[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Conductivities of Electrolytes in Anhydrous Acetic Acid*

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The recent contributions of Kraus, Fuoss and co-workers[2] on "The Properties of Electrolytic Solutions" have furnished the first satisfactory explanation of the unusual conductance phenomena exhibited by solutions of electrolytes in solvents with low dielectric constants. Since considerable interest has been shown in recent years in the properties of solutions in anhydrous acetic acid, which has a low dielectric constant,[3] $\epsilon = 6.25$, it was thought that additional studies[4] of conductivities in this solvent might prove of value especially in view of the above contributions.

In the present investigation conductance data have been obtained for solutions of certain quaternary ammonium salts, the chlorides and nitrates of the alkali metals and sodium acetate.

Experimental

The bridge assembly, thermostat and cells, as well as the method of purification of the solvent, were described previously.[4b] The specific conductivity of the acid used in the preparation of the solutions varied from 0.37 to 0.70 $\times 10^{-8}$ mho at 25°. Recently acid with a specific conductivity as low as 0.18 $\times 10^{-8}$ mho was obtained in quantity in this way.

Lithium chloride was prepared by the method of Richards and Willard.[5]

The chlorides of sodium, potassium and ammonium and the nitrates of lithium, sodium, potassium and cesium were purified by three recrystallizations of C. P. reagents from conductivity water and dried in an oven at 120° for three days.

Sodium acetate was prepared by the method of Davidson and McAllister.[6]

The quaternary ammonium compounds[7] were prepared by passing the corresponding halide into an alcoholic solution of trimethylamine. The second crop of crystals obtained from these solutions was then twice recrystallized from pure methyl alcohol and heated to constant weight at 120°.

The stronger solutions were made by adding weighed amounts of the dry salt to a known weight of pure acetic acid. The solutions of low concentration were obtained by dilution.

Discussion of Results

The experimental results are given in Tables I to XII. The concentrations are expressed in moles per liter. In calculating the equivalent conductances no solvent correction was applied.[8] The specific conductivity of the solvent is that measured at the completion of each dilution run. The starred values are for k-solvent varying between 0.40 and 0.70 $\times 10^{-8}$ mho. In each case at least two different samples of the solution were measured. In addition, duplicate dilution runs were made for several of the electrolytes. These results were in very good agreement with the data listed here but were omitted in order to conserve space.

A comparison with the results of Kolthoff and Willman[4a] is possible in the case of the sodium acetate and lithium chloride solutions. The data for sodium acetate are in satisfactory agreement but those obtained for lithium chloride in the present work are definitely higher. These differences might be due to a difference in the method of the preparation of the salt. Two separate preparations of lithium chloride were studied in the present work and the data obtained were in excellent agreement.

An examination of curves in which values of Λ were plotted against $\sqrt{c}$ indicated them to be of the type previously described[8] for solutions in solvents of low dielectric constants. In the dilute range the slope of such curves is chiefly determined by the ion pair equilibrium.[9] In the more concentrated solutions the effect of triple ion formation[10] is evident. The data for tetramethyl-

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(2) Series of publications in THIS JOURNAL and in *Trans. Faraday Soc.* Number XIX of this series, the latest to date, may be found in *Trans. Faraday Soc.*, **32**, 594 (1936). A review of the major portion of this work appears in *Chem. Rev.*, **17**, 29 (1935).

(3) Seward and Hamblet, THIS JOURNAL, **54**, 554 (1932).

(4) (a) Kolthoff and Willman, *ibid.*, **56**, 1007 (1934); (b) Weidner, Hutchison and Chandlee, *ibid.*, **56**, 1285 (1934).

(5) Richards and Willard, *ibid.*, **32**, 4 (1910).

(6) Davidson and McAllister, *ibid.*, **52**, 519 (1930).

(7) All the quaternary ammonium compounds were very kindly prepared by Mr. J. H. Jones of this Laboratory.

(8) Application of a solvent conductance correction showed a curvature in the log Λ *vs.* log c plots which seemed anomalous and also gave somewhat less satisfactory agreement with what might be expected from Walden's rule. Furthermore, some uncertainty exists regarding the nature of the solvent conductance. In view of these considerations it seemed best not to make a correction.

(9) Fuoss and Kraus, THIS JOURNAL, **55**, 476 (1933).

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

Table I

Lithium Chloride

k-solvent = 0.41×10^{-8}

C	Λ
0.02434	0.1852*
.01539	.1951*
.01084	.2243
.007224	.2512
.004100	.3089
$.0_{3}3703$	.8449
$.0_{3}2853$	.9470
$.0_{4}9322$	1.538
$.0_{4}5439$	1.928
$.0_{4}3136$	2.436
$.0_{4}2044$	2.916
$.0_{4}1206$	3.627
$.0_{5}801$	4.30
$.0_{5}497$	5.29
$.0_{5}354$	6.11
$.0_{5}252$	7.16

Table II

Sodium Chloride

k-solvent = 0.45×10^{-8}

C	Λ
0.003764	0.1651*
.002550	.1910
.001711	.2279
$.0_{3}5547$	.3822
$.0_{3}3383$	.4805
$.0_{3}2045$	.6092
$.0_{3}1251$	.7706
$.0_{4}7686$	.9787
$.0_{4}4769$	1.231
$.0_{4}2836$	1.592
$.0_{4}1666$	2.071
$.0_{4}1001$	2.66
$.0_{5}716$	3.14
$.0_{5}584$	3.46

Table III

Potassium Chloride

k-solvent = 0.47×10^{-8}

C	Λ
0.01060	0.1364*
.006675	.1620*
.004407	.1888*
.002507	.2574*
.001915	.2630*
$.0_{3}9772$	.3602
$.0_{3}5901$	.4543
$.0_{3}3434$	.5853
$.0_{3}1512$	.8636
$.0_{4}8452$	1.159
$.0_{4}4876$	1.533
$.0_{4}3040$	1.907
$.0_{4}1833$	2.442
$.0_{4}1188$	3.01
$.0_{5}688$	3.95
$.0_{5}448$	4.95
$.0_{5}300$	6.12

Table IV

Ammonium Chloride

k-solvent = 0.50×10^{-8}

C	Λ
0.002575	0.2241
.001704	.2680
$.0_{3}9797$	.3401
$.0_{3}5815$	.4357
$.0_{3}2907$	.5993
$.0_{3}1642$	.7751
$.0_{4}9789$	.9841
$.0_{4}5552$	1.287
$.0_{4}3171$	1.646
$.0_{4}1879$	2.100

Table V

Lithium Nitrate

k-solvent = 0.39×10^{-8}

C	Λ
0.02736	0.2355
.009935	.2389
.002933	.3129
$.0_{3}5423$	.4837
$.0_{3}3279$	.5510
$.0_{3}1501$	.687
$.0_{4}9154$	.829
$.0_{4}5568$	.102
$.0_{4}3653$	1.24
$.0_{4}2619$	1.49

Table VI

Sodium Nitrate

k-solvent = 0.43×10^{-8}

C	Λ
0.007934	0.2060*
.004541	.2423*
.003266	.2573
.001689	.3190
$.0_{3}9262$	.3906
$.0_{3}5066$	.4767
$.0_{3}2279$	.6231
$.0_{3}1426$	.739
$.0_{4}8747$	.882
$.0_{4}5053$	1.112
$.0_{4}3165$	1.365
$.0_{4}1875$	1.772
$.0_{4}1120$	2.270
$.0_{5}819$	2.69
$.0_{5}522$	3.34

Table VII

Potassium Nitrate

k-solvent = 0.47×10^{-8}

C	Λ
0.01246	0.2407*
.009466	.2435*
.006219	.2675*
.004190	.3047*
.001824	.4087
.001219	.4736
$.0_{3}5783$	.6278
$.0_{3}2121$	.929
$.0_{3}1134$	1.199
$.0_{4}6720$	1.477
$.0_{4}3910$	1.860
$.0_{4}2362$	2.32
$.0_{4}1452$	2.88
$.0_{5}906$	3.53
$.0_{5}635$	4.13
$.0_{5}433$	4.91
$.0_{5}315$	5.82

Table VIII

Cesium Nitrate

k-solvent = 0.50×10^{-8}

C	Λ
0.002329	0.3938*
.001310	.5033*
$.0_{3}7033$	.6514*
$.0_{3}5932$	.7003
$.0_{3}2913$	.9454
$.0_{3}1572$	1.228
$.0_{4}9061$	1.549
$.0_{4}4917$	2.010
$.0_{4}2789$	2.59
$.0_{4}1630$	3.22
$.0_{5}957$	3.97
$.0_{5}567$	4.90
$.0_{5}432$	5.59

Table IX

Tetramethylammonium Chloride

k-solvent = 0.56×10^{-8}

C	Λ
0.1153	1.551*
.05136	0.8053*
.01970	.5264*
.01227	.5064*
.008150	.5242*
.005610	.5630*
.002749	.6995
.001771	.820
$.0_{3}5373$	1.365
$.0_{3}1062$	2.806
$.0_{4}1974$	6.12
$.0_{4}1151$	7.36
$.0_{5}647$	9.23
$.0_{5}372$	10.97
$.0_{5}250$	12.29

Table X

Tetramethylammonium Bromide

k-solvent = 0.45×10^{-8}

C	Λ
0.002287	0.6813
.001247	.8505
$.0_{3}9725$	.9477
$.0_{3}6095$	1.155
$.0_{3}3223$	1.528
$.0_{3}1822$	1.976
$.0_{3}1044$	2.549
$.0_{4}679$	3.106
$.0_{4}474$	3.64

Table XI

Trimethyl-n-butylammonium Bromide

k-solvent = 0.57×10^{-8}

C	Λ
0.008222	0.5121
.004988	.5601
.003063	.6401
.001990	.7327
.001169	.9107
$.0_{3}4954$	1.303
$.0_{3}2710$	1.692
$.0_{3}1635$	2.12
$.0_{4}9668$	2.68
$.0_{4}5736$	3.42

Table XII

Sodium Acetate

k-solvent = 0.48×10^{-8}

C	Λ
0.02966	0.05347*
.02000	.07820*
.01676	.07901*
.009629	.09637
.005797	.1195
.001482	.2167
$.0_{3}8832$	.2773
$.0_{3}4635$	.3798
$.0_{3}2498$	.5149
$.0_{3}1296$	.7160
$.0_{4}6980$	.9748
$.0_{4}3920$	1.312
$.0_{4}2465$	1.664
$.0_{4}2149$	1.973
$.0_{4}1140$	2.682
$.0_{5}549$	3.96

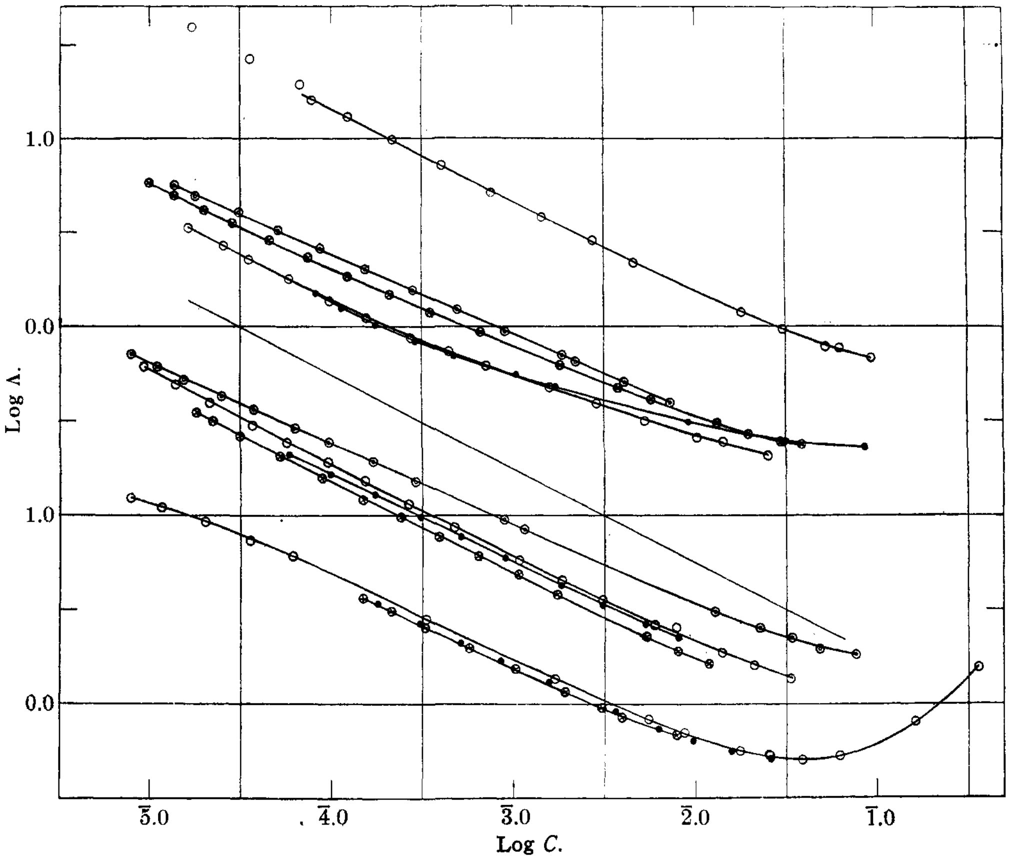

Fig. 1.—The ordinates have unit value. In plotting, the second and third groups of curves and the upper simple curve have been displaced by 1, 2 and 3 units, respectively. The straight line has a slope of $-1/2$. In the first group: ○, tetramethylammonium chloride; ⊗, tetramethylammonium bromide; and ●, trimethyl-*n*-butylammonium bromide. The second group are for the chlorides: ⊙, lithium; ○, potassium; ⊗, sodium; and ●, ammonium. The third group are nitrates: ⊙, cesium; ⊗, potassium; ●, lithium; and ○, sodium. The top curve is for sodium acetate.

ammonium chloride solutions show a distinct minimum due to this effect while in the case of the other substances investigated it is apparent that, though not reached, a minimum is being approached. More concentrated solutions were not investigated because of solubility limitations in the case of several of the materials used. Plots of log Λ against log *C*, Fig. 1, gave nearly straight lines indicative of small values for the ion pair dissociation constant.[9,11]

The limiting equivalent conductances and the ion pair dissociation constants for several of the salts were evaluated by the methods of Kraus and Fuoss.[2] Unfortunately these calculations must be based on the data obtained in the more dilute solutions where considerable uncertainty exists regarding the influence of the solvent conductances in the case of acetic acid. Because of this difficulty the numerical values obtained are of doubtful significance. The results, however, were in reasonable accord with the general predictions of the theory.

We wish to acknowledge the kindness of Professor C. A. Kraus in discussing with us certain points in regard to the interpretation of these data.

Summary

The specific conductances of a number of uni-univalent electrolytes have been determined in dilute solutions in acetic acid with a specific conductivity varying from 0.37 to 0.70×10^{-8} mho at 25°.

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(11) Kraus and Fuoss, THIS JOURNAL, 55, 21 (1933).