the ammonium ion with the solvent molecule in the less basic solvents. In pyridine the ammonium ion interacts markedly with the pyridine molecules, perhaps largely by way of hydrogen bonding; in nitrobenzene bonding with solvent molecules does not occur and the interaction of the ammonium ion with the picrate ion is accentuated as a result of hydrogen bonding as well as of Coulombic interaction. On substituting methyl groups for the hydrogen atoms, bonding does not occur and the interaction with the picrate ion is chiefly Coulombic.[7]

TABLE II

CONSTANTS OF SALTS IN ACETONE AT 25°

Salt	Λ_0	Λ_0^+	Λ_0^-	$K \times 10^3$
NH_4Pi	180.2	94.9	85.3[a]	1.11
Me_4NPi	183.1	97.8	....	11.2
Pr_4NI	190.6	78.3	112.3[a]	4.98
Am_4NBr	174.4	58.5	115.9[a]	4.25
$Octd\cdot Bu_3NI$	163.6	51.3	....	5.99
$Octd_2\cdot Bu_2NI$	157.2	44.9	....	6.77
Bu_4NCl	172.3	67.1[a]	105.2	2.28

[a] Reynolds, ref. 2.

The interaction of a given ion with solvent molecules, on the one hand, and with counter ions, on the other, is determinative of the dissociation constant of the ion pairs. It is, indeed, a striking fact that the dissociation constant of ammonium picrate in nitrobenzene, of dielectric constant 34.5, is only one-half that in pyridine, of dielectric constant 12.3.

2. Conductance and Ion Size.—The conductance of an ion in a given solvent is a function of the viscosity of the solvent medium and of the size and structure of the ion. If the viscosities of two media differ widely, the conductance in the less viscous medium will be the greater. However, if the viscosities do not differ too greatly, the conductance in the more viscous medium may be greater than in the less viscous medium.

So, also, for two ions in different media, the ratio of their conductances in one medium will, in general, differ from that in another. While we know the dimensions of the atoms, or groups of atoms, from which the ions are derived, we have no means of determining the dimensions of the free ions in

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(5) C. R. Witschonke and C. A. Kraus, THIS JOURNAL, **69**, 2472 (1947).

(6) D. S. Burgess and C. A. Kraus, *ibid.*, **70**, 706 (1948).

(7) For other examples of hydrogen bonding in nitrobenzene, see ref. 5, p. 2476, Table V.

solution. It is with the symmetrical quaternary ammonium ions that we might expect to approximate dimensions with some assurance on the basis of the dimensions of their constituent atoms.

In comparing the conductance of the symmetrical quaternary ammonium ions on the basis of the number of carbon atoms in their substituent alkyl groups, it is preferable to compare equivalent resistances rather than equivalent conductances, as Thompson has suggested.[8] In making comparisons between different solvents, it is advantageous to employ the reciprocal of the conductance viscosity product, $1/\Lambda_0^i\eta$.

In Fig. 1 are plotted values of $1/\Lambda_0^i\eta$ for the quaternary ammonium ions of Table II as a function of the number of carbon atoms in the positive ions. For purposes of comparison, similar plots are shown for the same ions in water and pyridine. The resistance curve for water is simpler than are those for the non-aqueous solvents. Thus, in water, the change of $1/\Lambda_0^i\eta$ in going from the ammonium to the tetraamylammonium ion in steps of four carbon atoms is marked and the curve is only slightly flexed. In pyridine, the resistance change, in going from the ammonium to the tetramethylammonium ion, is small. In acetone, the ammonium ion has a higher resistance (lower conductance) than the tetramethylammonium ion.

In pyridine and acetone, the reciprocal $\Lambda_0^i\eta$ product does not differ greatly for the tetrapropyl-, tetrabutyl- and tetraamylammonium ions. For the octadecyltributylammonium ion, the resistance becomes greater in pyridine than in acetone and for the dioctadecyldibutylammonium ion, the resistance in pyridine is much greater than in acetone. The conductance of these ions cannot be determined in water. It is a remarkable fact that for small ions, resistances are smaller in water than in non-aqueous solvents while, for larger ions, they are greater.

3. **Conductance Viscosity Product.**—It is of interest to compare values of the conductance viscosity product of ions in water with those of the same ions in other solvents.

The ratios of the $\Lambda_0^i\eta$ products of ions in different solvents to those of the same ions in water are presented in Table III for a number of different ions. If Walden's rule held, all ratios would have the value unity.

TABLE III

COMPARISON OF $\Lambda_0^i\eta$ PRODUCTS IN DIFFERENT SOLVENTS WITH THOSE IN WATER

Ion/solvt.	$\Lambda_0^i\eta$ solvt./$\Lambda_0^i\eta$ H_2O $C_6H_5NO_2$	C_5H_5N	$C_2H_4Cl_2$	$(CH_3)_2CO$
Cl^-	0.59	0.67	0.45	0.47
I^-	.54	.62	.34	.50
ClO_4^-	.62	.69	.52	.58
Pi^-	1.08	1.10	.90	.96
Me_4N^+	0.77	0.95	.83	.74
Bu_4N^+	1.38	1.39	1.42	1.33
$\eta H_2O/\eta$ solvt.	0.49	1.01	1.14	2.94

For the three simpler negative ions, the ratio of the conductance viscosity products is uniformly much less than unity; in other words, these ions are relatively much better conductors in water than in other solvents. It may be pointed out, in this connection, that the viscosity of pyridine is only one per cent. less than that of water. The ratios for the iodide ion are uniformly lower than those for the perchlorate ion; the $\Lambda_0^i\eta$ product for the iodide ion in ethylene chloride is only one-third that in water.

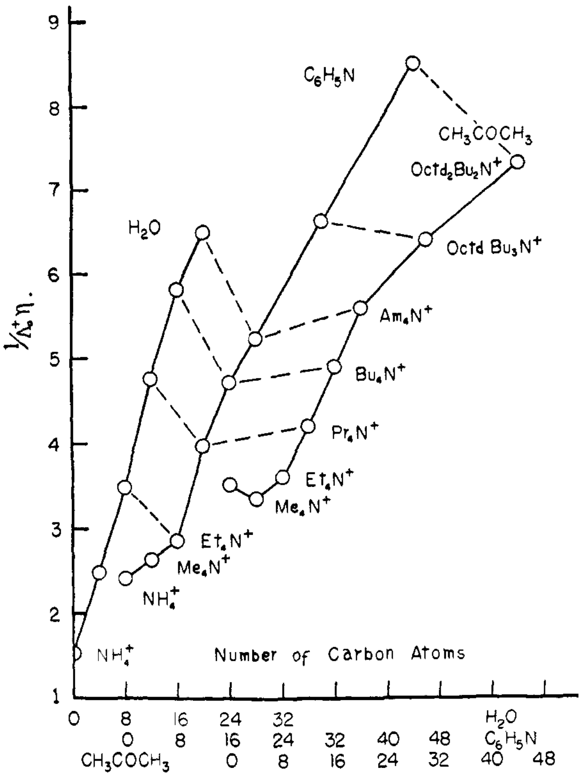

Fig. 1.—Plots of $1/\Lambda_0^i\eta$ for quaternary ammonium ions in three different solvents.

The conductance of the picrate ion is 10% greater in pyridine than in water although the two solvents have practically the same viscosity. The product is 8% greater in nitrobenzene than in water and in other solvents the product ratio does not differ greatly from unity. The product ratio for the tetramethylammonium ion is only a little less than unity in pyridine; in other solvents, the product ratios for the tetramethylammonium ion are less than unity but they are markedly greater than for the perchlorate ion which has the same symmetry and much the same size. For the tetrabutylammonium ion the product ratio in the different solvents varies between 1.33 for acetone and 1.42 for ethylene chloride. The conductance of this ion is 39% greater in pyridine than in water.

4. **Conductance Ratios in Different Solvents.**—The ratio of conductances of a given pair of ions varies markedly from solvent to solvent. In Table IV are presented ratios of conductances for a number of pairs of ions in five different solvents.

The perchlorate and the tetramethylammonium ions have the same symmetry and do not differ greatly in size. The ratio of their conductances varies from 0.96 in ethylene chloride to 1.51 in water. The conductance ratio of the picrate

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(8) W. E. Thompson, Thesis, Brown University, 1941.

TABLE IV

RATIO OF ION CONDUCTANCES IN DIFFERENT SOLVENTS

Ions/solvt.	$C_6H_5NO_2$	H_2O	C_5H_5N	$C_2H_4Cl_2$	$(CH_3)_2CO$
ClO_4^-/Me_4N^+	1.22	1.51	1.11	0.96	1.18
Pi^-/Bu_4N^+	1.38	1.59	1.40	1.19	1.27
Me_4N^+/Am_4N^+	1.61	2.62	1.99	1.99	1.67
Cl^-/I^-	1.09	0.995	1.06	1.36	0.94

and the tetrabutylammonium ions, having 16 and 17 atoms, respectively, other than hydrogen, varies from 1.19 in ethylene chloride to 1.59 in water. The conductance ratio of the tetramethylammonium and the tetraamylammonium ions varies between 1.61 in nitrobenzene and 2.62 in water. For the first three pairs of ions in the table, the ratio is greatest for water, with the exception of the first pair in ethylene chloride. In the case of the chloride and iodide ions, the ratio differs little from unity in water. In other solvents it varies from 0.94 in acetone to 1.31 in ethylene chloride. In this connection, it may be noted that in methanol the ratio is 0.85.[9]

The marked change in the ratio of ion conductances from solvent to solvent indicates quite clearly that the mobility of ions cannot be accounted for adequately on the basis of viscosity alone. With the exception of ethylene chloride, the conductance of the negative ions is greater than that of comparable positive ions. This is illustrated by the conductance ratio of the perchlorate and the tetramethylammonium ions; only in ethylene chloride is the tetramethylammonium ion a better conductor (4%) than the perchlorate ion. The picrate ion is a much better conductor than the tetrabutylammonium ion; the conductance ratio is smallest for ethylene chloride where the ratio is 1.19.

The halide ions are of particular interest. We should expect these ions to have a minimum tendency to form solvates. Yet, the order of ion conductances for these ions varies greatly in different solvents. In ethylene chloride, the conductance of the chloride ion is 31% greater than that of the iodide ion; in methanol,[7] the conductance of the iodide ion is 18% greater than that of the chloride ion.

It seems safe to conclude that to account for the mobility of ions in different solvents, we must take into account constitutional and structural factors of the solvent molecules as well as those of the ions themselves. It is not to be expected that ion conductances may be accounted for on the basis of macroscopic analysis alone.

PROVIDENCE, R. I. RECEIVED JANUARY 4, 1951

(9) Private communication from Dr. E. C. Evers, of the University of Pennsylvania.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CLARK UNIVERSITY]

Ionic Conductances in Ethylidene Chloride[1]

BY FRANK H. HEALEY[2] AND ARTHUR E. MARTELL

Electrical conductance measurements in ethylidene chloride of tetraethyl-, tetra-*n*-propyl-, tetra-*n*-butyl-, tetra-*n*-amyl-, octadecyltrimethyl- and octadecyltri-*n*-butylammonium picrates, and tetraethylammonium perchlorate, nitrate and thiocyanate are reported. The conductances at infinite dilution, dissociation constants of ion pairs and ionic conductances at infinite dilution were calculated. The conductance-viscosity products were found to be nearly the same as those of the same ions in ethylene chloride, but the dissociation constants of ion pairs differ widely for these two solvents.

Introduction

In the case of ethylene chloride and ethylidene chloride we have an example of two isomeric solvents with practically the same dielectric constant and similar chemical constitution, but with quite different boiling points, viscosities and densities. These solvents offer, therefore, an unusual opportunity to measure the effects of constitutional factors on the properties of solutions. In this paper ionic conductances and dissociation constants of ion pairs are reported and compared with corresponding values for ethylene chloride as determined by Kraus[3-7] and co-workers. A previous comparison of ionic behavior in these solvents resulted from the work of Ramsey and Colichmann,[8] who measured the electrical conductance of *o*-chlorophenyltrimethylammonium perchlorate. They reported the dissociation constant in ethylidene chloride to be only about one-tenth of the value in ethylene chloride. Also, preliminary conductance measurements by Foy[9] indicated that dissociation constants of ion pairs of other salts are considerably lower in ethylidene chloride. In this connection, therefore, ethylidene chloride solutions appeared to be worthy of further study.

Experimental

Apparatus.—The conductance bridge has been described by Foy and Martell.[10] A 0–20,000 cycle audio oscillator (General Radio No. 913-C) was used in all measurements. Temperature of the conductance cell was maintained at 25.00° by means of a constant-temperature oil-bath. Measurement and bath control were greatly aided by dehumidification and regulation of room temperature in the range 21–22°. The conductance cell was designed according to the specifications of Kraus and co-workers,[11] and

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(1) Abstracted from a Dissertation submitted by Frank H. Healey to the Faculty of Clark University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1939.

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(4) L. F. Gleysteen and C. A. Kraus, *ibid.*, **69**, 451 (1947).

(5) L. M. Tucker and C. A. Kraus, *ibid.*, **69**, 454 (1947).

(6) E. R. Kline and C. A. Kraus, *ibid.*, **69**, 814 (1947).

(7) W. E. Thompson and C. A. Kraus, *ibid.*, **69**, 1016 (1947).

(8) J. B. Ramsey and E. L. Colichmann, *ibid.*, **69**, 3041 (1947).

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