the negative ions; the picrate and perchlorate yield consistent results for the methyltri-*n*-butylammonium ion.

Replacement of one of the butyl groups in the tetra-*n*-butylammonium ion by a propyl and a methyl group, respectively, results in a small conductance increase in each case, as was to have been expected.

The dissociation constant of tetra-*n*-butylammonium picrate has been found to be 2.28×10^{-4}.[8] Comparing this value with the values for the dissociation constants of propyltributylammonium and methyltributylammonium picrates, it is seen that the dissociation constants decrease as the effective ion dimensions decrease.

The substitution of arsenic for phosphorus in the ethyltriphenylonium ions causes but little change in the ion conductance. The steric effect of the phenyl groups appears to be the predominant factor in determining the conductance of these ions.

The substituent groups, rather than the central atom, appear to determine the extent of ion interaction; the dissociation constants for corresponding phosphonium and arsonium salts differ but little. It is somewhat surprising that the dissociation constants of the phosphonium salts are all slightly greater than those of the corresponding arsonium salts. As will be shown in a later paper, the same inversion is found in the case of the aliphatic substituted onium ions of the same elements.

The influence of the anion on the dissociation constant varies considerably, depending upon the structure of the cation. Thus, in the case of the ethyltriphenyl-phosphonium and arsonium picrates and perchlorates, the dissociation constants have almost the same value. In the case of the methyltributylammonium ion, however, the picrate is much stronger than the perchlorate. The same holds true for the tetra-*n*-butylammonium ion where the picrate is much stronger than the perchlorate. The small nitrate ion gives rise to greater ionic interactions than does either the picrate or perchlorate ion as was to have been expected.

V. Summary

1. The conductance of ethylene chloride solutions of the following salts has been measured at 25°: tetra-*n*-butylammonium perchlorate, *n*-propyltri-*n*-butylammonium picrate, methyltri-*n*-butylammonium picrate and perchlorate, ethyltriphenylphosphonium picrate, perchlorate and nitrate, ethyltriphenylarsonium picrate, perchlorate and nitrate.
2. At low concentrations, these salts conform to the laws governing the pairwise interaction of ions.
3. Limiting equivalent conductances and dissociation constants have been calculated for the above salts.
4. The approximate ion conductances have been calculated according to the method of Fowler.
5. The influence of the structure of the ions upon the dissociation constant is discussed.

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[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XXIV. Conductance of Some Substituted Ammonium Salts in Ethylene Chloride(1)

BY LAWRENCE M. TUCKER(2) AND CHARLES A. KRAUS

I. Introduction

Continuing the investigation of the influence of the chemical nature and structure of ions on their mutual interactions, a homologous series of quaternary ammonium picrates and nitrates has been investigated in ethylene chloride solution. The effect of a gradual increase of cationic size has thus been determined. In addition, measurements have been made with pyridonium picrate and perchlorate and phenylpyridonium picrate with a view to ascertaining a possible effect of hydrogen bonding on the dissociation constant of a salt.

II. Experimental

Apparatus and Procedure.—The apparatus and experimental procedure have been fully described in earlier papers of this series. The ethylene chloride was purified as before and its specific conductance was of the order of 10^{-11}; corrections for solvent conductance were negligible even in the most dilute solutions. Desorption effects become appreciable in the neighborhood of 1×10^{-5} N(3) and measurements were not extended below this concentration. All measurements were made at 25 ± 0.01°.

Salts.—Tetraethylammonium picrate (m. p. 255.5–255.8°), tetra-*n*-propylammonium picrate (m. p. 117–117.5°), tetra-*n*-amylammonium picrate (m. p. 73–74°) and tetra-*i*-amylammonium picrate (m. p. 87–87.5°) were prepared by metathesis of silver picrate with the corresponding quaternary ammonium iodides in alcoholic solution. The products were first recrystallized from 95% ethanol, until a maximum melting point was reached. Further purification of each salt was carried out by two successive precipitations from hot alcohol by addition of water and of ethyl acetate, respectively.

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(1) This paper is based on a portion of a thesis presented by L. M. Tucker in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University, May, 1938.

(2) University Fellow at Brown University, 1936–1937; Metcalf Fellow, 1937–1938.

(3) Cox, Kraus and Fuoss, *Trans. Faraday Soc.*, **31**, 749 (1935).

Tetraethylammonium nitrate (dec. 280°), tetra-*n*-propylammonium nitrate (dec. 260°), tetra-*n*-butylammonium nitrate (m. p., 120.5–121.0°), tetra-*n*-amylammonium nitrate (m. p., 115–115.5°) and tetra-*i*-amylammonium nitrate (m. p., 138–138.5°) were prepared by metathesis of the corresponding iodides with silver nitrate in alcoholic solution. The products were repeatedly recrystallized from chloroform–petroleum ether mixtures and also from ethanol–ethyl acetate mixtures.

Pyridonium picrate was prepared by reaction of equivalent amounts of picric acid and pyridine. The salt was recrystallized from ethanol (m. p. 165.5 and 166.0°). Pyridonium perchlorate was similarly obtained from perchloric acid and pyridine and was recrystallized from water (m. p. 293–293.5°).

Pure phenylpyridonium picrate had been prepared earlier by metathesis of the chloride with silver picrate. The chloride was prepared according to the method of Zincke.[4] The picrate was recrystallized from ethanol (m. p. 121.5–122.0°).

The salts were recrystallized between successive runs until the conductance values agreed within 0.1%.

TABLE I

CONDUCTANCE OF VARIOUS ELECTROLYTES IN ETHYLENE CHLORIDE AT 25°

$C \times 10^5$	Λ	$C \times 10^5$	Λ
Tetraethylammonium picrate		Tetraethylammonium nitrate	
21.81	41.99	35.83	32.55
8.696	50.71	13.14	43.66
2.841	59.28	5.002	54.86
1.179	63.95	2.173	63.34
0.5134	66.36	0.7199	71.67
Tetra-*n*-propylammonium picrate		Tetra-*n*-propylammonium nitrate	
22.39	39.47	32.28	33.32
10.62	45.74	13.19	42.54
5.068	51.16	5.465	51.60
2.418	55.34	2.320	59.12
1.133	58.36	0.8686	65.28
Tetra-*n*-butylammonium nitrate		Tetra-*n*-amylammonium picrate	
22.57	35.30	24.59	34.99
12.74	42.03	8.623	42.27
6.352	48.49	2.328	48.83
2.922	54.68	1.162	50.98
1.096	60.27		
Tetra-*n*-amylammonium nitrate		Tetra-*i*-amylammonium picrate	
47.39	29.19	50.43	30.00
17.28	38.14	19.27	37.18
5.481	48.17	7.811	43.33
2.121	54.64	3.124	44.15
0.8441	58.78	1.401	51.01
Tetra-*i*-amylammonium nitrate		Phenylpyridonium picrate	
23.99	34.55	57.79	47.47
11.70	41.16	32.77	52.63
5.987	47.06	14.73	58.56
2.811	52.76	6.941	62.56
1.321	57.01		

III. Results

The data for one series for each salt are given in Table I. In all cases, except that of phenylpyridonium picrate, at least two independent series of measurements were made. Concentrations are given in moles per liter of pure solvent, assuming 1.2455 as the density of ethylene chloride at 25°. In the computation of constants, the viscosity was taken to be 0.00785 and the dielectric constant 10.23.

Pyridonium picrate and perchlorate are very difficultly soluble in ethylene chloride but conductance measurements with nearly saturated solutions of these salts yielded Λ values of 1.4 and 2.0, respectively; the concentrations were 1.3×10^{-4} and 7.4×10^{-4} mole per liter, respectively.

IV. Discussion

Application of the Fuoss conductance function[5] to the data leads to verification of the linear relationship for solutions less concentrated than $3.4 \times 10^{-4}N$—the critical concentration.

From large scale plots were determined the intercept on the $1/\Lambda$ axis and the slope of the line. With these values, the limiting equivalent conductance, Λ_0, and the dissociation constant, K, for each salt were computed. The results are presented in Table II. The plots are not reproduced in this paper since all are linear and conform to the experimental values within the limit of experimental error; examples of such plots will be found in earlier papers.[3,6,7]

Values of K for pyridonium picrate and pyridonium perchlorate are included in the table. They were obtained by assuming approximate Λ_0 values of 70 and 75, respectively, for the two salts and computing K by means of the Ostwald dilution law.

TABLE II

CONSTANTS OF ELECTROLYTES IN ETHYLENE CHLORIDE

Salt	Λ_0	Λ_0^+	$K \times 10^4$
$(CH_3)_4NPi$[6]	73.81	42.6	0.32
$(C_2H_5)_4NPi$	69.44	38.2	1.59
$(n\text{-}C_3H_7)_4NPi$	62.66	31.5	1.94
$(n\text{-}C_4H_9)_4NPi$[6]	57.40	26.2	2.26
$(n\text{-}C_5H_{11})_4NPi$	54.50	23.3	2.38
$(i\text{-}C_5H_{11})_4NPi$	55.00	23.8	2.39
$(C_6H_5)(C_5H_5N)Pi$	67.94	36.7	0.86
$(C_2H_5)_4NNO_3$	78.43		.74
$(n\text{-}C_3H_7)_4NNO_3$	71.48		.95
$(n\text{-}C_4H_9)_4NNO_3$	66.31		1.18
$(n\text{-}C_5H_{11})_4NNO_3$	63.33		1.29
$(i\text{-}C_5H_{11})_4NNO_3$	63.57		1.20
C_5H_5NHPi			0.0004
$C_5H_5NHClO_4$			.005

In the preceding communication of this series, Gleysteen and Kraus[7] arrived at a value of 31.2 for the limiting conductance of the picrate ion.

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[4] Zincke, *Ann. Chem.*, **333**, 328 (1904).

[5] Fuoss, THIS JOURNAL, **57**, 488 (1935).

[6] Mead, Fuoss and Kraus, *Trans. Faraday Soc.*, **32**, 594 (1936).

[7] Gleysteen and Kraus, THIS JOURNAL, **69**, 451 (1947).

From the present Λ_0 values for the tetra-alkylammonium picrates, we have arrived at values for the limiting cation conductances for a series of salts. These values are given in column 3 of Table II. Using these values of cation conductance in conjunction with Λ_0 values for the tetra-alkylammonium nitrates (from tetraethyl to tetra-*i*-amylammonium, inclusive), we obtain five values for the conductance of the nitrate ion: 40.2, 40.0, 40.1, 40.0 and 39.8. The discrepancy in the last value is probably due to the presence of traces of impurities left in one or both of the tetra-*i*-amylammonium salts after final recrystallization. The other four values are in agreement within the experimental error and a value of 40.1 may safely be adopted for the limiting conductance of the nitrate ion.

The conductance of the homologous series of tetra-alkyl-ammonium ions is of considerable interest. While the conductance of the ions falls off with increasing number of carbon atoms in the substituent groups, the decrease in going from the methyl to the ethyl derivative is exceptionally low. The decrease, on introducing an additional CH_2 group in going successively from methyl to *n*-amyl substituted ions, is as follows: 4.4, 6.7, 5.3, 2.9. The decrease is greatest from ethyl to propyl, but even in going from propyl to butyl, the decrease, 5.3, is greater than in going from methyl to ethyl, 4.4. In other words, the conductance of the tetramethylammonium ion is much too low on the basis of its dimensions.

That tetramethylammonium is a very small ion is indicated by the exceptionally low value of the dissociation constant (0.32×10^{-4}) of tetramethylammonium picrate, as against that of 1.59×10^{-4} for tetraethylammonium picrate. Clearly, of the two ions, tetramethylammonium is much the smaller. It would seem, therefore, that in its motion among the solvent molecules, the tetramethylammonium ion experiences interactions which are largely absent in the case of the larger tetra-alkylammonium ions. It may be suspected that, with the tetramethylammonium ion, interaction occurs to a significant extent between the charge on the ion and the dipoles of adjacent solvent molecules. The phenomenon is worthy of further study.

The dissociation constants of the salts show a gradual increase as their ionic conductance decreases. On account of its smaller size, the nitrate ion gives rise to much stronger ionic interaction than does the picrate ion and the dissociation constants of the nitrates are approximately one-half those of the corresponding picrates.

That the nature and structure of both cation and anion are involved in determining the magnitude of the dissociation constant, becomes apparent when we consider the K values of the normal and *i*-tetra-amylammonium salts. In the case of the picrates, we find a very slight increase in the dissociation constant in going from the normal to the *i*- salt; in the case of the nitrates, a well defined decrease occurs in going from the normal to the *i*- derivative.

The exceptionally low dissociation constants of the pyridonium salts may indicate that hydrogen bonding is involved. It seems highly probable, however, that an acid–base dissociation also occurs, similar to that found by Elliott and Fuoss[8] for anilinium salts in tricresyl phosphate. Such phenomena will be discussed at length in a future paper in connection with solutions in nitrobenzene. It is of interest to note that pyridonium perchlorate is a much stronger electrolyte than the picrate.

The influence of structure on the ion-pair equilibrium is clearly shown on comparing the constant found for phenylpyridonium picrate with those obtained for tetra-alkylammonium picrates possessing approximately the same number of carbon atoms in the cation. The dissociation constant of tetraethylammonium picrate, with eight carbon atoms, is 1.59×10^{-4}, that of tetrapropylammonium picrate, with twelve carbon atoms, is 1.94×10^{-4}, while, in contrast to these, the constant of phenylpyridonium picrate, with eleven carbon atoms, is only 0.85×10^{-4}; clearly steric factors have a marked influence upon the dissociation constant. The arrangement of the carbon atoms around the nitrogen atom in the pyridonium ion permits of closer approach of the anion than does the more densely packed and more symmetrical structure of the tetra-alkylammonium ions.

In general, the results obtained with salts having ions of varying dimensions and structure are in accord with concepts underlying the theory of short-range ion-interaction.

V. Summary

1. The conductance of homologous series of tetra-alkylammonium picrates and nitrates in ethylene chloride has been investigated, and the limiting conductance of the nitrates at 25° in ethylene chloride has been determined.
2. Values of Λ_0 and K have been computed from the experimental results.
3. The Λ_0 values are found to decrease and the K values to increase with increasing size of the constituent ions of the electrolytes investigated.
4. The dissociation constants of pyridonium picrate and perchlorate have been approximated. Both are very weak electrolytes, with the perchlorate the stronger of the two.

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[8] Elliott and Fuoss, THIS JOURNAL, **61**, 294 (1939).