tive ketones, esters, alcohols, ethers, amines and carboxylic acids ionize when dissolved in methanesulfonic acid. Many of these compounds are completely ionized, the degree of ionization being a function of their respective basic strengths. Several compounds which display complex ionization in sulfuric acid have normal *i*-factors in methanesulfonic acid. The *i*-factor of triphenylcarbinol is four in both solvents. Methanesulfonic acid has a cryoscopic constant of 5.69 and an acidity function, H_0, of about -6.0.

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[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XLV. Conductance of Some Salts in Benzene at Higher Concentrations[1]

BY LAURENCE E. STRONG[2] AND CHARLES A. KRAUS*

I. Introduction

In solvents of high dielectric constant, such as water, the equivalent conductance of normal salts decreases continuously with increasing concentration. In solvents of low dielectric constant, the conductance initially decreases, passes through a minimum and thereafter passes through a maximum. The maximum is due to the rapidly increasing viscosity of the solution. In solvents of intermediate dielectric constant, having values in the neighborhood of 15 or 20, the conductance passes through a minimum for some salts and levels off and then decreases rapidly for others.

The conductance of a number of salts in benzene has been measured by several investigators in this Laboratory.[3,4,5] They found the conductances of different salts to vary over a rather wide range, depending on the constitution of their ions. However, measurements were not carried to high concentrations. It seemed worthwhile, therefore, to measure a number of salts at higher concentrations in order to determine how their conductance is related to various constitutional factors. Accordingly, eight salts were measured up to the limit of their solubility. Two of these, tetraisoamylammonium thiocyanate[3] and triisoamylammonium picrate[4] had been measured earlier at lower concentrations. Tetra-*n*-butylammonium thiocyanate and bromide were measured to compare with tetraisoamylammonium thiocyanate, as was also amyltributylammonium iodide. Dioctadecyldimethyl- and methyltributylammonium thiocyanate were measured for comparison with dioctadecyldibutylammonium thiocyanate. The solubility of the last named salt is rather low; measurements were therefore carried out at 35° as well as at 25° in order to extend these measurements to somewhat higher concentrations. Dioctadecyldimethylammonium thiocyanate was measured at 35° for the same reason.

The densities of solutions of the five most soluble salts were determined in order to be able to express conductances on a volume basis. The viscosity of solutions of tetraisoamylammonium thiocyanate was measured. The dielectric constant of solutions of several salts was measured for the purpose of comparison of molecular polarization values with earlier results.

II. Experimental

1. **Materials.**—Salts were prepared by conventional methods and purified by recrystallization from suitable solvents. The dioctadecyl salts were prepared according to the method of Evers[6] by treating the iodide with the dialkylamine. Octadecyl iodide was heated with dibutylamine at 70° in a sealed tube for a week. The iodide was converted to nitrate with silver nitrate and the nitrate was converted to the thiocyanate by metathesis with potassium thiocyanate in absolute ethanol. The following salts were prepared: tetraisoamylammonium thiocyanate (m. p. 104°); tetra-*n*-butylammonium thiocyanate (m. p. 124°); di-*n*-butyldi-*n*-octadecylammonium thiocyanate (m. p. 83-5°); tri-*n*-butylmethylammonium thiocyanate (m. p. 101°); *n*-amyltri-*n*-butylammonium iodide (m. p. 107°); tetra-*n*-butylammonium bromide (m. p. 118°); triisoamylammonium picrate (m. p. 127°). The sample of dimethyldi-*n*-octadecylammonium thiocyanate was prepared by Dr. E. C. Evers[6] by a method similar to that used for the corresponding butyl derivative.

In computations, the density of benzene was taken to be 0.8737 at 25° and 0.8627 at 35°. The dielectric constant of benzene was taken to be 2.268 at 25°.

2. **Apparatus and Procedure.**—Conductances in the lower resistance range were measured by means of a Jones bridge; high resistances were measured by means of a specially designed, shielded parallel arm bridge constructed by the Leeds and Northrup Company. This bridge was also used in measuring the dielectric constant of several solutions.

Seven different cells were employed varying in design and free volume as well as cell constant. The constants ranged from 0.3 to 0.003. For the more dilute solutions the usual dilution procedure was employed[6a]; for some of the more concentrated solutions the salt was weighed directly into the cell.

Densities of solutions of the more soluble salts were determined with a Westphal balance.

Viscosities of solutions of tetraisoamylammonium thiocyanate were measured with a modified Ostwald viscometer. The solutions were made up in the viscometer.

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

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

[4] Fuoss and Kraus, *ibid.*, **55**, 3614 (1933).

[5] Luder, Kraus, Kraus and Fuoss, *ibid.*, **58**, 255 (1936).

[6] E. Charles Evers, Thesis, Brown University, May, 1941.

[6a] Mead, Fuoss and Kraus, *Trans. Faraday Soc.*, **32**, 594 (1936).

TABLE I

CONDUCTANCE OF SALTS IN BENZENE AT 25°

A. Tetra-*n*-butylammonium thiocyanate

C	Λ
2.054	0.6355
1.718	1.008
1.348	1.162
1.240	1.139
1.069	1.042
0.691	0.642
.0606	.02893
.0838	.0475
.1325	.0841
.2025	.1358
C	$\Lambda \times 10^3$
0.00599	0.679
.01378	1.549
.02916	6.405
.04515	17.21
.06415	32.58
$C \times 10^4$	$\Lambda \times 10^4$
66.55	7.498
30.96	4.785
13.38	3.503
3.600	2.314
1.799	1.790
0.711	1.207
.3844	0.955
.1871	.822

B. Tetraisoamylammonium thiocyanate

C	Λ
1.138	0.3938
1.040	.3580
0.909	.2998
1.045	.3473
0.7068	.2213
.4535	.1235
.2471	.07086
.0960	.04228
$C \times 10^3$	$\Lambda \times 10^3$
1.185	0.894
3.052	1.155
6.670	1.718
15.71	4.529
30.69	15.07
$C \times 10^4$	$\Lambda \times 10^4$
23.63	10.61
6.82	7.68
3.042	5.557
1.013	2.368
0.3651	1.105

C. Tetra-*n*-butylammonium bromide

C	Λ
0.8420	0.1880
.8145	.1827
.6240	.1384
.4610	.1017
.3456	.0791
$C \times 10^2$	$\Lambda \times 10^3$
0.864	0.340
1.472	.588
2.440	1.243
4.145	5.21
9.03	25.19
11.23	31.64
13.24	36.64
15.59	41.28
20.55	49.70
26.00	60.15
$C \times 10^4$	$\Lambda \times 10^4$
255.4	14.63
113.4	4.460
37.04	2.161
21.36	1.822
8.01	1.423
4.315	1.249
1.953	1.026
0.856	0.811
.290	.674
.099	.57

D. *n*-Amyltri-*n*-butylammonium iodide

C	Λ
1.34	0.374
0.475	.189
.1774	.0754
.2640	.1138
.1084	.0505
.06095	.02422
.03318	.00655
$C \times 10^2$	$\Lambda \times 10^3$
2.261	2.488
3.876	9.71
6.445	26.42
12.89	59.15
18.75	82.9
$C \times 10^3$	$\Lambda \times 10^4$
17.25	15.17
7.60	5.960
2.876	3.422
1.014	2.580
0.3344	2.078
.1148	1.623
.0407	1.211

E. Tri-*n*-butylmethylammonium thiocyanate

$C \times 10^3$	$\Lambda \times 10^5$
19.19	38.40
6.88	9.81
4.50	6.91
1.660	4.078
0.581	3.173
.2295	2.895
.1019	2.74

F. Dimethyldioctadecylammonium thiocyanate

$C \times 10^2$	$\Lambda \times 10^5$
0.2736	1.21
.5220	1.25
1.645	1.922
4.282	3.584
10.42	11.32

G. Tri-isoamylammonium picrate

C	Λ
0.2225	0.004935
.352	.01351
.2180	.004441
.3794	.01683
.7370	.04270
1.079	.04754
1.190	.0448
0.6095	.03526

H. Dioctadecyldibutylammonium thiocyanate

$C \times 10^3$	$\Lambda \times 10^2$
1.977	1.20
3.962	2.74
9.67	3.38
15.49	3.38
9.19	3.33
7.04	3.23
5.14	2.98
3.09	2.11
$C \times 10^4$	$\Lambda \times 10^5$
21.98	55.73
8.628	27.48
3.119	14.62
1.232	9.16
0.5090	6.395
0.1777	4.92
(at 35°)	
$C \times 10^2$	$\Lambda \times 10^2$
0.4040	0.1421
1.790	1.387
4.125	3.720
6.315	4.330
13.82	5.06
18.32	5.22
25.92	5.59
35.41	6.38
0.3818	6.51

III. Results

A. Conductances.—The results of conductance measurements are presented in Table I. Concentrations in moles per liter of solution appear in the first column and equivalent conductances in the second.

B. Densities.—Densities for five salts that have a fairly high solubility in benzene are given in Table II. The molal concentration, in moles of salt per thousand grams of solvent, appears in the first column, the density in the second and the molar concentration in the last column.

TABLE II

DENSITY OF SOLUTIONS OF SALTS IN BENZENE AT 25°

m	*d*	*c*
A. Tetra-*n*-butylammonium thiocyanate		
5.081	0.925	1.860
1.553	.9025	0.9559
0.4246	.8845	.3331
0.0115	.8737	.0100
B. Tetraisoamylammonium thiocyanate		
2.058	0.897	1.065
0.4180	.8808	0.3205
.1828	.8777	.1505
.0	.8737	.0
C. Tetra-*n*-butylammonium bromide		
1.411	0.9289	0.8420
0.759	.9110	.5555
.5740	.9027	.4360
.3574	.8925	.2824
.2650	.8887	.2278
.1717	.8854	.1440
D. *n*-Amyltri-*n*-butylammonium iodide		
0.3484	0.9027	0.2778
.2664	.8962	.2166
.1732	.8886	.1442
E. Triisoamylammonium picrate		
1.791	0.973	0.971
0.9123	.9375	.6095
.5523	.9176	.4073
.2820	.8978	.2251
.1499	.8872	.1247
.0892	.8819	.0757
.0354	.8771	.0306

C. Dielectric Constants.—The dielectric constant of solutions of three salts was measured in benzene at 25°. The results are presented in Table III where the concentration of the solution appears in the first column, the observed dielectric constant in the second and the molecular polarization of the solute in the last column.

D. Viscosities.—The viscosity of solutions of tetraisoamylammonium thiocyanate was measured at several concentrations at 25°. Values of the viscosity relative to that of pure benzene are given in Table IV.

IV. Discussion

1. Conductance as a Function of Concentration and Constitution.—Conductance curves of the eight salts measured are shown in Figs. 1 and

TABLE III

DIELECTRIC CONSTANTS OF SOLUTIONS OF SALTS IN BENZENE AT 25°

A. Dioctadecyldibutylammonium thiocyanate

$C \times 10^3$	D_{12}	P_2
3.106	2.285	1100
2.198	2.284	1600
0.863	2.277	1900

B. *n*-Amyltri-*n*-butylammonium iodide

$C \times 10^3$	D_{12}	P_2
2.876	2.280	800
1.014	2.275	1200

C. Tetra-*n*-butylammonium bromide

$C \times 10^3$	D_{12}	P_2
3.704	2.276	450
2.136	2.274	550
0.801	2.272	1000
.432	2.271	1400
.800[a]	...	1260[a]
.431[a]	...	1510[a]

[a] Geddes and Kraus ref. 10.

TABLE IV

RELATIVE VISCOSITY OF SOLUTIONS OF TETRAISOAMYLAMMONIUM THIOCYANATE IN BENZENE

C	η/η_0
0.0842	1.531
.1832	2.109
.2744	2.607
.3418	2.941
1.028	9.76

2; logarithms of equivalent conductance are plotted against logarithms of concentration.

Although the conductance curves for different salts differ greatly in detail, they have certain elements in common. All pass through a minimum in the neighborhood of 10^{-4} *N* and all approach a maximum in the neighborhood of 1 *N*, although the maximum can be reached only with those salts that have a sufficiently high solubility. Thus, triisoamylammonium picrate has a minimum at about 3×10^{-4} *N* where its conductance is approximately 2.5×10^{-7}; it has a maximum at 1.08 *N* where its conductance is 0.047. Tetrabutylammonium thiocyanate has a minimum at about 1×10^{-5} *N* where its conductance is approximately 1×10^{-4}; it has a maximum at 1.35 *N* where its conductance is 1.16. For the first salt, the conductance, in going from the minimum to the maximum, increases 2×10^5 times, for the second, it increases 1.16×10^4 times. The ratio of conductance of the two salts at the minimum is 400; at the maximum, it is 25.

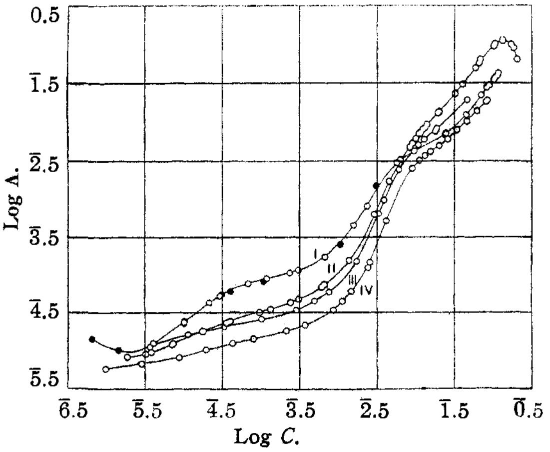

Fig. 1.—Conductance of salts in benzene at 25°: I, tetraisoamylammonium thiocyanate (black circles, Fuoss and Kraus[4]); II, tetra-*n*-butylammonium thiocyanate; III, *n*-amyltri-*n*-butylammonium iodide; IV, tetra-*n*-butylammonium bromide.

Triisoamylammonium is a small ion as is indicated by the small polar moment of salts of this and of similar ions; the tetrabutylammonium ion, on the other hand, is a large ion as is indicated by the large polar moment of its salts. At low concentrations, salts of the triisoamylammonium ion are ionized to a much smaller extent than are salts of larger ions. This is illustrated by the conductance curves of Figs. 1 and 2. At concentrations well below the minimum, the salts conform to the requirements of the Bjerrum–Fuoss theory; at high concentrations, where the conductance increases with increasing concentration, an acceptable theory is lacking. Judging by the viscosity of tetraisoamylammonium thiocyanate, the relative viscosity of the tetrabutylammonium thiocyanate solution at the maximum of conductance is of the order of 10 or more; the equivalent conductance is 1.16. This corresponds to an equivalent conductance of 10, or more, in pure benzene. On the basis of the viscosity of benzene, the limiting conductance of a binary salt of the type here under consideration would be of the order of 70. Thus, at the maximum, a large proportion of the salt is concerned in the conduction process.

At the highest concentration (2.05 *N*) of tetrabutylammonium thiocyanate, the conductance is 0.64 and the relative viscosity may be estimated as of the order of 50. Taking the viscosity of ben-

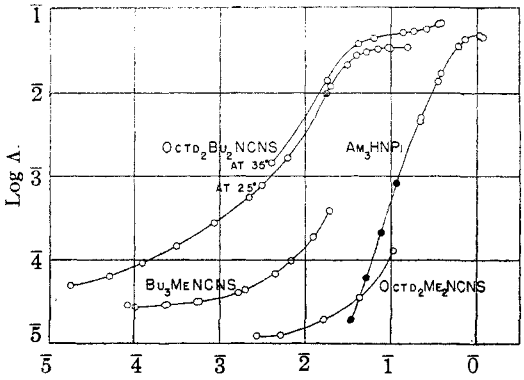

Fig. 2.—Conductance of salts in benzene at 25° (black circles, Fuoss and Kraus[4]).

zene as 6.11×10^{-3} poise, the conductance–viscosity product for this solution is of the order of 0.2. For fused salts at higher temperatures, the product has a value in the neighborhood of 1.0.[7] For tetrabutylammonium thiocyanate in ethylene chloride solution,[8] using $\Lambda_0 = 68.6$, the product has a value of 0.55. The conductance–viscosity product of tetrabutylammonium thiocyanate in benzene at the highest concentration is of the order of that of a highly, if not completely, dissociated salt.

With tetrabutylammonium thiocyanate at the concentration of the maximum (1.35 N), there are 6.5 moles of benzene per mole of salt. At the highest concentration measured (2.054 N), there are two moles of benzene per mole of salt or one mole of benzene per ion. Clearly, it becomes a question as to which component is to be considered as solvent and which as solute.

As already noted above, for a given anion, salts are the weaker the smaller the cation. The same holds true for salts of different anions. This is shown most clearly by the earlier measurements of Fuoss and Kraus[4] with the four halides, the thiocyanate and the picrate of the tetraisoamylammonium ion.

Salts of the symmetrical quaternary ammonium ions with simple anions have very complex conductance curves, having 3, or more, inflection points between the minimum and the maximum. The curves of corresponding picrates have a much simpler structure as Fuoss and Kraus[4] have shown.

The curves for dioctadecyldibutylammonium thiocyanate are less inflected than those of corresponding tetrabutyl- or tetraamylammonium salts. However, with the first mentioned salt, the conductance rises to a high value at a lower concentration. The solubility of the long chain salt was not high enough to permit of carrying the curve to high concentrations. At 35°, the curve shows an upward trend near the end, indicating that the conductance might increase markedly at higher concentrations.

It may be pointed out that our measurements with triisoamylammonium picrate and tetraisoamylammonium thiocyanate by an alternating current method are in good agreement with the earlier measurements of Fuoss and Kraus[4] by a direct current method (Figs. 1 and 2).

2. Dielectric Constants and Molecular Polarizations.—The parallel arm bridge, which was used for dielectric constant measurements in the audio-frequency range, was not sufficiently sensitive to yield reliable results at the low concentration necessary for the determination of limiting polarization values for salts. However, it is of interest to compare the results of present measurements at higher concentration with those of earlier investigations by a resonance method.

As may be seen from the polarization values recorded in Table III, present measurements are in accord with those of Hooper[9] and Geddes[10] for similar salts. The values for tributylammonium bromide agree with those of Geddes within the limits of experimental error of the present method.

The decrease of polarization with increasing concentration is due to the formation of quadrupoles or of more complex structures. In the case of salts with large ions, the quadrupoles exist down to concentrations as low as 1×10^{-4} N. With weaker electrolytes, such as the salts of trialkylammonium ions, quadrupoles are present in only small amount at concentrations below 1×10^{-3} N.[11,12]

3. Nature of Concentrated Salt Solutions.—Let us consider a fused salt to which we gradually add a solvent until we have reached any desired low concentration of salt in solvent, and let us examine the change in the properties of the system as we pass from pure salt to dilute solution, bearing in mind such knowledge as we have concerning electrolytic systems. We have three types of such systems: I. The solvent has highly polar molecules and a dielectric constant of such high value that the salt is completely dissociated into its ions at all concentrations. II. The solvent is composed of non-polar molecules and its dielectric constant is such that the salt is not completely dissociated into its ions at the lowest concentration practically attainable. III. The solvent is composed of polar molecules but its dielectric constant is such that, although the salt is practically completely dissociated into its ions at very low concentrations, at intermediate concentrations the ions interact to form ion-pairs and, perhaps, more complex structures.

Before entering upon an analysis of these three types of systems, let us first consider the properties of fused salts. We may assume that typical salts are completely dissociated into their ions in the fused state. The order of magnitude of their equivalent conductance, when allowance is made for viscosity, is much the same as that of the same salts in solution.[7] In other words, their conductance viscosity product is of the order of that of their solutions in ordinary solvents in which they are completely dissociated into their ions. Moreover, the conductance–viscosity product of fused salts shows very little temperature dependence.[7]

Type I.—Although most salts have such a high melting point that solutions of solvents in the fused salt cannot well be studied, it has been shown that lithium chlorate (m. p. 129°) is completely miscible with water.[13] The fused salt is a very viscous liquid at its melting point and its viscosity decreases on addition of water; for this reason the conductance of the solution increases

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(7) Goodwin and Mailey, *Phys. Rev.*, **25**, 469 (1907).

(8) Thompson and Kraus, THIS JOURNAL, **69**, 1016 (1947).

(9) Hooper and Kraus, *ibid.*, **56**, 2265 (1934).

(10) Geddes and Kraus, *Trans. Faraday Soc.*, **32**, 585 (1936).

(11) Fuoss and Kraus, THIS JOURNAL, **57**, 1 (1937).

(12) Batson and Kraus, *ibid.*, **56**, 2017 (1934).

(13) Kraus and Burgess, *ibid.*, **49**, 1226 (1927).

continuously with increasing water content.[14] If we add water to a fused salt, the conductance increases continuously until such concentration is reached that further increase occurs in conformity with the limiting law of Onsager.

Type II.—Solutions of salts in benzene are examples of systems of this type. The solvent molecules are non-polar and the dielectric constant is 2.268. In conformity with the low dielectric constant of the solvent, salts are only slightly dissociated to free ions even at the lowest concentration at which reliable measurements can be made. The strongest salts are ionically dissociated to the extent of only one part per million at a concentration of 1×10^{-5} N. Fuoss and Kraus[4] have shown that, at concentrations somewhat below the minimum, an equilibrium exists between free ions and ion-pairs which equilibrium conforms to the law of mass action. Hooper[9] and Geddes[10] have measured the polar moments of salts in benzene. They found values ranging from 7.17×10^{-18} to 19.7×10^{-18} debye unit, depending on the size and structure of the constituent ions.

Measurements of the molecular polarization and the freezing point depression of salt solutions in benzene have shown that at higher concentration the ion-pairs interact to form quadrupoles and more complex aggregates. In some instances, as cryoscopic measurements have shown, the aggregates, on an average, may contain as many as 30 or 40 formula weights of salt.[15] This is true of salts of very large ions only. Salts of small ions are much less highly associated.[11]

With salts of larger ions, the mean molecular weight reaches a maximum value between 0.1 and 0.3 molar after which it decreases with increasing concentration. Apparently, the maximum is displaced toward lower concentrations with increasing size of the ions.[15]

As we have seen above, the conductance of salts in benzene reaches significant values at high concentrations. If allowance is made for viscosity, it follows that, in highly concentrated solutions, a considerable fraction of the salt exists as free ions that function as carriers of the electric current.

We can now picture what happens as we add benzene to a fused salt. Initially, the conductance increases due to the decreasing viscosity of the solution. When a sufficient amount of benzene has been introduced, which may be in the neighborhood of one or a few moles of benzene per mole of salt, ion-pairs begin to be formed. When the rate of formation of ion pairs is such that it overbalances the conductance increase due to viscosity decrease, the conductance passes through a maximum.

At the same time, the ion-pairs interact with one another to form more complex aggregates; these probably carry an excess of one or more units of charge. As more benzene is added, the aggregates build up to a maximum of complexity after which they begin to dissociate as more benzene is added.[15]

When the aggregates have largely dissociated to ion-pairs, triple ions are formed, as well as simple ions. The triple ions, as Fuoss and Kraus[16] have shown, are formed as a result of interaction of ions with ion-pairs. The minimum in the conductance curves is due, at least in part, to the formation of triple ions. Finally, at concentrations well below the minimum, the triple ions have disappeared and on further addition of benzene, the equivalent conductance increases in conformity with the laws of Bjerrum–Fuoss and of Debye–Hückel–Onsager.

Type III.—Systems of this type are very common; they include all cases in which the solvent is composed of polar molecules and the dielectric constant is sufficiently low to permit of the formation of ion-pairs. If the ions are sufficiently small and, particularly, if they carry multiple charges, ion-pairs may be formed even in aqueous solutions. In solvents of dielectric constant in the neighborhood of 35, ion-pairs are formed except in the case of salts of very large ions.[17]

With polar solvents of dielectric constant below 15 and above 6 or 8, nearly all salts form ion-pairs to such an extent that the conductance passes through a minimum. The conductance curves of salts in such solvents resemble those of salts in benzene except that the conductance at the minimum is much higher and that, at very low concentrations, ion-pairs are present in very small amount.

Whenever a minimum occurs in the conductance curve, a maximum also occurs at higher concentration if the salt is sufficiently soluble. This maximum is due to the increasing viscosity of the solution. As solvent is added to the fused salt, the conductance increases as a result of decreasing viscosity. When sufficient solvent has been added, ion-pairs are formed as a result of which conductance is decreased until it overbalances the viscosity effect, when the conductance passes through a maximum. On further addition of solvent, the ion-pairs dissociate and the conductance passes through a minimum. At still lower concentrations the conductance conforms to the requirements of the Bjerrum–Fuoss theory.

V. Summary

1. The conductance of eight salts has been measured in benzene at 25° at concentrations up to the limit of their solubility. Of them, two, tetra-*n*-butylammonium thiocyanate and tri-*n*-amylammonium picrate, were sufficiently soluble to permit of measurements through the maximum at 1.35 and 1.08 N, respectively. The thiocyanate was measured up to a concentration of 2.054 N where the solution contained one mole of benzene per ion of salt.

2. As these and earlier measurements show, all

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[14] W. M. Burgess, Thesis, Brown University, May, 1925.

[15] David T. Copenhafer, Thesis, Brown University, May, 1942; Howard S. Young, Thesis, Brown University, May, 1948.

[16] Fuoss and Kraus, THIS JOURNAL, 55, 2387 (1933).

[17] Pickering and Kraus, *ibid.*, 71, 3288 (1949).

salts exhibit a minimum in their conductance curves and the conductance increases sharply at higher concentrations. The increase is the more pronounced the lower the conductance at the minimum.

3. For salts with large anions, such as the picrate ion, the conductance curves are comparatively simple. With salts of simple ions, the curves are highly inflected.

4. It is suggested that concentrated salt solutions may be looked upon as solution of solvent in fused salt. The properties of concentrated solutions are discussed from this point of view.

PROVIDENCE, R. I. RECEIVED JULY 9, 1949

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Mechanism of Rotation of Long-chain Alkyl Bromides and Other Molecules in the Solid State[1]

BY JOHN D. HOFFMAN[2] AND CHARLES P. SMYTH[*]

It has been found that the normal long-chain alcohols rotate about their long molecular axes in the solid state provided the chain contains fourteen or more carbon atoms.[3] Observation of orientation polarization due to molecular rotation was rendered difficult in the study on alcohols by a direct current conductivity effect which resulted in Maxwell–Wagner polarization at low frequencies. Since it is to be expected that the proton transfer mechanism of conductivity postulated for the alcohols could not occur in the bromides the study of molecular rotation in the latter should not be hampered by conductivity effects.

Müller[4] has shown by X-ray techniques that rotation about the long axis in the solid is not observed in the normal long-chain hydrocarbons on warming until the chain contains twenty-two or more carbon atoms. The explanation tentatively advanced by Müller for the onset of rotation in the paraffins at about twenty-two carbon atoms was that the molecules achieved sufficient chain length to overcome end-group forces. It has seemed desirable to reconsider this hypothesis. Data on transition temperatures have been collected from the literature for alcohols, iodides and paraffins for purposes of comparison.

It was also found by Müller[5] that certain long-chain ketones showed a gradual increase in orientation polarization at 1.5 × 10^8 cycles/sec. prior to melting. This increase was marked even 30° below the melting point, and considerably exceeded the polarization of the corresponding paraffin, thus indicating molecular freedom in the solid state. The term "prerotation" will be used to describe the gradual onset of molecular rotational freedom below the transition or melting point.[6]

In this work, dielectric evidence of prerotation was sought in *n*-dodecyl, *n*-hexadecyl, *n*-octadecyl and *n*-docosyl bromides down to liquid nitrogen temperatures. *n*-Hexadecane was measured for purposes of comparison. The wide temperature range over which prerotation phenomena were observed suggested that Fowler's treatment of rotating diatomic molecules,[7] with extensive modifications, might predict the dielectric constants and rotational specific heats in the solid state at and below the transition point. Formation of liquid due to impurities and premelting[8] does not constitute a true prerotation effect, as has been discussed in a previous paper on molecular freedom in amines,[9] and care has been taken to minimize these effects by using pure materials.

Purification of Materials

We are indebted to Dr. E. Emmet Reid for the samples of pure *n*-dodecyl, *n*-hexadecyl and *n*-octadecyl bromides,[10] and to Dr. Nathan L. Drake of the University of Maryland for the sample of *n*-docosyl bromide. In addition, *n*-octadecyl bromide from the Matheson Co. (Paragon Div.) was purified by twice crystallizing from the melt, and then distilling under vacuum three times, each distillate being cut into five fractions and the product designated as II in Table I. This product is compared with that supplied by Dr. Reid which is designated as I. The sample of *n*-docosyl bromide supplied by Dr. Drake was further purified by high vacuum distillation. *n*-Hexadecane obtained from Paragon

TABLE I

PHYSICAL PROPERTIES OF THE ALKYL BROMIDE SAMPLES

Bromide	Densities 30°	Densities 60°	n_D		M. p.
n-Dodecyl	1.029	1.005	1.45747	(25°)	−9.70°
n-Hexadecyl	0.986	0.962	1.46075	(25°)	17.33°
n-Octadecyl(I)	.9760	.952	1.46145	(30°)	27.35°
n-Octadecyl(II)	.9754	.952	1.46105	(30°)	27 15°
n-Docosyl	....	...	1.46 (est.)	(40°)	42.7°

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[*] Harvard University Ph.D., 1921.

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(3)(a) Hoffman and Smyth, THIS JOURNAL, **71**, 431 (1949); (b) Baker and Smyth, *ibid.*, **60**, 122 (1938); (c) Ott, *Z. physik. Chem.*, **193**, 218 (1944).

(4) Müller, *Proc. Roy. Soc.* (*London*), **A138**, 514 (1932).

(5) Müller, *ibid.*, **A158**, 403 (1937).

(6) Smyth, *Trans. Faraday Soc.*, **42A**, 175 (1946).

(7) Fowler, *Proc. Roy. Soc.* (*London*), **A1419**, 1 (1935).

(8) Oldham and Ubbelohde, *ibid.*, **A176**, 50 (1940).

(9) Hoffman and Smyth, THIS JOURNAL, **71**, 3591 (1949).

(10) Meyer and Reid, *ibid.*, **55**, 1574 (1933).