Solubility.—The compounds prepared were found to be insoluble in water, slightly soluble in acetone and cold ethanol and soluble in ether, benzene, toluene, chloroform, petroleum ether and hot ethanol.

Summary

1. Seven new compounds of germanium, methyl-, ethyl-, *n*-propyl-, *n*-butyl-, *n*-amyl- and benzyltricyclohexylgermane, and hexacyclohexyldigermane have been prepared and some properties described.

2. Possible steric effects were encountered in attempts to introduce the isopropyl, the phenyl and the cyclohexyl group as the fourth group into tricyclohexylgermane.

3. Hexacyclohexyldigermane was prepared from bromotricyclohexylgermane by the Wurtz synthesis.

MINNEAPOLIS, MINN. RECEIVED NOVEMBER 17, 1947

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XXXII. Conductance of Some Long Chain Salts in Ethylene Chloride and Nitrobenzene at 25°[1]

BY HAROLD E. WEAVER[2] AND CHARLES A. KRAUS

I. Introduction

Conductance measurements with aqueous solutions[3] of salts containing hydrocarbon chains of progressively increasing length indicate that the characteristic effect—ascribed to micelle formation—first becomes noticeable with the *n*-nonyl group. In order to determine whether similar effects occur in solutions of such electrolytes in non-aqueous solvents, measurements were carried out with several salts in ethylene chloride and nitrobenzene. At the time that this investigation was initiated, no data were available on the conductance of long chain salts in solvents other than water; in the meantime, however, results of measurements by several investigators have appeared.[4]

The following salts have been studied: octadecyltrimethylammonium and octadecyltributylammonium nitrates in ethylene chloride and dioctadecyldimethylammonium, octadecyltributylammonium and octadecylpyridonium nitrates in nitrobenzene. The octadecyl salts are well adapted to the purpose of the present investigation since octadecyl alcohol of high purity is readily available and the quaternary salts are readily crystallized from a variety of solvents.

II. Experimental

Apparatus and Procedure.—These have been fully described in earlier papers of this series. Bright platinum electrodes were used.

Materials.—Ethylene chloride was purified according to the method described by Mead.[5] The specific conductance was always less than 5×10^{-11}, making solvent corrections unnecessary.

Nitrobenzene was purified as described by Witschonke.[6] The specific conductance of the material was less than 5×10^{-10} so that corrections were unnecessary.

n-Octadecyl alcohol served as the starting material in the preparation of the salts used in this investigation. One recrystallization of the alcohol from nitromethane gave a product which melted at 57.5–58.5°.

n-Octadecyl iodide was obtained by heating the alcohol with iodine and red phosphorus in a sealed tube at 180° for one hour according to the method of Levene, West and van der Scheer.[7] The resulting mixture was extracted with hexane, in which the iodide is very soluble; the excess phosphorus was separated by filtration. The *n*-octadecyl iodide was recrystallized from hexane by slow cooling to 0° in a refrigerator; m. p., 34–35°.

n-Octadecyltri-*n*-butylammonium iodide was prepared by heating *n*-octadecyl iodide with tri-*n*-butylamine (10% excess) in a stoppered flask at 60° for from four to six days. The salt was recrystallized from hexane containing a trace of alcohol; m. p., 97–98°.

n-Octadecyltrimethylammonium iodide was prepared by heating *n*-octadecyl iodide with trimethylamine (20% excess) in a water–alcohol solution in a sealed tube at 60° for from a week to ten days. The salt was recrystallized from hexane containing 3–5% of alcohol; m. p., 234.5–236°.

n-Octadecylpyridonium iodide was prepared by heating *n*-octadecyl iodide with excess pyridine for from twelve to eighteen hours at 60° in a stoppered flask. The excess pyridine was evaporated and the salt was recrystallized from hexane containing a trace of alcohol; m. p., 101.5–103°.

Di-*n*-octadecyldimethylammonium iodide was prepared by Dr. E. C. Evers by heating *n*-octadecyl iodide with excess dimethylamine in water–alcohol solution. The product was recrystallized from hexane containing a trace of alcohol; m. p., 154°.

The corresponding nitrates were obtained from the iodides by metathesis with silver nitrate in an alcohol–water mixture containing 75% alcohol. As a rule, several hours of digestion at 60° were required to coagulate the colloidal silver iodide. Care was exercised to avoid peptization of the coagulated silver iodide on filtration. The solutions were evaporated to dryness and the salts redissolved and crystallized from suitable solvents.

Di-*n*-octadecyldimethylammonium nitrate is very soluble in pure hexane but crystallizes on cooling to Dry Ice temperatures; m. p., 79–81°.

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[1] This paper is based on a portion of a thesis presented by Harold E. Weaver in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Graduate School of Brown University, May, 1940.

[2] University Fellow at Brown University, 1938–1939; Metcalf Fellow, Brown University, 1939–1940.

[3] E. L. McBain, Dye and Johnson, THIS JOURNAL, **61**, 3210 (1939).

[4] Ward, *J. Chem. Soc.*, I, 522 (1939); *Proc. Roy. Soc.* (*London*), **176A**, 512 (1940); Ralston and Hoerr, THIS JOURNAL, **68**, 2460 (1946); Thompson and Kraus, *ibid.*, **69**, 1016 (1947).

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

[6] Witschonke and Kraus, THIS JOURNAL, **69**, 2472 (1947).

[7] Levene, West and van der Scheer, *J. Biol. Chem.*, **20**, 525 (1915).

The other nitrates were recrystallized from hexane containing alcohol in amounts varying from a trace for the *n*-octadecylpyridonium and *n*-octadecyltri-*n*-butylammonium salts to two or three per cent. for *n*-octadecyltrimethylammonium nitrate. The solutions were cooled to 0° in a refrigerator. The melting points were: *n*-octadecyltrimethylammonium nitrate—softens at 170°—melts to a clear liquid at 190°; *n*-octadecyltri-*n*-butylammonium nitrate, 90–91°; *n*-octadecylpyridonium nitrate, 71–73°.

It may be noted that accurate observation of the melting point of long chain salts is often difficult because of gradual changes in the crystalline structure. In addition, pronounced shrinkage occurs between 90 and 100° and in some cases this extends as far as the actual melting point.

III. Results

Values of the equivalent conductance, Λ, and the concentration, *C*, in moles per liter of solution, are presented in Tables I and II. In Table I are given the results in ethylene chloride solution; the densities of the solutions have been taken as that of the pure solvent, 1.2455.[8] In Table II are given the results for nitrobenzene solutions; the densities of the solutions have been taken as 1.1986,[9] the value for pure nitrobenzene. All measurements were at 25 ± 0.01°. Although two series of measurements were made with each salt, with one exception, results from only one of these are reported here; the additional determinations, however, are shown on the plots.

TABLE I

CONDUCTANCE OF LONG CHAIN SALTS IN ETHYLENE CHLORIDE

n-Octadecyltri-*n*-butylammonium nitrate		*n*-Octadecyltrimethylammonium nitrate	
$C \times 10^5$	Λ	$C \times 10^5$	Λ
118.8	20.31	65.73	10.68
35.86	28.86	34.06	13.90
7.989	41.26	11.79	20.93
3.365	47.55	4.559	29.24
2.098	50.19	3.594	31.52
0.7825	54.38	2.050	37.34
0.5478	55.39	1.467	60.68

TABLE II

CONDUCTANCE OF LONG CHAIN SALTS IN NITROBENZENE

n-Octadecyltri-*n*-butylammonium nitrate		Di-*n*-octadecyldimethylammonium nitrate		*n*-Octadecylpyridonium nitrate	
$C \times 10^5$	Λ	$C \times 10^5$	Λ	$C \times 10^5$	Λ
116.7	28.10	107.8	26.78	156.4	27.78
29.93	29.74	32.56	28.50	61.28	29.63
8.761	30.53	12.40	29.40	23.61	30.82
5.366	30.73	82.13	27.31	10.47	31.57
3.196	30.87	27.84	28.72		
1.976	31.04	12.13	29.42		

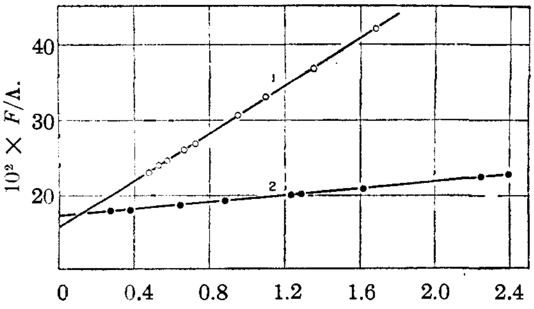

Fig. 1.—Fuoss plots for long chain salts in ethylene chloride: 1, *n*-octadecyltrimethylammonium nitrate; 2, *n*-octadecyltri-*n*-butylammonium nitrate.

IV. Discussion

1. Ethylene Chloride.—The conductance data for ethylene chloride solutions have been analyzed by the method of Fuoss. The results are shown graphically in Fig. 1; values of Λ_0 and *K* for each salt are presented in Table III. Solutions of long chain salts begin to show deviations from the theoretical at concentrations of approximately 1.5×10^{-4} *N*.

TABLE III

CONSTANTS OF SOME LONG CHAIN ELECTROLYTES IN ETHYLENE CHLORIDE

Salt	Λ_0	Λ_0^+	$K \times 10^4$
$(n\text{-C}_{18}\text{H}_{37})(\text{CH}_3)_3\text{NNO}_3$	63.7	23.6	0.157
$(n\text{-C}_{18}\text{H}_{37})(n\text{-C}_4\text{H}_9)_3\text{NNO}_3$	58.2	18.1	1.27

The cation conductances shown in Table IV have been obtained using Tucker's value of 40.1 for the limiting conductance of the nitrate ion.[10]

Since the plots of F/Λ against $C\Lambda f^2/F$ are straight lines in the concentration range investigated, it appears that, at these concentrations, the behavior of solutions of long chain salts is normal. There is no evidence of micelle formation at concentrations up to several thousandths normal.

The interrelation between ion conductances and chain length remains qualitative until additional data are available. It may be pointed out here that the conductance of the octadecyltrimethylammonium ion with 21 carbon atoms is slightly higher than that of the tetra-*n*-amylammonium ion[10] with 20 carbon atoms.

The dissociation constants of the long chain salts exhibit no exceptional properties. When only one long hydrocarbon group is present in the

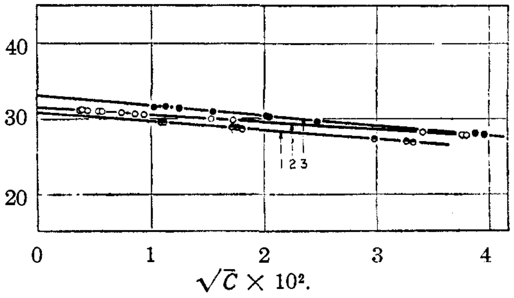

Fig. 2.—Square root plots for long chain salts in nitrobenzene: 1, *n*-octadecyltrimethylammonium nitrate; 2, *n*-octadecyltri-*n*-butylammonium nitrate; 3, *n*-octadecylpyridonium nitrate.

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[8] Walden and Busch, *Z. physik. Chem.*, **140A**, 89 (1929).

[9] Walden and Birr, *ibid.*, **163A**, 281 (1932).

[10] Tucker and Kraus, THIS JOURNAL, **69**, 457 (1947).

cation, the value of the dissociation constant is approximately that which might have been expected for an ion-pair in which the distance of closest approach is determined by the field around the three smaller alkyl groups.

2. **Nitrobenzene.**—In Table IV are given the limiting conductances of three quaternary ammonium nitrates containing long hydrocarbon chains in the cation. The cation conductances are given in column 3 and have been calculated on the assumption that the nitrate ion has a conductance of 22.6.[6]

TABLE IV

LIMITING CONDUCTANCES OF ELECTROLYTES IN NITROBENZENE

Salt	Λ_0	Λ_0^+
$(n\text{-}C_{18}H_{37})_2(CH_3)_2NNO_3$	30.7	8.1
$(n\text{-}C_{18}H_{37})(n\text{-}C_4H_9)_3NNO_3$	31.5	8.9
$(n\text{-}C_{18}H_{37})(C_5H_5N)NO_3$	32.9	10.3

The above Λ_0 values for the three salts have been obtained by extrapolation of the plots shown in Fig. 2, in which values of Λ_0 are plotted against values of $C^{1/2}$. These plots are linear over a considerable range of concentrations although the slopes of the lines are somewhat greater than the theoretical; this is doubtless due to ion-pair formation. Ion conductances decrease with increasing number of carbon atoms in the cation but rather less than one might otherwise expect.

V. Summary

1. The conductance of octadecyltrimethylammonium and octadecyltributylammonium nitrates in ethylene chloride and of octadecyltributylammonium, dioctadecyldimethylammonium and octadecylpyridonium nitrates in nitrobenzene have been measured.

2. These long chains salts are normal electrolytes over the concentration range studied in both ethylene chloride and nitrobenzene.

3. Limiting conductances and dissociation constants have been evaluated in ethylene chloride and limiting conductances in nitrobenzene.

4. Ion conductances have been evaluated in both solvents.

PROVIDENCE, R. I. RECEIVED DECEMBER 16, 1947

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XXXIII. The Conductance of Some Salts in Acetone at 25°[1]

BY MYRON B. REYNOLDS[2] AND CHARLES A. KRAUS

I. Introduction

Acetone is a solvent that differs markedly in type from those previously investigated in this Laboratory; it has a dielectric constant of 20.5 and is a fair solvent for a number of uni-univalent inorganic salts. Solutions in this solvent have been investigated earlier by several different investigators[3] but with the exception of Lannung, who was chiefly concerned with solubilities, their results are uncertain because of the high conductance of the solvent which introduced large and often uncertain corrections with solutions of low concentration. In this connection, it may be pointed out that, since the only laws that are known to apply to electrolytic solutions are of limiting type, it is of particular importance that experimental errors be kept at a minimum at low concentrations. *If a solvent cannot be adequately purified, there is little point in carrying out conductance measurements.*

In the present investigation, the solvent has been purified to a point where correction for solvent conductance was negligible. The electrolytes investigated were, for the most part, salts of the tetrabutylammonium ion with various negative ions. The picrates of lithium, sodium and potassium were measured as were also potassium iodide and thiocyanate. It may be noted that numerous salts which have been measured by earlier investigators were found to be too difficultly soluble in the pure solvent to permit of ready measurement.[3b]

Owing to uncertainties in the value of the physical constants of acetone, these (dielectric constant, viscosity and density) were redetermined.

The results of conductance measurements have been treated by the method of Fuoss[4] and values of the limiting conductance, Λ_0, and the dissociation constant, K, have been derived. Ion conductances have been evaluated according to the method of Fowler.[5]

II. Experimental

Apparatus.—Conductance measurements were carried out as described in earlier papers of this series, using a Jones type a. c. bridge and Erlenmeyer conductance cells with bright platinum electrodes. All measurements were carried out at 25 ± 0.01 °.

The dielectric constant of acetone was measured at 25°,

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(1) This paper comprises a portion of a thesis presented by Myron B. Reynolds in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Graduate School of Brown University, June, 1947.

(2) Anthony Fellow at Brown University, 1946–1947; present address: Research Laboratory, General Electric Company, Schenectady, N. Y.

(3) (a) Walden, Ulich and Busch, *Z. physik. Chem.*, **123**, 429 (1926); (b) Lannung, *ibid.*, **161A**, 255 (1932); (c) Hughes and Hartley, *Phil. Mag.*, **15**, 610 (1933); and others.

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

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