curve for monosodium diphenylketyl does not correspond to that of a simple binary electrolyte.

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Properties of Electrolytic Solutions. IX. Conductance of Some Salts in Benzene

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I. Introduction

In the first paper of this series,[1] the conductances of tetraisoamylammonium thiocyanate and of tri-isoamylammonium picrate in benzene were reported. With the apparatus then available, it was impossible to investigate the conductance at concentrations below the minimum; in fact, it was only possible to argue by inference from the behavior in mixed solvents that the conductance in a strictly non-polar solvent such as benzene would show a minimum. The appearance of inflection points in the conductance curves in the neighborhood of 0.001 N for some salts and not for others also made further experimental work desirable. It seemed especially important to determine, experimentally at least, how the complexity of the curve depended upon the ions of the electrolyte.

By constructing cells with constants as low as 0.003 and by improving the electrical measuring system, it has been possible to measure conductances at concentrations below 10^{-6} N with an accuracy of several per cent. We report herewith the conductance of tetraisoamylammonium thiocyanate, picrate, iodide, bromide, chloride and fluoride in benzene at 25°. Actual minima in conductance, followed by slopes approximating that required by the law of mass action, were found in the case of the picrate, thiocyanate, iodide and bromide; and the minimum was located for the chloride and fluoride. Dissociation constants calculated from the conductance data are of the order of 10^{-18}; among the halides, the iodide is the strongest salt ($K = 5 \times 10^{-18}$) and the fluoride is the weakest ($K = 6 \times 10^{-19}$), which is the order one might expect in non-polar (not solvating) solvents.

II. Materials, Apparatus and Method

Salts.—The preparation of tetraisoamylammonium thiocyanate and iodide has already been described. The iodide used as the starting material for this series of experiments melted at 141°, which is 5° higher than our previous value. The picrate, bromide, chloride and fluoride were prepared by neutralizing the hydroxide with the corresponding acid in alcoholic solution. The picrate was recrystallized from alcohol; the other salts were used directly as obtained from (room temperature) evaporation of

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[1] Kraus and Fuoss, THIS JOURNAL, **55**, 21 (1933).

the solution in which they were prepared. The fluoride is *extremely* hygroscopic; for the conductance experiments, samples were placed in a small weighing bottle which was heated to constant weight *in vacuo* at 70°. Dry air was admitted to the vacuum oven before capping the weighing bottle, which, after weighing, was emptied into a conductance cell previously evacuated and filled with dry air.

Benzene.—In addition to the treatment previously described, the benzene for these experiments was refluxed for six hours over (molten) potassium.

Conductance Cells.—For concentrations greater than 10^{-4} N, cells of several designs were used, much like those previously described. For the most dilute solutions, a different model was constructed (Fig. 1). The electrodes are three platinum cylinders, 5 cm. long and 8, 10 and 12 mm. in diameter, held concentrically by means of lead glass beads fused around light platinum wires welded to the cylinders. The seams are soldered with gold. The inner and outer cylinders are connected by platinum wires, so that both surfaces of the central cylinder are used. The lead wires from the cylinders are connected to thin platinum tubes which are sealed through the Pyrex glass envelope[2] at one end as shown in the figure, the exterior copper leads being soldered to the ends of the platinum tubes. The cell constant was found to be 0.003049 by indirect comparison with a cell standardized by means of 0.1 demal potassium chloride solution. The volume of the electrode compartment is about 17 cc.

Manipulation was as follows: benzene was pumped by dry air pressure from a 250-cc. storage cell (into which it was distilled immediately before the conductance experiment) onto a sample of salt weighed into the cell. After weighing the cell, and determining the conductance, the cell was wiped free from thermostat oil and weighed. Then, by means of dry air pressure applied through the stopcock in the cap, about half of the solution was blown out through the sealed-in capillary siphon. The cell was weighed, and a portion of pure benzene was pumped in. The dilution ratio could be varied from 0.3 to 0.6, depending on the relative amounts of solution emptied and benzene added.

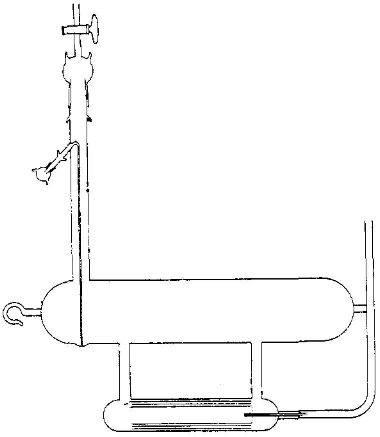

Fig. 1.—Conductance cell.

Electrical Equipment.—The previous method of using a sensitive galvanometer as ammeter has been discarded in favor of a Wheatstone bridge circuit. The cell formed one arm of the bridge, a megohm wire-wound coil[3] the second, a 0–10,000 ohm dial resistance box the third, and either a 10^4, 10^5 or 10^6 ohm coil the fourth. The bridge current was furnished by three 45-volt radio B-batteries and balance was determined by means of a galvanometer whose sensitivity was 10^{-10} amp./cm. at 2 meters scale distance. Corrections for solvent conductance, and for conductance of the glass between the electrodes and other leaks amounted to about 3×10^{-15} mho.

III. Experimental Results

The experimental results are given in Tables I–VI, and are shown graphically in Fig. 2. It will be noted that the conductances in the dilute region for the thiocyanate are somewhat higher than those previously

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(2) C. A. Kraus, Conducting-Seal for Vacuum-Containers, U. S. Patent 1,093,997, patented April 21, 1914.

(3) Shallcross Manufacturing Company, Collingdale, Pa.

reported. The measurements were extended to concentrations as low as 10^{-7} N, but, with the present methods, were somewhat erratic at concentrations below 10^{-6} N. The low concentration conductances, in general, appeared to be too high, perhaps due to traces of moisture. We intend to investigate the low concentration region in solvents of low dielectric constant in a closed system where even slight contamination can be

TABLE I

TETRAISOAMYLAMMONIUM PICRATE IN BENZENE AT 25°

$c \times 10^3$	$\Lambda \times 10^4$	$c \times 10^4$	$\Lambda \times 10^4$	$c \times 10^5$	$\Lambda \times 10^4$	$c \times 10^6$	$\Lambda \times 10^4$
13.20	108.1	9.25	3.26	15.07	1.11	14.80	1.07
9.31	60.5	6.86	2.46	11.93	1.02	14.66	1.02
6.79	36.24	6.75	2.53	10.53	1.00	14.32	1.12
4.57	20.01	4.77	1.88	8.30	0.96	9.41	1.22
3.34	12.92	4.53	1.87	6.27	.92	8.43	1.18
3.29	13.09	3.10	1.54	5.64	.92	4.33	1.65
2.405	8.47	3.07	1.45	3.85	.91	2.31	2.14
2.265	8.18	2.27	1.31	3.72	.91	1.20	3.04
1.488	5.06	2.17	1.28	2.54	.94	0.66	4.5
1.025	3.52	1.94	1.19	2.20	.94	..	..

TABLE II

TETRAISOAMYLAMMONIUM THIOCYANATE IN BENZENE AT 25°

$c \times 10^6$	$\Lambda \times 10^4$
102.2	2.43
41.9	1.26
14.32	1.02
6.55	1.43
2.808	2.29
1.152	4.0

TABLE III

TETRAISOAMYLAMMONIUM IODIDE IN BENZENE AT 25°

$c \times 10^6$	$\Lambda \times 10^4$	$c \times 10^6$	$\Lambda \times 10^4$
11.88	3.32	13.40	1.28
5.34	2.25	8.45	1.27
3.44	1.78	5.91	1.55
3.21	1.69	4.87	1.54
2.075	1.38	3.09	2.03
1.682	1.40	1.68	3.17

TABLE IV

TETRAISOAMYLAMMONIUM BROMIDE IN BENZENE AT 25°

$c \times 10^3$	$\Lambda \times 10^4$	$c \times 10^4$	$\Lambda \times 10^4$	$c \times 10^5$	$\Lambda \times 10^4$	$c \times 10^6$	$\Lambda \times 10^4$
34.22	58.0	29.74	3.86	16.85	2.60	18.73	0.96
22.25	20.7	20.35	3.58	9.86	2.07	15.38	.94
15.02	10.49	12.77	3.48	8.59	1.84	6.34	1.18
9.97	6.74	7.29	3.32	5.79	1.51	2.29	1.85
6.81	5.18	4.56	3.17	3.83	1.14	0.98	3.1
4.58	4.32	3.11	3.03	3.61	1.15	..	..

TABLE V

TETRAISOAMYLAMMONIUM CHLORIDE IN BENZENE AT 25°

$c \times 10^3$	$\Lambda \times 10^4$	$c \times 10^4$	$\Lambda \times 10^4$	$c \times 10^5$	$\Lambda \times 10^4$
33.02	42.0	33.98	3.82	14.71	1.69
23.17	18.40	23.09	3.47	9.68	1.26
15.57	9.45	15.51	3.22	6.65	1.07
10.72	6.40	5.97	2.90	3.87	0.68
7.21	4.83	3.67	2.50	2.01	.56
4.80	3.99	2.20	2.10	..	..

TABLE VI

TETRAISOAMYLAMMONIUM FLUORIDE IN BENZENE AT 25°

$c \times 10^3$	$\Lambda \times 10^4$	$c \times 10^4$	$\Lambda \times 10^4$	$c \times 10^5$	$\Lambda \times 10^4$
28.15	22.49	25.61	4.26	20.33	1.03
18.88	12.26	16.83	3.74	13.78	0.72
13.00	8.55	11.46	3.29	9.01	.52
8.88	6.57	8.41	2.92	5.61	.39
5.91	5.36	5.85	2.44	3.18	.32
3.88	4.60	4.35	2.02	1.58	.32
..	..	2.97	1.47	..	..

avoided. In the present communication, therefore, no data are given for the extremely dilute range. No attempt was made to carry the conductances to very high concentrations. It might be mentioned, however, that all of the halides appear to be quite soluble except the iodide, whose saturation concentration at 25° is less than 10^{-3} N. The picrate liquefies on the addition of a small amount of benzene, but the liquid phase produced requires a considerable volume of benzene for complete solution. Saturation is less than 0.1 N.

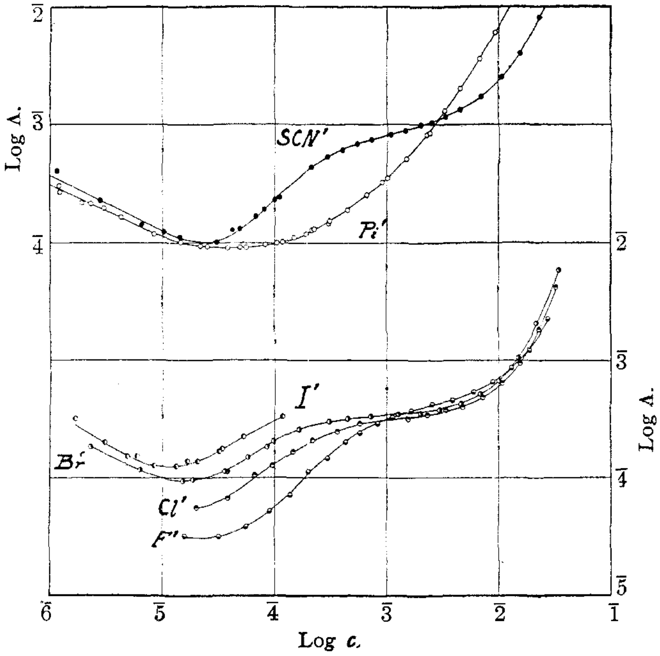

Fig. 2.—Conductance curves for tetraisoamylammonium salts in benzene at 25°.

IV. Discussion

As may be seen from Fig. 2, all the salts exhibit a conductance minimum at concentrations between 10^{-4} and 10^{-5} N, and in those cases (picrate, thiocyanate, iodide, bromide) where the specific conductance was sufficiently large to permit measurement at low concentrations, the rise in conductance below the minimum is in agreement with the slope of -0.5 required by the law of mass action. We conclude, therefore, that electrolytes exhibit a normal behavior in non-polar solvents.

At concentrations above 0.01 N, the equivalent conductance in all cases shows the very rapid increase with concentration which is characteristic of electrolytic solutions in solvents of low dielectric constant. Between the minimum and the higher concentration range is the region where inflection points may occur in the conductance curve. Their appearance seems to depend very much on the nature of the electrolyte: they are very noticeable for the bromide and are entirely lacking for the picrate. In the case of the halides, it is only in the neighborhood of the first inflection after the minimum that the curves show any marked differences from each other. Evidently, this region is controlled primarily by the specific properties of the ions involved. Two of these have been identified, namely: the distance parameters a and a_3 which, together with the dielectric constant and the temperature, are sufficient to describe the binary equilibrium $A^+ + B' \rightleftharpoons AB$ and the triple ion equilibrium $AB_2' + A_2B^+ \rightleftharpoons 3AB$.

By means of equation (8) of our previous paper,[4] it is possible to calculate $K\Lambda_0^2$ from the data locating the minimum in conductance. Although values of the limiting conductance Λ_0 are not known for electrolytes in benzene, a good estimate of the order of magnitude of the mass action constant K can be made by setting $\Lambda_0 = 100$ for all the salts. This value is based on the viscosity of benzene,[5] $\eta_{25} = 0.0060$, and a round value of Walden's constant for the product $\Lambda_0\eta$ for salts of the type studied here. This estimate for Λ_0 can hardly be in error by more than $\pm 50\%$, which corresponds to only ± 0.4 in $\log K$. The results of this calculation are given in the third column of Table VII, which also includes, for the sake of comparison, values for the ternary isoamyl picrate.[6]

TABLE VII

CONSTANTS FOR SALTS IN BENZENE AT 25°

Salt	$-\log K\Lambda_0^2$	$-\log K$	$-\log k$
$(C_5H_{11})_4NOC_6H_2(NO_2)_3$	13.05	17.05	4.85
$(C_5H_{11})_4NSCN$	13.25	17.25	5.15
$(C_5H_{11})_4NI$	13.30	17.30	5.40
$(C_5H_{11})_4NBr$	13.45	17.45	5.30
$(C_5H_{11})_4NCl$	13.90	17.90	5.20
$(C_5H_{11})_4NF$	14.20	18.20	5.10
$(C_5H_{11})_3HNOC_6H_2(NO_2)_3$	16.60	20.60	3.40

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[4] Fuoss and Kraus, This Journal, **55**, 2390 (1933).

[5] Landolt–Börnstein, Tables, p. 145.

[6] Kraus and Fuoss, This Journal, **55**, 21 (1933).

The quaternary picrate is the strongest salt of the group and the ternary picrate is much the weakest. Particularly interesting is the series presented by the four halides: $K\ (\mathrm{I}') > K(\mathrm{Br}') > K(\mathrm{Cl}') > K(\mathrm{F}')$. In a non-polar solvent we might expect complete absence of solvation (in the sense of orientation of solvent dipoles in the fields of the ions). In this event the halides should show a regular decrease in apparent ion size from iodide to fluoride, and the latter should be the weakest salt among the halides. This is precisely what we find experimentally. The decrease of K with decreasing atomic number is, in fact, probably greater than that calculated above, because the value of the *product* $K\Lambda_0^2$ *decreases* from iodide to fluoride, while the limiting conductance presumably increases.

The values of the parameter a calculated from the above constants and equations (5) and (6) of our third paper[7] range from 5.75×10^{-8} cm. for the quaternary picrate to 4.8×10^{-8} cm. for the ternary picrate.

The shift of the minimum with changing salt constitution is described by the constant k, given in the last column of Table VII. This constant[8] describes the equilibrium between free ions and ion pairs (dipoles), on the one hand, and ion triples, on the other. A large value of k (*i. e.*, small negative logarithm) corresponds to a low probability for the formation of an ion triple. The constant increases with increasing dissymmetry, either in relative size or in location of charge, of the ions which make up the salt; k is smallest for the quaternary iodide and greatest for the ternary picrate. The halide ions may all be represented as charged spheres, and here k increases as the size of the negative ion decreases, the size of the (rather large) positive ion remaining the same. It is interesting to note that, while the iodide and thiocyanate have nearly the same K for the binary equilibrium, the k for the triple equilibrium is larger for the thiocyanate, as is shown by the appearance of the minimum at a higher concentration. In the negative ion of the quaternary picrate, the charge is located on one end of the negative ion, and this reduces the chances of formation of ion triples; correspondingly, among the quaternary salts measured, k is greatest for the picrate. In the ternary picrate both ions could best be represented by ellipsoids with charges at one end of the longest axis, rather than by spheres, and this marked dissymmetry leads to a very large k. If we represent all ions as spheres, and calculate parameters a_3 by means of equations (14) and (16) of our fourth paper[8] we obtain $a_3 = 7.4 \times 10^{-8}$ for the quaternary iodide and 14.8×10^{-8} for the ternary picrate.

The appearance of inflection points on the high concentration side of the minimum also appears to be directly related to the symmetry of the salt. In the neighborhood of 10^{-3} N, the conductance curve of the bromide is almost horizontal, and the slope of this inflection region increases to chloride and fluoride, so much so in the latter case, that the fluoride curve,

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(7) Fuoss and Kraus, THIS JOURNAL, **55**, 1019 (1933).

(8) Fuoss and Kraus, *ibid.*, **55**, 2387 (1933).

which lies below the others at high and at low concentrations, cuts across the others twice in this region. The thiocyanate has nearly the same inflection slope as the fluoride and the picrate curve exhibits no inflection points whatsoever. Preliminary calculations indicate that the complete conductance function is of the form

$$\Lambda = A_{-1}c^{-1/2} + A_1c^{1/2} - A_2c + A_3c^{3/2} - A_4c^2 + - \ldots$$

where the even powers of the square root of concentration correspond to the formation of ion clusters containing an even number of ions. The formation of the latter corresponds to a decrease in conductance with increasing concentration, and, depending on the relative magnitudes of the coefficients A_n, the inflection points are more pronounced, the greater the negative coefficients. There is at least qualitative agreement between the apparent molecular weights determined from freezing point measurements[9] and the apparent association calculated from conductance data. It therefore seems likely that it will be possible to account generally for the properties of electrolytic solutions up to moderate concentrations on the basis of equilibria between simple ions and more complex structures formed from them due to the action of Coulomb forces.

Summary

1. Conductances are reported for tetraisoamylammonium picrate, thiocyanate, iodide, bromide, chloride and fluoride in benzene at 25° in the concentration range 0.02–0.000001 *N*.

2. It is shown that the conductance of electrolytes in a non-polar solvent conforms to the law of mass action at low concentrations.

3. Relationships between the structure of electrolytes and their conductance curves in solvents of low dielectric constant are discussed.

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(9) R. A. Vingee, Thesis, Brown University, 1932; F. M. Batson, unpublished work in this Laboratory.