with Strubl's conclusion that each wave in ammonium carbonate solution corresponds to an electron transfer of 2.

The diffusion current of uranyl chloride in ammonium carbonate medium is not proportional to the concentration of uranium. The diffusion current constant at −1.4 v. decreases quite markedly as the concentration of uranium is increased. For example, in 1 *M* ammonium carbonate solution the diffusion current decreased from 5.0 to 3.62 microampere millimole liter when the concentration of uranyl chloride was increased from 2.6×10^{-5} to 3.07×10^{-3} *M*. For this reason we do not recommend ammonium carbonate as supporting electrolyte for the polarographic determination of U^{VI}. We recommend for this purpose approximately 0.1 *M* hydrochloric acid in which medium the diffusion current is proportional to the uranyl concentration.[2]

Instead of ammonium carbonate as the complex forming agent sodium carbonate can be used. In 0.1 *M* sodium carbonate the polarographic reduction wave of uranium appears to be well defined (see Fig. 4). There is no indication of a second reduction similar to that found when ammonium carbonate is used. Although the reduction wave appears to be well defined in 0.1 *M* sodium carbonate the diffusion current again is not proportional to concentration of uranium.

Summary

1. From polarograms obtained in solutions of uranyl chloride containing 0.1 *M* potassium chloride, either without or with small amounts of acid or alkali it is concluded that the first wave corresponds to the reduction of UO_2^{++}. The hydrolysis product UO_2OH^+ from UO_2^{++} is not reduced at the first wave, but is reduced at the second wave together with U^V. The UO_2OH^+ is reduced to pentavalent and not to tetravalent uranium. It is assumed that under the specified conditions UO_2 and UO_2OH separate as insoluble films at the surface of the dropping mercury.

2. The hydrolysis constant of the uranyl ion at 25° is 8.1×10^{-5}.

3. Amperometric titration of uranyl chloride with sodium hydroxide yields complete precipitation long before the stoichiometric end point $UO_2(OH)_2$ is reached.

4. At the proper concentration of ammonium carbonate two well-defined waves of U^{VI} are found. Contrary to statements in the literature each reduction wave corresponds to an electron transfer of one. Carbonate is not recommended as supporting electrolyte for the polarographic determination of U^{VI} because the diffusion current is not proportional to the concentration.

MINNEAPOLIS, MINNESOTA RECEIVED JUNE 24, 1946

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XXIII. Conductance of Several Quaternary Onium Salts in Ethylene Chloride at 25°[1]

BY LELAND F. GLEYSTEEN[2] AND CHARLES A. KRAUS

I. Introduction

Earlier papers of this series have served to elucidate the interaction between ions in solution as a function of their dimensions, on the one hand, and of the dielectric constant of the solvent medium, on the other. There are, however, specific factors that remain to be examined, more particularly, the detailed structure and constitution of the ions, the constitution of the molecule of the solvent medium and the interaction of ions with molecules of a third component.

This is the first of a series of papers in which will be presented the results of investigations intended to elucidate how the factors mentioned above influence the ionic equilibria in several solvents. The solvents chosen are ethylene chloride, pyridine, nitrobenzene and benzene. The dielectric constants of the first three solvents (10.23, 12.01 and 34.5, respectively) are sufficiently high to permit direct evaluation of the limiting conductance for all but very weak electrolytes. One of these solvents, pyridine, is a basic solvent while the others have neither acidic nor basic properties.

The dielectric constants for pyridine and ethylene chloride differ but little and afford a favorable opportunity for studying the influence of solvent constitution on ionic equilibria. The higher dielectric constant of nitrobenzene and its larger molecules, with respect to ethylene chloride, permits of a study of these factors for two inactive solvents otherwise very similar. Numerous inorganic salts may be studied in pyridine and a few are sufficiently soluble in nitrobenzene to permit of their investigation.

Limiting conductances cannot be reliably evaluated in benzene; however, the behavior of concentrated solutions of electrolytes in benzene is of great interest because of the light that these solutions throw on the problem of concentrated solutions of electrolytes. The molecular weights of electrolytes in benzene have likewise been investigated up to fairly high concentrations and

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(1) This paper is based on a portion of a thesis presented by L. F. Gleysteen in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University, May, 1936.

(2) University Fellow at Brown University, 1934–1936.

the results of these studies will be reported in this series.

Ion conductances have been evaluated in ethylene chloride, pyridine and nitrobenzene. These values are of interest in that they throw light on the interaction of free ions and solvent molecules or molecules of added substances.

The present paper deals with the influence of the asymmetry of certain ammonium ions on the ionic equilibrium as also with the influence of the central atom of onium ions on such equilibria. The salts investigated were: methyltri-*n*-butylammonium picrate and perchlorate, *n*-propyltri-*n*-butylammonium picrate, tetra-*n*-butylammonium perchlorate, ethyltriphenylphosphonium picrate, perchlorate and nitrate and ethyltriphenylarsonium picrate, perchlorate and nitrate.

II. Experimental

Apparatus and Procedure.—The apparatus used and the experimental procedure were the same as those already described in earlier papers of this series. Measurements were made at 25 ± 0.01°. The specific conductance of the solvent was of the order of 10^{-11} and no correction was necessary for solvent conductance. The purification of the solvent has already been described.[3]

In making up solutions, approximately 100 mg. of salt was introduced into a small weighing bottle, pumped to constant weight *in vacuo* and thereafter introduced into the conductance cell.

Materials.—Ethyltriphenylphosphonium picrate was prepared by treating an alcoholic solution of the iodide with moist silver oxide, filtering and thereafter neutralizing the filtrate with picric acid. The resulting solution was evaporated until the greater part of the picrate had crystallized. The crystals, after separation, were recrystallized from hot alcohol; m. p., 135°.

Ethyltriphenylphosphonium perchlorate was prepared by treating an aqueous-alcoholic solution containing the calculated quantity of silver perchlorate with an alcohol solution of ethyltriphenylphosphonium iodide. The perchlorate separated out along with the silver iodide and was extracted with ethylene chloride. After evaporating to dryness, the salt was recrystallized from hot alcohol; m. p., 163.5°.

Ethyltriphenylphosphonium nitrate was obtained by metathesis of the iodide with silver nitrate in alcohol solution. The product was recrystallized from alcohol at 0° by addition of petroleum ether; m. p., 127°.

Arsonium salts were prepared according to the same procedure as that used for the preparation of the corresponding phosphonium salts. In the case of ethyltriphenylarsonium picrate, the sirupy product obtained on evaporation of the alcoholic solution was concentrated as far as possible by warming and pumping in vacuum. It was then dissolved in a minimum quantity of hot alcohol and precipitated by addition of water and cooling. After three such recrystallizations, it was recrystallized from 95% alcohol; m. p. 125.5–126.0°.

Ethyltriphenylarsonium perchlorate was recrystallized from a mixture of ethylene chloride and alcohol by addition of alcohol and petroleum ether; m. p., 143°.

Ethyltriphenylarsonium nitrate was recrystallized from ethylene chloride by addition of petroleum ether; m. p., 123°.

Tetra-*n*-butylammonium perchlorate was obtained by metathesis of the iodide with silver perchlorate in alcoholic solution. After filtration from the silver iodide, the solution was evaporated to dryness and the residue recrystallized from ethyl acetate; m. p., 209.7°.

Propyltri-*n*-butylammonium picrate was prepared from the iodide by metathesis with silver picrate in alcoholic solution. After separating from the silver iodide, the solution was evaporated and the product recrystallized from alcohol; m. p., 89°.

Methyltri-*n*-butylammonium picrate was prepared by treating the iodide with silver picrate in alcoholic solution. After separating from silver iodide, evaporation yielded a sirupy mass which was dissolved in aqueous alcohol. On cooling, the mixture separated into two phases, of which the lower one became crystalline on cooling. This procedure was repeated eight times after which it was possible to recrystallize the salt from alcohol; m. p. 28°.

Methyltri-*n*-butylammonium perchlorate was prepared from the iodide by metathesis with silver perchlorate in alcohol solution. The product was recrystallized from alcohol; m. p., 159°.

III. Results

The experimental results are presented in Table I. Two, or more, independent series of measurements were made in all cases. The agreement was of the order of 0.1%. Data are given for only one series for each salt. Concentrations are expressed in moles per liter of solvent. The solutions are so dilute that their densities, in all cases, may be taken as that of the pure solvent at 25°, namely, 1.2455[4] without incurring appreciable error.

In the computations, the dielectric constant of ethylene chloride was taken as 10.23[5] and the viscosity as 0.00785.[6]

TABLE I

CONDUCTANCE OF DIFFERENT SALTS IN ETHYLENE CHLORIDE AT 25°

Methyltri-*n*-butylammonium picrate		Methyltri-*n*-butylammonium perchlorate	
$C \times 10^4$	Λ	$C \times 10^4$	Λ
8.501	22.61	12.50	19.46
3.942	28.44	5.356	25.67
1.919	34.65	2.547	32.29
1.289	38.06	1.172	39.95
0.6715	43.58	0.4866	48.75
.3238	48.91	0.2287	55.32
.1775	52.51		
n-Propyltri-*n*-butylammonium picrate		Tetra-*n*-butylammonium perchlorate	
8.808	27.16	3.925	33.72
4.252	32.69	1.863	40.54
3.204	37.94	0.9355	46.76
1.110	43.25	.5073	51.72
0.4817	48.81	.2840	55.64
.2363	52.47	.1515	58.90
Ethyltriphenylphosphonium picrate		Ethyltriphenylphosphonium perchlorate	
10.36	30.92	12.39	33.32
5.034	36.11	5.814	39.32
2.358	41.64	3.121	44.49
1.150	46.46	1.558	50.00
0.5509	50.54	0.7555	54.99
.2813	53.35	.3652	58.90
		.1752	61.73

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(3) Mead, Fuoss and Kraus, *Trans. Faraday Soc.*, **32**, 594 (1936).

(4) G. S. Bien, Thesis, Brown University, 1934.

(5) Hooper, Thesis, Brown University, 1936.

(6) Walden and Busch, *Z. physik. Chem.*, **140**, 89 (1929).

TABLE I (*Concluded*)

$C \times 10^4$	Λ	$C \times 10^4$	Λ
Ethyltriphenylphosphonium nitrate		Ethyltriphenylarsonium picrate	
5.133	37.14	5.921	33.92
2.445	43.66	2.974	39.01
1.186	49.86	1.312	44.76
0.5151	55.93	0.5796	49.56
.2679	59.64	.2688	52.90
.1515	62.60	.1338	55.02
Ethyltriphenylarsonium perchlorate		Ethyltriphenylarsonium nitrate	
10.99	33.56	14.44	27.26
4.690	40.45	6.828	33.13
2.273	46.47	3.176	39 86
1.186	51.48	1.490	46.62
0.6189	55.77	0.6982	52.78
.3222	59.12	.3505	57.35
.1772	61.31		

IV. Discussion

The experimental data have been analyzed graphically according to the method of Fuoss.[7] Figures 1 and 2 establish the linear relationships between F/Λ and $C\Lambda f^2/F$ for dilute solutions of the above-mentioned salts. The lowest concentrations measured were, in general, in the neighborhood of 2×10^{-5} N and appreciable deviations from linearity do not ordinarily appear below a concentration of 5×10^{-4} N.

From the intercepts and slopes of the curves (using large scale plots), values of the limiting conductance, Λ_0, and of K, the dissociation constant of the ionic equilibrium, have been calculated. These values are given in Table II, columns two and four.

TABLE II

CONSTANTS OF ELECTROLYTES IN ETHYLENE CHLORIDE AT 25°

Salt	Λ_0	Λ_0^+	$K \times 10^4$
$(n\text{-}C_4H_9)_4NClO_4$	65.40	26.2[a]	1.54
$(n\text{-}C_3H_7)(n\text{-}C_4H_9)_3NPi$	59.07	27.9	2.03
$(CH_3)(n\text{-}C_4H_9)_3NPi$	60.30	29.1	1.20
$(CH_3)(n\text{-}C_4H_9)_3NClO_4$	68.30	29.1	0.80
$(C_2H_5)(C_6H_5)_3PPi$	58.63	27.4	3.77
$(C_2H_5)(C_6H_5)_3PClO_4$	66.03	26.8	3.60
$(C_2H_5)(C_6H_5)_3PNO_3$	67.00	26.9	2.18
$(C_2H_5)(C_6H_5)_3AsPi$	58.63	27.4	3.43
$(C_2H_5)(C_6H_5)_3AsClO_4$	65.69	26.5	3.45
$(C_2H_5)(C_6H_5)_3AsNO_3$	66.68	26.6	2.14

[a] Value due to Fowler and Kraus (ref. 8).

From conductance measurements of tetra-*n*-butylammonium triphenylborohydroxide and the corresponding triphenylborofluoride, Fowler and Kraus[8] have obtained a value of 26.2 units for the limiting conductance of the tetra-*n*-butylammonium ion. Using this value and the Λ_0 values of Mead, Fuoss and Kraus,[9] for tetra-*n*-butylammonium picrate, we arrive at a value of 31.2 for the limiting conductance of the picrate ion. The limiting conductance of tetra-*n*-butylammonium perchlorate, reported in the present investigation, thus leads to a value of 39.2 for the conductance of the perchlorate ion. Unpublished measurements of Tucker[10] on the nitrates of a series of tetra-alkylammonium ions show that the most probable value for the conductance of the nitrate ion is 40.1. Using the above values of the limiting conductance of the picrate, perchlorate and nitrate ions, we have calculated the conductance of the cations of the salts in the present investigation. They are given in column three of Table II.

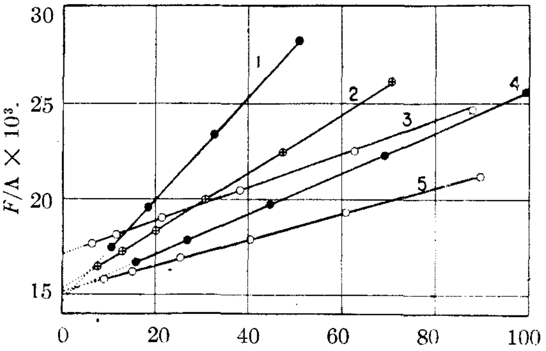

Fig. 1.—Extrapolation plots for: 1, methyltri-*n*-butylammonium perchlorate; 2, tetra-*n*-butylammonium perchlorate; 3, ethyltriphenylarsonium picrate; 4, ethyltriphenylarsonium nitrate; 5, ethyltriphenylarsonium perchlorate.

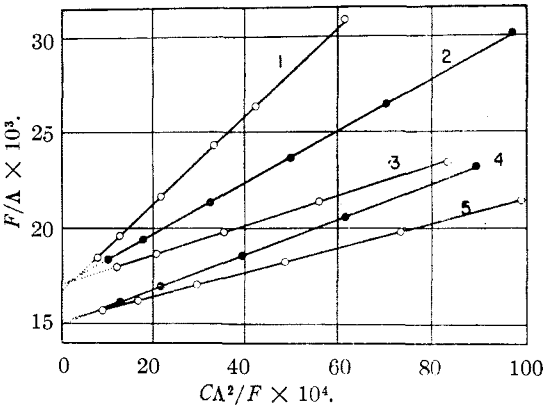

Fig. 2.—Extrapolation plots for: 1, methyltri-*n*-butylammonium picrate; 2, *n*-propyltri-*n*-butylammonium picrate; 3, ethyltriphenylphosphonium picrate; 4, ethyltriphenylphosphonium nitrate; 5, ethyltriphenylphosphonium perchlorate.

Except for ethyltriphenylphosphonium picrate and ethyltriphenylarsonium picrate, the results are consistent. The discrepancies are probably due to impurities present in these salts; they are recrystallized with difficulty. There is no reason for suspecting errors in the values adopted for

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(7) Fuoss, THIS JOURNAL, **57**, 488 (1935).

(8) Fowler and Kraus, *ibid.*, **62**, 2237 (1940).

(9) Mead, Fuoss and Kraus, *Trans. Faraday Soc.*, **32**, 594 (1936).

(10) L. M. Tucker, Thesis, Brown University, 1938.

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.

PROVIDENCE, R. I. RECEIVED OCTOBER 21, 1946

[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).