V. Summary

1. The conductance of solutions of a number of quaternary ammonium salts having different anions has been measured in nitrobenzene at 25° and values of Λ_0 and K determined.

2. The conductance of solutions of an ammonium salt, as well as of some partially substituted ammonium salts, has been measured and values of Λ_0 and K determined; all are weak electrolytes.

3. The conductance of solutions of lithium, sodium and potassium picrates has been measured and Λ_0 and K values computed. All three salts are weak, with the lithium salt much the weakest ($K = 6 \times 10^{-8}$).

4. The constants for phenyldimethylhydroxyammonium picrate and trimethylhydroxyammonium picrate have been derived from conductance measurements. Both salts are very weak electrolytes.

5. Ion conductances have been evaluated for all but the weakest electrolytes by the method of Fowler.

6. The acid–base dissociation of phenylammonium, phenyldimethylammonium and pyridonium picrates has been studied by the conductance method, the pyridonium salt in detail. Constants of the ionic and the acid–base equilibria have been evaluated for the three salts.

7. The effect of bases on the dissociation constant of partially substituted ammonium salts and of quaternary salts containing a hydroxyl group attached to the nitrogen of the cation has been investigated. The effect is often large, depending on the constitution of the cation and the strength of the added base.

8. The conductance of triphenylmethyl chloride, bromide, fluoride and borofluoride has been measured. The halogen derivatives are very weak electrolytes; the borofluoride is a fairly strong electrolyte.

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[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XXX. Conductance of Some Inorganic and Organic Electrolytes in Pyridine at 25°[1]

BY WILLIAM F. LUDER[2] AND CHARLES A. KRAUS

I. Introduction

In view of the fact that pyridine exhibits a strong basic function, accurate conductance measurements with solutions of electrolytes in this solvent should yield valuable and new information as to the interaction of solvent molecules with ions, particularly with certain inorganic cations. The dielectric constant of pyridine, 12.01,[3] is such that accurate Λ_0 and K values readily can be obtained for all but very weak salts. These constants often serve to throw light on the nature of the ions and their interactions in solution. It is possible, moreover, to carry out measurements with several inorganic salts which are readily soluble in pyridine although practically insoluble in ethylene chloride.

Previous conductance measurements in pyridine are uncertain because of the high conductance of the solvent—usually greater than 2×10^{-8}. In the present investigation, it has been found possible to obtain pyridine, the specific conductance of which was less than 1×10^{-9}. Solvent corrections were unnecessary even in the most dilute solutions.

The salts measured were: silver nitrate and perchlorate, tetra-*n*-butylammonium bromide, iodide and picrate and ethyltriphenylarsonium picrate. Several other salts were investigated, but difficulty was experienced in obtaining reproducible results. The underlying source of the difficulty will be elucidated in a following communication.

II. Experimental

Materials.—For initial purification of pyridine, a modification of the method of Heap, Jones and Speakman[4] was adopted. Zinc chloride forms a molecular compound containing two molecules of pyridine per molecule of zinc chloride. This compound was precipitated by the interaction of the appropriate quantities of anhydrous zinc chloride and pyridine in alcohol solution. The precipitate was filtered off, washed with alcohol and then recrystallized from alcohol containing 20% of water. The crystallized product was washed with alcohol; m. p. 207°. The pyridine was regenerated by the addition of an aqueous solution of sodium hydroxide. The mixture was filtered, solid sodium hydroxide was added to the filtrate and the water layer removed in a separatory funnel. Most of the water remaining in the pyridine was removed by several treatments with sodium hydroxide. After storing over barium oxide for several days, the pyridine was shaken with activated alumina for a further period and finally distilled from activated aluminum oxide in an all-glass apparatus which was protected against the entrance of carbon dioxide and moisture.

Tetra-*n*-butylammonium picrate and ethyltriphenylarsonium picrate had been previously prepared and employed by other workers in this laboratory.

Tetra-*n*-butylammonium iodide (m. p. 145°) and tetra-

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(1) This paper is based on a portion of a thesis presented by William F. Luder in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University, May, 1937.

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(3) Le Fèvre, *J. Chem. Soc.*, Part I, 776 (1935).

(4) Heap, Jones and Speakman, THIS JOURNAL, **43**, 1936 (1921).

n-butylammonium bromide (m. p. 115°) were prepared in the usual manner.

Reagent grade silver nitrate was recrystallized twice from water while silver perchlorate was prepared by the method described in an earlier paper.[5]

Apparatus and Procedure.—These have, for the most part, been described adequately in earlier papers. Due to the presence of pronounced polarization effects when bright platinum electrodes were used to measure resistances less than 10,000 ohms, it was found desirable to use lightly platinized electrodes in the more concentrated region. While measurements were carried out with both cells, data will be presented only for those with the unplatinized cell since we are concerned only with dilute solutions where polarization effects are inappreciable. All experiments were carried out at 25 ± 0.01°.

III. Results

The experimental data are presented in Table I where concentrations are expressed in moles per liter of pure solvent, the density of which was taken to be 0.97792.[6]

IV. Discussion

The data of Table I have been treated by the method of Fuoss[7] to obtain the limiting conductances and dissociation constants presented in Table II. The plots of F/Λ against $C\Lambda f^2/F$ are shown in Fig. 1. The viscosity and dielectric constant of pyridine have been taken as 0.008824[6] and 12.01,[3] respectively.

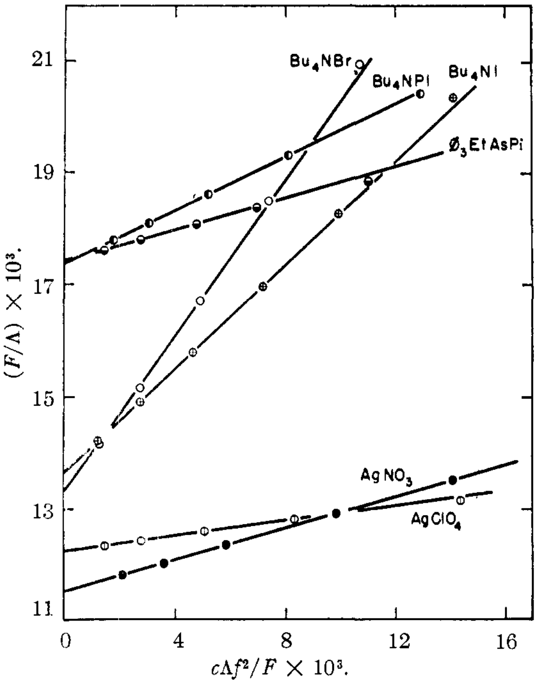

Fig. 1.—Fuoss plots for salts in pyridine at 25°.

As may be seen from Fig. 1, the Fuoss plots are all linear in the dilute region. The intercept and slope of the plots yield values of Λ_0 and K for the different salts. At higher concentrations, the experimental points begin to deviate above and below the straight line, depending upon the salt. For strong salts, the deviations are toward higher and for weak salts, toward lower conductance values. Silver nitrate gives a straight line up to the critical concentration,[8] 5×10^{-4}.

TABLE I

CONDUCTANCE OF SOME ELECTROLYTES IN PYRIDINE AT 25°

$C \times 10^4$	Λ	$C \times 10^4$	Λ
Tetra-*n*-butylammonium picrate		Tetra-*n*-butylammonium bromide	
6.694	41.35	15.61	29.84
2.969	46.26	7.360	37.23
1.540	49.53	4.247	43.11
0.7616	52.52	2.242	50.06
.3985	54.00	1.199	56.45
		0.5392	63.28
		.2169	68.67
Tetra-*n*-butylammonium iodide		Ethyltriphenylarsonium picrate	
6.466	43.04	4.669	45.86
3.362	49.61	2.261	49.25
1.998	54.54	1.336	51.23
1.071	59.74	0.6622	53.25
0.5315	64.33	0.3111	54.79
.2155	68.29		
Silver nitrate		Silver perchlorate	
7.637	59.80	4.008	67.58
3.851	66.48	1.762	72.29
2.183	71.43	0.9235	75.09
1.058	76.53	0.4406	77.41
0.5786	79.69	.2157	78.92
.3044	82.09		

TABLE II

CONSTANTS OF SOME SALTS IN PYRIDINE AT 25°

Salt	Λ_0	Λ_0^+	Λ_0^-	$K \times 10^4$
$(C_4H_9)_4NPi$	57.7	(24.0)[9]	33.7	12.8
$(C_4H_9)_4NBr$	75.3	..	51.3	2.5
$(C_4H_9)_4NI$	73.1	..	49.1	4.1
$(C_2H_5)(C_6H_5)_3AsPi$	57.7	24.0	..	19.4
$AgNO_3$	86.9	34.3	(52.6)[9]	9.3
$AgClO_4$	81.9	..	47.6	19.1

The ion conductances given in columns three and four of Table II have been calculated on the basis of conductance measurements to be presented in the next paper of this series.[9] These measurements have yielded values of 24.0 and 52.6 for the conductance of the tetrabutylammonium and the nitrate ion, respectively.

The conductance of the three inorganic anions differs but little and is in accordance with atomic dimensions. The tetrabutylammonium and the ethyltriphenylarsonium ions have the same conductance although the latter ion contains four more carbon atoms. The conductance of the picrate ion, with 16 atoms other than hydrogen, is much greater than that of the tetrabutylammo-

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[5] Luder, P. B. Kraus, C. A. Kraus and Fuoss, This Journal, **58**, 255 (1936).

[6] Walden, Audrieth and Birr, *Z. physik. Chem.*, **160A**, 337 (1932).

[7] R. M. Fuoss, This Journal, **57**, 488 (1935).

[8] Fuoss, *ibid.*, **57**, 2604 (1935).

[9] David S. Burgess, Thesis, Brown University, May, 1940.

nium ion containing 17 atoms other than hydrogen. These facts point to specific interactions which are dependent on constitutional and structural factors that cannot be elucidated without more extensive data than are presently available.

The dissociation constants of the quaternary onium salts are such as might be expected with a solvent of a dielectric constant of 12. With decreasing size of the negative ion, the dissociation constant diminishes. The high value of the dissociation constant for the two silver salts is puzzling. The silver ion is not an exceptionally slow ion when compared with the ethyltriphenylarsonium ion, for example. Yet the dissociation constant of silver perchlorate is practically the same as that of ethyltriphenylarsonium picrate. The conductance of the perchlorate ion is 47.3 and that of the silver ion is 34.1, while, in contrast, the conductance of the ethyltriphenylarsonium ion is 24.0 and that of the picrate ion is 33.7.

V. Summary

1. The conductance of the following salts has been measured in pyridine at 25°: silver nitrate and perchlorate, tetra-*n*-butylammonium picrate, bromide and iodide and ethyltriphenylarsonium picrate.

2. Values of Λ_0 and K for these salts have been derived by the method of Fuoss.

3. Ion conductances have been evaluated by the method of Fowler.

4. The dissociation constants of the silver salts are unexpectedly high.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

The Thermodynamics and Molecular Structure of Cyclopentane[1]

BY JOHN E. KILPATRICK,[2] KENNETH S. PITZER[3] AND RALPH SPITZER[4]

The five-membered saturated ring is an important unit in organic chemistry. It is also particularly interesting because the torsional forces about the single bonds are in opposition to the forces tending to retain tetrahedral bond angles. Thus the latter forces tend to keep all five carbon atoms co-planar while the torsional forces tend to pucker the ring.

Aston, Schumann, Fink and Doty[5] have measured the entropy of gaseous cyclopentane and shown that it indicates a puckered ring, while one of us has found that calculations based on normal values of the force constants,[6] give lower energy to a puckered than to a planar ring. Douslin and Huffman[7] have also measured the entropy of cyclopentane and confirm the value of Aston and co-workers. Two of us[8] have recently measured the heat capacity of gaseous cyclopentane. It is the purpose of the present paper to analyze all of these and other data in order to give, if possible, a complete and reliable picture of the structure of the molecule and set of tables of thermodynamic properties.

Bond Distances and Angles.—Hassel and Viervoll[9] have recently reinvestigated cyclopentane by the electron diffraction method, using a rotating sector. They find C–C to be 1.54 Å. and C–H to be 1.09 Å. While they assumed a plane pentagonal model, the small puckering we shall find would have only a minor effect at this point. Indeed a study of their curves indicates that the fit at larger distances might be even more perfect if the slight changes due to puckering were taken into account. In any event this work gives us reliable distances; also it confirms approximate tetrahedral angles.

Vibration Frequencies.—The Raman spectrum of cyclopentane has been reported by Rosenbaum and Jacobson[10] who summarize earlier work. They remark about the unusual diffuseness of the lines. This we will find to be significant. The infrared spectrum has been reported by several laboratories.[11]

Since detailed and complete normal coördinate calculations would be excessively laborious for the puckered ring model, we first made calculations for the planar model which has the symmetry D_{5h}. At this point we are indebted to Dr. C. S. Lu and Dr. C. W. Beckett[12] who were studying certain features of the vibrational spectrum of the series cyclopropane through cyclohexane. Using force constants from this study, chiefly from cyclo-

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[1] This work was supported by Research Project 44 of the American Petroleum Institute with headquarters at the National Bureau of Standards.

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[4] National Research Fellow in Chemistry, 1945–46. Now at Department of Chemistry, Oregon State College, Corvallis, Oregon.

[5] J. G. Aston, S. C. Schumann, H. L. Fink and P. M. Doty, THIS JOURNAL, **63**, 2029 (1941); Aston, Fink and Schumann, *ibid.*, **65**, 341 (1943).

[6] K. S. Pitzer, *Science*, **101**, 672 (1945).

[7] D. R. Douslin and H. M. Huffman, THIS JOURNAL, **68**, 173 (1946).

[8] R. Spitzer and K. S. Pitzer, *ibid.*, **68**, 2537 (1946).

[9] O. Hassel and H. Viervoll, *Tids. Kjemi Bergvesen*, **3**, 31 (1946).

[10] E. J. Rosenbaum and H. F. Jacobson, THIS JOURNAL, **63**, 2841 (1941).

[11] Spectrograms 343 and 446 distributed by Project 44 of the American Petroleum Institute, National Bureau of Standards. 343 is from the Radiometry section of the Bureau of Standards, which also supplied data at wave lengths greater than 15μ. 446 is from the Shell Development Company, Emeryville, Calif.

[12] These results including these force constants will be published separately.