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.

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(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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(3) D. L. Fowler and C. A. Kraus, THIS JOURNAL, **62**, 2237 (1940).

(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).

(9) W. L. Foy, Dissertation, Clark University, 1947.

(10) W. L. Foy and A. E. Martell, *Rev. Sci. Instruments*, **19**, 628 (1948).

(11) N. L. Cox, C. A. Kraus and R. M. Fuoss, *Trans. Faraday Soc.*, **31**, 749 (1935).

the cell constant was determined by measurement of the conductance of tetraethylammonium picrate in ethylene chloride, taking as standard the measurements of Tucker and Kraus.[5] The value thus determined was 0.03208.

Solvent.—The best solvent was obtained by further purification of ethylidene chloride obtained directly from the Dow Chemical Company. This contained a trace of methanol as stabilizer. The solvent was refluxed six hours over activated alumina pellets and then distilled through a column designed to suppress entrainment. The intermediate fraction was siphoned directly from the receiver into the cell, and gave a conductance of 1.7×10^{-9} mho. The density of the solvent was taken as 1.1667 g./ml. as given in data received from the Dow Chemical Company. This value was checked at 1.166 g./ml. The viscosity of the solvent was determined as 0.00466 poise by comparison with purified carbon tetrachloride in an Ostwald viscosimeter. This agreed well with the figure listed in the "Critical Tables"[12] as 0.00465 poise. The latter figure was used in all calculations. The dielectric constant was measured at Brown University through the courtesy of Dr. C. A. Kraus. The value was reported to be 10.00.

Salts.—Procedures for the preparation of salts not previously reported are given below. The melting points of other salts prepared were in good agreement with values in the literature.

Tetraethylammonium perchlorate was prepared by metathesis of tetraethylammonium iodide with silver perchlorate in ethanol, and was recrystallized three times from ethanol (m.p. 345° dec.).

Tetraethylammonium thiocyanate was prepared by metathesis of tetraethylammonium nitrate with potassium thiocyanate in absolute ethanol, and purified by recrystallization from chloroform–petroleum ether mixtures. A trace of moisture was sufficient to prevent formation of crystals (m.p. 247° (dec.)).

Octadecyltrimethylammonium picrate was prepared by metathesis of octadecyltrimethylammonium iodide with silver picrate in methanol, and purified by three recrystallizations from methanol (m.p. 134° dec.).

Octadecyltributylammonium picrate was prepared by metathesis of octadecyltributylammonium iodide with silver picrate, and recrystallized three times from ethanol–water solutions (m.p. 50–50.5° dec.).

Procedure.—An amount of salt calculated to give a 0.0002 to 0.0006 molar solution was weighed on a microbalance and added to the previously weighed cell. After the addition of about 100 ml. of solvent, the cell was weighed again. After complete solution of the solute and determination of resistance, the outer surface of the cell was cleaned, the cell was weighed, and about half of the solution was removed. After again weighing the cell, sufficient solvent was added to bring the volume to about 100 ml. and the weight determined once more. Measurements at four or five concentrations were made in each determination. The equivalent conductance was then calculated assuming the density of the ethylidene chloride solution to be equal to that of the pure solvent.

Results

Two runs were also made with tetramethylammonium picrate. In both cases no resistance equilibrium could be reached. The resistance gradually increased, the solution became colorless, and orange droplets deposited on the outside (shiny) surfaces of the platinum electrodes.

Measurements were made on two samples of tetra-*n*-butylammonium triphenylborofluoride prepared independently by W. B. Martin, Jr., and R. C. Plumb of this Laboratory. In both cases resistance equilibrium was not obtained. The resistance showed a steady decrease, the effect being more noticeable in dilute solution and apparently was independent of the amount of alternating current sent through the solution. It would appear that some interaction occurs with the solvent, and that this may or may not be catalyzed by the presence of platinum black.

TABLE I

EQUIVALENT CONDUCTANCES IN ETHYLIDENE CHLORIDE

$C \times 10^4$	Λ
Tetraethylammonium picrate	
1.8534	45.00
1.4952	48.53
1.1143	53.22
0.9878	55.30
.7067	61.07
.6402	62.92
.5085	66.94
.4761	68.22
Tetra-*n*-butylammonium picrate	
8.6134	24.37
5.2397	29.01
4.6956	30.21
2.7136	36.38
2.2466	38.78
1.0833	48.71
0.9280	51.01
.7110	54.69
.5715	58.13
Tetraethylammonium nitrate	
5.7117	18.79
4.5742	20.52
3.4060	23.16
2.2965	27.32
1.5689	31.92
1.2182	35.58
0.8996	40.04
Tetraethylammonium thiocyanate	
3.8710	25.16
3.0172	27.79
2.5060	30.02
1.8660	33.64
1.6641	35.20
1.3855	38.14
1.0607	41.47
0.7806	47.08
Tetra-*n*-propylammonium picrate	
4.9913	29.78
2.1289	40.43
1.0588	50.05
0.9970	51.44
.5896	52.29
.5344	61.29
.4332	64.37
Tetra-*n*-amylammonium picrate	
4.2416	30.06
2.0653	38.26
1.9842	38.65
0.8638	49.73
.7341	51.81
.5433	55.96
.5338	56.33
Tetraethylammonium perchlorate	
2.5849	32.74
2.2401	35.13
1.4159	41.74
0.7679	51.99
.7072	53.45
.5521	58.34
Octadecyltrimethylammonium picrate	
3.9266	13.36
2.6885	15.42
1.8462	18.25
1.5290	19.46
0.8650	24.75
.8230	24.97
.5228	29.71
.4951	30.62
Octadecyltributylammonium picrate	
5.7976	24.62
4.0980	27.85
2.9187	31.15
1.4029	39.37
1.3689	39.61
0.7261	47.26

Discussion

In the range of concentrations listed in Table I, it was found that the Fuoss conductance function[13,14] gives a linear relationship. This is illustrated by Fig. 1 in the case of tetra-*n*-amylammonium picrate. Thus it was possible by means of large scale plots to accurately determine Λ_0, the equivalent conductance at infinite dilution. From the slope of the plot the value of K, the dissociation constant of ion pairs, was determined. Values of Λ_0 and K are listed in Table II.

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(12) "International Critical Tables," Vol. VII, McGraw-Hill Book Co., Inc., New York, N. Y., 1926, p. 213.

(13) R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 476 (1933).

(14) R. M. Fuoss, *ibid.*, **57**, 488 (1935).

TABLE II

DISSOCIATION CONSTANTS AND EQUIVALENT CONDUCTANCES AT INFINITE DILUTION

Salt	Λ_0	Λ_0^+	Λ_0^-	$K \times 10^5$	$\frac{K_{CH_2ClCH_2Cl}}{K_{CH_3CHCl_2}}$
Tetraethylammonium picrate	116.6	63.9	..	3.48	4.5
Tetra-*n*-propylammonium picrate	103.7	51.0	..	3.97	4.9
Tetra-*n*-butylammonium picrate	96.9	44.2	52.7	4.54	5.0
Tetra-*n*-amylammonium picrate	90.4	37.7	..	4.94	4.8
Octadecyltrimethylammonium picrate	86.4	33.7	..	0.843	5.8
Octadecyltributylammonium picrate	80.4	27.7	..	5.39	...
Tetraethylammonium nitrate	149.0	..	85.1	0.75	9.9
Tetraethylammonium thiocyanate	137.4	..	73.5	1.17	...
Tetraethylammonium perchlorate	128.9	..	65.0	1.76	...

It was found that in comparing the conductances of the tetraalkylammonium picrates in ethylidene chloride with the values given by Tucker and Kraus in ethylene chloride, Walden's[15] rule was followed most nearly in the case of the tetrabutyl derivative. This allowed the conductance of the tetra-*n*-butylammonium ion in ethylidene chloride to be calculated from the conductance of this ion in ethylene chloride as given by Fowler and Kraus.[3]

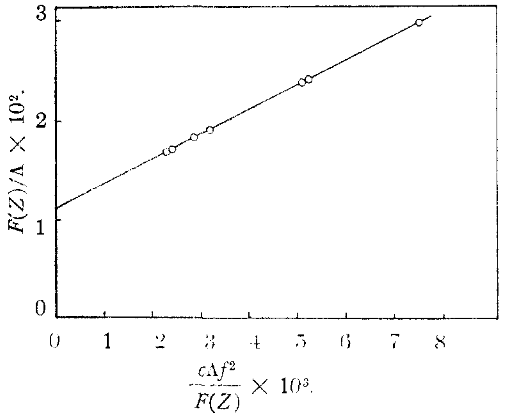

Fig. 1.—Tetra-*n*-amylammonium picrate in ethylidene chloride at 25°.

The adherence of the tetrabutylammonium ion to Walden's rule is strikingly illustrated by comparison of conductance–viscosity products in the solvents ethylene chloride,[5] nitrobenzene,[15a] pyridine[16] and acetone.[17] The quantities have a maximum deviation of ±3.8% from the average value of 1.38. Therefore, it may reasonably be supposed that the assumption of the application of Walden's rule to ethylene and ethylidene chlorides results in the calculation of an ionic conductance of the tetrabutylammonium ion which is correct within about ±3.8%. Pickering and Kraus[15a] have suggested this ion as the best for the purpose of estimating ion conductances. This is further borne out in the comparison by McDowell and Kraus[17] of $\Lambda_0\eta$ products of a number of salts in these solvents. The picrate ion, for example, is not nearly as constant, its $\Lambda_0\eta$ values having a deviation from the mean of ± 11%.

It is noteworthy that the ratio of picrate to tetrabutylammonium ion conductances (1.19) in ethylidene chloride is the same as that in ethylene chloride. This is perhaps significant in view of the fact that the ratios of ion conductances reported by McDowell and Kraus[17] showed wide variations in various solvents.

Comparison between the conductances of these ions in ethylene and ethylidene chlorides is made by plotting the reciprocal of the conductance–viscosity product against the number of carbon atoms in the quaternary ammonium ions (Fig. 2). The graph shows that in both solvents there is a fairly linear increase of equivalent resistance with number of carbon atoms in the region from eight to twenty carbon atoms. No value for the tetramethylammonium ion was obtained in ethylidene chloride. It is not surprising that the ion resistance of the octadecyltrimethylammonium ion does not fall on the same straight line with symmetrical ions and the octadecyltributylammonium ion in ethylidene chloride. It is also remarkable that the butyl derivative lies practically on the straight line which passes through the symmetrical ions.

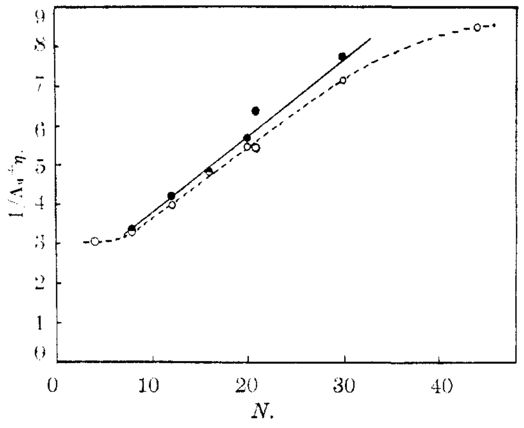

Fig. 2.—Equivalent resistance *vs.* ion size (number of carbon atoms): ●, ethylidene chloride; ○, ethylene chloride.

The conductance–viscosity products of the ions investigated are compared for ethylene and ethylidene solutions in Table III. It is seen that the agreement is within 5% for all positive and negative ions listed with the exception of the nitrate and octadecyltrialkylammonium ions. The anion conductances used in the calculation of $\Lambda_0^{\pm}\eta$ for ethylene chloride were given by Thompson and Kraus.[7] In view of the general agreement with Walden's rule it may be presumed that the ions,

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[15] P. Walden, *Z. physik. Chem.*, **55**, 246 (1906).

[15a] H. L. Pickering and C. A. Kraus, THIS JOURNAL, **71**, 3288 (1949).

[16] W. F. Luder and C. A. Kraus, *ibid.*, **69**, 2481 (1947).

[17] M. J. McDowell and C. A. Kraus, *ibid.*, **73**, 0000 (1951).

TABLE III

$\Lambda_0^{\pm}\eta_0$ PRODUCTS IN ETHYLIDENE CHLORIDE AND ETHYLENE CHLORIDE AT 25°

Ion	Ethylidene chloride	Ethylene chloride
Tetraethylammonium	0.297	0.300
Tetra-*n*-propylammonium	.237	.247
Tetra-*n*-butylammonium	.206[a]	.206[a]
Tetra-*n*-amylammonium	.175	.183
Picrate	.245	.245
Perchlorate	.302	.314[b]
Thiocyanate	.342	.333
Nitrate	.396	.315
Octadecyltrimethylammonium	.157	.186
Octadecyltributylammonium	.129	.140

[a] The seemingly perfect agreement here is due to the assumption that Walden's rule holds for tetrabutylammonium ion in these solvents. [b] Calculated using 40.0 mhos as the equivalent conductance of the perchlorate ion (privately communicated by Dr. Charles A. Kraus of Brown University).

with the exceptions noted, have the same effective volume in both solvents. The conductance-viscosity product of the nitrate ion in ethylidene chloride is approximately 25% higher than the product in ethylene chloride, indicating much less ion–solvent interaction in the former solvent. In Fig. 3 the conductance of the nitrate ion in various solvents is plotted in terms of the percentage of the perchlorate ion conductance, the data on ethylidene chloride extending a similar comparison made by Kraus.[18] It may be seen that the relative conductance of the nitrate ion varies considerably, and is higher in ethylidene chloride than in any of the alkylammonium picrates are in general agreement with the theoretical predictions of Bjerrum,[19] of Fuoss and Kraus[20a] and of Fuoss.[20b] As the size of the symmetrical cations increases, the dissociation constant increases. As would be expected, octadecyltributylammonium picrate has the highest dissociation constant of all the salts measured. On the other hand, the octadecyltrimethylammonium picrate has a relatively very low dissociation constant, indicating possible orientation effects in the formation of ion pairs. Similar behavior has been reported for the dissociation of methyltributylammonium picrate in ethylene chloride.[4] The dissociation constants of the four tetraethylammonium salts measured increases in the order nitrate < thiocyanate < perchlorate < picrate. The same relative order for these anions has been observed in ethylene chloride. The relatively low dissociation constant of the nitrate is in conformity with the high relative conductivity of this ion.

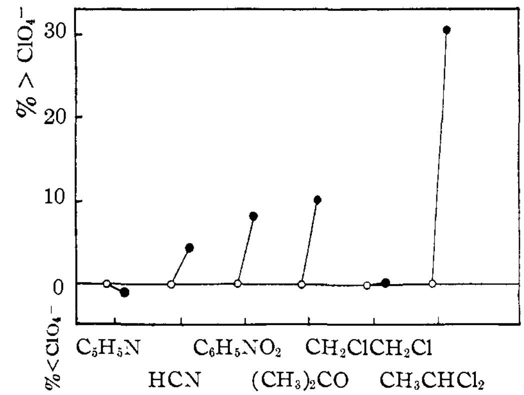

Fig. 3.—Relative NO_3^-–ClO_4^- conductances: ●, NO_3^-; O, ClO_4^-.

It is seen that the dissociation constants in ethylene chloride are about five times as great as in ethylidene chloride, except in the case of the nitrate ion, for which the constants differ by a factor of about ten. This is not readily explained. Certainly it cannot be justified on the basis of a 2% difference in the dielectric constants. Pyridine, with a dielectric constant 18% higher than that of ethylene chloride, shows only a sevenfold increase in the dissociation constant of tetrabutylammonium picrate.[21] Apparently there are constitutive differences in ethylene and ethylidene chlorides which influence the dissociation of ion pairs differently. In this connection it should be noted that (1) the polarizability of ethylene chloride is greater than that of ethylidene chloride and (2) the freely rotating dipoles of ethylene chloride may be partially stabilized in the *cis* form in the vicinity of an ion whereas this would not be possible in the case of ethylidene chloride. Further suggestions for explaining the differences of dissociating power of these two solvents have been made by Denison and Ramsey[22] on the basis of an "effective" dielectric constant which is considerably higher than the measured value for ethylene chloride.

Acknowledgments.—The authors are greatly indebted to Dr. C. A. Kraus of Brown University for suggesting this research topic, for invaluable advice, for measurement of the dielectric constant of the solvent, and for supplying samples of octadecyltrimethylammonium and octadecyltributylammonium iodides; to the Cyrus M. Warren Fund of the American Academy of Arts and Sciences for two grants, in 1947 and 1948, which were used in the purchase of equipment; and to the Dow Chemical Company for supplying the ethylidene chloride.

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

(19) N. Bjerrum, *Kgl. Danske Videnskab. Selskab. Mat.-Phys. Medd.*, **7**, No. 9 (1926).

(20) (a) R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 1019 (1933); (b) R. M. Fuoss, *Trans. Faraday Soc.*, **30**, 967 (1934).

(21) W. F. Luder and C. A. Kraus, THIS JOURNAL, **69**, 2483 (1947).

(22) J. T. Denison and J. B. Ramsey, *J. Chem. Phys.*, **18**, 770 (1950).