ment of this method by Dr. J. C. Clark and Dr. Harold Mestre, formerly of Stanford University.

Summary

By means of a new photoelectric spectrophotometric apparatus the absorption spectra of highly purified alpha-carotene, beta-carotene and lycopene dissolved in 20% ether in ethanol and in carbon bisulfide have been determined. The absorption coefficients found agree well with the results obtained previously for the ether–ethanol solutions but differ considerably from those reported for carbon bisulfide solutions. The causes for the differences in carbon bisulfide solutions are not apparent.

An explanation has been offered for the variations in positions of the absorption maxima of alpha-carotene and beta-carotene determined spectrophotometrically and spectroscopically, supplemented with a copper ammonium filter. The cause probably lies in the superposition of the absorption of the filter on that of the pigment. Because of the variations possible in the latter method of measurement due to changes in concentrations of the solutions, only the positions of the absorption maxima determined photometrically should be reported.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XVII. The Conductance of Some Salts in Benzene and Dioxane

BY WILLIAM F. LUDER AND PHILIP B. KRAUS[1] WITH CHARLES A. KRAUS AND RAYMOND M. FUOSS

In a previous paper of this series,[2] data were presented which demonstrated the existence of simple binary equilibria for 1-1 salts in benzene, a non-polar solvent. This paper contains data for silver perchlorate, tetrabutylammonium acetate and tetrabutylammonium perchlorate in benzene at 25°, for tetraisoamylammonium iodide in benzene at 60° and for tetrabutylammonium acetate and perchlorate in dioxane at 25°. All of these salts show minima in the equivalent conductance at small concentrations, below which the conductance rises in approximate agreement with the limiting form of the law of mass action

$$c\Lambda^2 = \text{const.}$$

which is valid when association to ion pairs is nearly complete.

I. Materials, Apparatus and Method

Solvents.—Benzene was purified as described by Fuoss and Kraus;[2] m. p. 5.4°, specific conductance 3–10 $\times$ 10^{-15} mho. Dioxane was purified by the method of Kraus and Vingee;[3] m. p. 11.65°, specific conductance 2–6 $\times$ 10^{-15} mho.

Salts.—The tetraisoamylammonium iodide was the same as that used by Fuoss and Kraus.[2] Silver perchlorate was made by dissolving silver oxide (from silver nitrate and potassium hydroxide) in 60% perchloric acid. After evaporation to incipient crystallization, the salt was dried at 115°, dissolved in benzene and filtered and the solution was then evaporated to dryness under reduced pressure. The product apparently contained some impurity, possibly benzene, according to the analyses: found 51.31, 51.17, 50.16% Ag; calculated, 52.03%. Erratic conductance results were obtained with silver perchlorate which was recrystallized from water, and it was only after it had been treated with benzene and filtered from a small amount of insoluble residue that reproducible values were obtained. Tetrabutylammonium iodide was made by the method of Cox, Kraus and Fuoss,[4] m. p. 142° (This is 2° lower than Cox's value.) The perchlorate was made from the iodide by metathesis with silver perchlorate in 95% alcohol; after standing overnight to coagulate colloidal silver iodide, the solution was filtered and allowed to evaporate at room temperatures. The product was recrystallized from anhydrous ethyl acetate (6 cc. of ethyl acetate per gram of salt, 90% yield on first crop); m. p. 207°. Tetrabutylammonium acetate was made by neutralizing with acetic acid an alcoholic solution of the hydroxide (from the iodide and silver oxide). After room temperature evaporation in a desiccator containing first calcium chloride and subsequently phosphorus pentoxide, the salt was twice recrystallized from benzene (50 cc. benzene per gram of salt; 95% yield on first crop); m. p. 116°.

Apparatus and Procedure.—The electrical equipment was that used by Fuoss and Kraus.[2] The cells were of the Erlenmeyer type described by Kraus and Fuoss;[5] the cell constants were 0.1811, 0.02027 and 0.01743. The procedure was essentially that described by Kraus and Fuoss:[4] concentrated solutions from weight burets were

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[1] The data for tetraisoamylammonium iodide at 60° and for silver perchlorate at 25° are contained in a thesis, submitted by Philip B. Kraus in partial fulfilment of the requirements for the degree of Master of Science in the Graduate School of Brown University, June, 1933.

[2] Fuoss and Kraus, THIS JOURNAL, **55**, 3614 (1933).

[3] Kraus and Vingee, *ibid.*, **56**, 511 (1934).

[4] Cox, Kraus and Fuoss, *Trans. Faraday Soc.*, **31**, 749 (1935).

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

added in successive portions to pure solvent in the conductance cell, or pure solvent was weighed in successive portions into the cell into which a sample of salt had previously been weighed. Precautions were taken to exclude moisture in all cases. The 25° determinations were made in the large oil thermostat, which is regulated to ±0.002°. The 60° determinations were made in a small thermostat where the fluctuations were about ±0.5°.

Polarization Effects.—One obvious source of error in determining conductances by direct current is the back e. m. f. at the electrodes, due to polarization. In order to investigate this effect, a 0.055 M solution of tetraisoamylammonium nitrate in dioxane was placed in one of the conductance cells, which was put in series with a galvanometer (sensitivity 0.0333 $\times 10^{-6}$ amp./cm.) and a source of variable d. c. voltage. The current i for different voltages V was then measured, and the apparent resistance R' was calculated by Ohm's law, $R' = V/i$. As is shown in Table I, the apparent resistance decreased with increasing voltage, and approached R = 0.0981 megohm, the resistance determined on the a. c. bridge at 1000 cycles, as the limiting value. If the back e. m. f. is E, then

$$V - E = iR = iR' - E$$

or

$$E = i(R' - R)$$

For this solution, the average value of E was 1.83 volts, so that the absolute error is greater than 1% at 150 volts, which was the voltage used in our d. c. bridge readings. Tests on other solutions and at other resistances gave back e. m. f.'s of the same order of magnitude. In order to obtain reliable results, we are convinced that an alternating current method should be used. Wien[6] has developed one such method; it should also be possible to measure high resistances with fair accuracy by means of a Schering bridge.[7]

TABLE I

VOLTAGE DEPENDENCE OF APPARENT D. C. RESISTANCE

V	$i \times 10^6$	R' (megs.)	E
2.12	8.53	0.2485	1.28
4.23	26.59	.1590	1.62
6.35	46.27	.1372	1.81
8.46	66.8	.1266	2.00
12.68	108.4	.1169	2.04
19.0	169.8	.1118	2.16
31.8	306.1	.1038	1.75
48.4	470.8	.1028	2.21
			Av. 1.83

II. Results

The experimental results are given in Tables II–VII and are shown graphically in Fig. 1.

TABLE II

SILVER PERCHLORATE IN BENZENE AT 25°

$c \times 10^4$	$\Lambda \times 10^6$	$c \times 10^2$	$\Lambda \times 10^6$
0.230	2.20	0.473	0.72
0.953	1.47	0.703	.83
2.10	1.12	1.030	.99
4.04	0.87	1.33	1.17
7.53	.71	1.62	1.35
12.6	.63	3.49	2.41
15.3	.64	5.77	4.93
23.0	.63	9.05	11.70
33.0	.66	14.10	36.3

TABLE III

TETRAISOAMYLAMMONIUM IODIDE IN BENZENE AT 60°

$c \times 10^6$	$\Lambda \times 10^4$	$c \times 10^4$	$\Lambda \times 10^4$
3.01	6.49	0.88	6.22
4.97	4.99	1.82	9.59
8.85	4.44	3.11	12.9
14.20	4.21	6.88	16.8
20.6	4.21	13.90	19.9
43.3	4.66	28.2	23.3

TABLE IV

TETRABUTYLAMMONIUM ACETATE IN DIOXANE AT 25°

$c \times 10^6$	$\Lambda \times 10^5$	$c \times 10^5$	$\Lambda \times 10^5$
1.120	1.230	17.67	0.494
2.218	0.861	32.1	.484
3.98	.712	45.8	.515
8.97	.581		

TABLE V

TETRABUTYLAMMONIUM ACETATE IN BENZENE AT 25°

$c \times 10^4$	$\Lambda \times 10^5$	$c \times 10^4$	$\Lambda \times 10^5$
0.1136	2.13	1.778	0.685
.1666	1.81	2.095	.596
.336	1.36	2.335	.609
.407	1.190	2.591	.643
.555	1.060	2.779	.602
.615	1.040	3.136	.622
.846	0.870	3.693	.644
1.132	.804	4.405	.688
1.225	.698	4.926	.758
1.502	.677	5.505	.764

TABLE VI

TETRABUTYLAMMONIUM PERCHLORATE IN DIOXANE AT 25°

$c \times 10^4$	$\Lambda \times 10^4$	$c \times 10^4$	$\Lambda \times 10^4$
0.0294	1.24	1.660	1.023
.0414	1.18	1.810	1.025
.0611	0.861	2.21	1.116
.0833	.792	3.09	1.301
.1251	.687	3.34	1.307
.1530	.649	4.26	1.45
.231	.636	5.53	1.64
.379	.661	7.74	1.83
.388	.654	9.01	1.97
.413	.688	19.20	2.68
.840	.787	23.7	2.96
.912	.833	46.2	4.14
1.001	.836	104.5	7.32

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(6) Wien, *Physik. Z.*, **35**, 652 (1934).

(7) Schering, *Z. Instrumentenk.*, **40**, 124 (1920).

TABLE VII

TETRABUTYLAMMONIUM PERCHLORATE IN BENZENE AT 25°

$c \times 10^4$	$\Lambda \times 10^4$	$c \times 10^4$	$\Lambda \times 10^4$
0.01716	2.34	0.0194	2.16
.0361	1.46	.0413	1.38
.0676	1.20	.0675	1.22
.1216	1.23	.1425	1.30
.223	1.45	.280	1.58
.366	1.67	.490	1.84
1.125	2.19	.683	2.00
2.168	2.46	1.870	2.43
4.06	2.65	4.15	2.69
7.75	2.88	7.86	2.92
12.89	3.14	14.30	3.24
36.6	4.40	54.9	5.65
61.7	6.10	105.7	10.40
129.4	13.30		

III. Discussion

Probably the most striking result of the investigation is the marked effect of structure on the conductance in solvents of low dielectric constant, as is illustrated in Fig. 1. In solvents of higher dielectric constant, conductance curves conform fairly well to standard patterns, and specific influences are visible only in different Λ_0 and K values. In solvents of lowest dielectric constant, however, an enormous spread of K values appears and the region on the high concentration side of the minimum differs in a characteristic way from salt to salt. Thus in benzene, silver perchlorate has a minimum conductance $\Lambda = 6.3 \times 10^{-7}$ at about 1.8×10^{-3} N, while tetrabutylammonium perchlorate has a minimum conductance $\Lambda = 1.2 \times 10^{-4}$ at 8.0×10^{-6} N. Above the minimum, the conductance curve rises with steadily increasing slope for the silver salt, while in the case of the quaternary salt, two inflection points appear, between which the conductance increases only slowly with increasing concentration. But when the latter salt is studied in dioxane, this pair of inflection points has moved so close together that only a change of curvature appears. The same difference between benzene and dioxane curves has been observed for tetraisoamylammonium thiocyanate.

Approximate values of the various constants are given in Table VIII. Using the result derived by Fuoss and Kraus[8]

$$4K\Lambda_0^2 = (c\Lambda^2)_{min.}$$

it was possible to evaluate the products $K\Lambda_0^2$ from the data at the conductance minimum. Then assuming $\Lambda_0 = 100$ for the quaternary salts and $\Lambda_0 = 150$ for $AgClO_4$ in benzene, and using Walden's rule, $\Lambda_0\eta \doteq$ constant, Λ_0 values for dioxane at 25° and benzene at 60° were computed.[9]

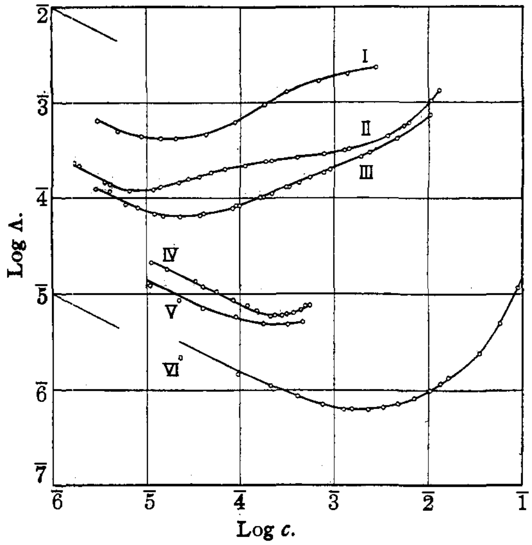

Fig. 1.—Conductance curves: I, i-Am_4NI in C_6H_6 at 60°; II, Bu_4NClO_4 in C_6H_6 at 25°; III, Bu_4NClO_4 in $C_4H_8O_2$ at 25°; IV, Bu_4NAc in C_6H_6 at 25°; V, Bu_4NAc in $C_4H_8O_2$ at 25°; VI, $AgClO_4$ in C_6H_6 at 25°.

Having determined the K-values, a, the average ion size was computed, using Fuoss and Kraus' equations

$$a = \epsilon^2/bDkT$$

$$K^{-1} = \frac{4\pi N}{1000}\left(\frac{\epsilon^2}{DkT}\right)^3 Q(b)$$

where $Q(b)$ is a function for which numerical values have been tabulated, and where the other symbols have their usual meanings.[10] For later discussion, the dipole moments in Debye units are also given in Table VIII for the cases where they have been measured.[11]

TABLE VIII

System	Λ_0	$K \times 10^{18}$	μ_D	$a \times 10^8$
$AgClO_4$–C_6H_6 at 25°	150	0.0078	10.7	4.89
Am_4NI–C_6H_6 at 25°	100	5.0	..	5.67
Am_4NI–C_6H_6 at 60°	155	32.0	..	5.47
Bu_4NAc–$C_4H_8O_2$ at 25°	51	0.56	..	5.61
Bu_4NAc–C_6H_6 at 25°	100	.23	11.2	5.25
Bu_4NClO_4–$C_4H_8O_2$ at 25°	51	.11	..	5.40
Bu_4NClO_4–C_6H_6 at 25°	100	2.9	14.1	5.60

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(8) Fuoss and Kraus, THIS JOURNAL, **55**, 2387 (1933), Equation 8).

(9) For benzene, $\eta_{25} = 0.006132$, $\eta_{60} = 0.003956$, by interpolation on a log $\eta - 1/T$ plot from Thorpe and Rodger's data, *Phil. Trans.*, **185A**, 397 (1894). For dioxane, $\eta_{25} = 0.011969$; Geddes, THIS JOURNAL, **55**, 4832 (1933).

(10) For benzene, $D_{25} = 2.267$ and $D_{60} = 2.196$; Matsuike, *Proc. Imp. Acad., Tokyo*, **5**, 29 (1929). For dioxane, $D_{25} = 2.181$; Hooper and Kraus, THIS JOURNAL, **56**, 2265 (1934).

(11) Hooper and Kraus, *ibid.*, **56**, 2265 (1934); Geddes, unpublished observations in THIS LABORATORY.

We note first that silver perchlorate is by far the weakest electrolyte of the group and hence has the smallest diameter. It also has the smallest moment, but the ratio of the moments of silver and tetrabutylammonium perchlorates, 0.76, is smaller than the ratio of a-values, which is 0.87. Evidently, the simple model of uniformly charged spheres is inadequate. Silver perchlorate is unusual in another respect; its minimum in conductance at 1.8×10^{-3} N appears at a higher concentration than any previously observed in benzene for the conductance minimum. In terms of the triple ion hypothesis, this means that triple ion formation is a very improbable event for silver perchlorate; if we calculate the corresponding a_3-value, we obtain the absurd result that $a_3 = 60 \times 10^{-8}$, which simply means that the spherical model fails completely to describe silver perchlorate at the minimum and that other effects, such as polarization forces, should also be taken into account. The value 4.89×10^{-8} for the ion size derived from the binary equilibrium is somewhat smaller than one might expect from lattice data, but even so, it is much larger than 2.26×10^{-8}, the value obtained by dividing the moment by $\epsilon = 4.774 \times 10^{-10}$ e. s. u. In general, we find that ion sizes calculated from K are larger than those calculated from μ, but are less sensitive to salt structure while, at the same time, they have more plausible magnitudes. At concentrations below the minimum, silver perchlorate behaves like a normal 1-1 salt, as is shown by the slope of $-1/2$ on a log Λ–log c plot.

The change of conductance of tetraisoamylammonium iodide at concentrations up to the minimum is fairly well accounted for on the basis of association theory, but the change of a with temperature seems greater than would correspond to experimental error, and also is greater than the change observed in a-values for tetrabutylammonium nitrate in anisole.[12] Obviously, more work must be done on temperature coefficients. If our model were correct, a would be a true constant, so a study of a as a function of temperature should eventually lead to an improvement of our ideas about electrolytes.

The benzene–dioxane comparison is quite interesting. The perchlorate is a weaker electrolyte in dioxane than in benzene, as would be expected from the lower dielectric constant of dioxane, and this is the primary effect, because the ion size calculated from the K values in the two solvents is about the same. But the acetate is stronger in dioxane, the solvent of lower dielectric constant, than in benzene. This observation indicates solvation of the acetate ion by dioxane, which, although it has a net moment of zero, still has two polar ether–oxygens in its molecule. A similar effect was found in ethylene chloride;[13] the limiting conductance of tetrabutylammonium acetate in ethylene chloride is 52.8 and that of tetrabutylammonium picrate[14] is 57.40. The only plausible explanation for the fact that the acetate ion has a smaller mobility than the picrate ion is solvation of the former ion.

The data presented in this paper show that specific effects due to the structure of solute and solvent play an important part in determining the properties of electrolytic solutions in solvents of low dielectric constant. In dilute solutions in solvents of high dielectric constant, the magnitude of the charges (*i. e.*, valence type) is the determinative factor; in solvents of intermediate dielectric constant, deviations from the laws of strong electrolytes can be accounted for by the theory of association, using a spherical ionic model and Coulomb's law; in solvents of low dielectric constant, this method is still successful at very low concentrations, but at concentrations above that corresponding to the conductance minimum it is obvious that more parameters, which give a more detailed description of the system, must be introduced. It will be necessary to collect more data on a wide variety of systems before we can hope to discover any regularity.

Summary

1. Conductance data for the following systems are presented: tetraisoamylammonium iodide in benzene at 60°; silver perchlorate, tetrabutylammonium perchlorate and acetate in benzene at 25°; and tetrabutylammonium perchlorate and acetate in dioxane at 25°.
2. The conductance curves show minima at low concentrations, below which the conductance rises in accordance with the law of mass action for binary equilibria.
3. The marked specific effect of structure on conductance in solvents of very low dielectric constant is pointed out.

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[12] Bien, Kraus and Fuoss, THIS JOURNAL, **56**, 1860 (1934).

[13] Cox, Kraus and Fuoss, *Trans. Faraday Soc.*, **31**, 749 (1935).

[14] Mead, unpublished observations in THIS LABORATORY.