to the reaction mixture effected by opening stopcock D and clamp N. The rate of delivery was reasonably constant, since a high head of mercury (30") was used; and stirring was quite vigorous, at approximately 1800 r.p.m. Nitrogen was passed through during the entire addition. The volume of solution delivered between the calibration marks was measured in blank runs at the same delivery speed. After addition of the approximately 25-ml. portion of ferrous solution from the delivery tube, the latter was removed from the reaction vessel, and a second portion of ferrous solution (normally ten times as concentrated as the first), was added rapidly from an ordinary volumetric pipet in order to consume the persulfate and leave an excess of ferrous solution which could be titrated.

The apparatus shown in Fig. 2 was designed to permit the collection of any oxygen which might be evolved in the slow addition experiments. The solutions were freed from oxygen before the start of the experiment by evacuation for 20 minutes. The technique employed for the slow addition was similar to that used with the apparatus of Fig. 1. After completion of the reaction, the contents of the reaction vessel were forced up into the evacuated buret N and any gas which had formed was there measured.

Calculations.—The calculations for the rapid mixing experiments (Tables II–V) are straightforward. For the slow addition experiments of Table I the calculations were performed as follows: Let A = ml. Ce^{+4} equivalent to total volume of Fe^{+2} added rapidly. Let B = ml. Ce^{+4} equivalent to Fe^{+2} remaining in reaction mixture at end of rapid reaction. Then $A - B = C$ = ml. Ce^{+4} equivalent to portion of rapidly added Fe^{+2} which reacted = ml. Ce^{+4} equivalent to $S_2O_8^=$ left unreacted after slow addition.

Let D = ml. Ce^{+4} equivalent to total $S_2O_8^=$ taken. Then $D - C = E$ = ml. Ce^{+4} equivalent to total $S_2O_8^=$ reacted.

Let F = Ce^{+4} equivalent to total vol. of Fe^{+2} added slowly. Then $F/E \times 2 = Fe^{+2}$ reacted/$S_2O_8^{-2}$ reacted = molar reaction ratio during slow addition. For the slow addition experiments of Table VI, the over-all reaction ratio was calculated simply as $((A + F) - B)^2/D$.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, THE UNIVERSITY OF PENNSYLVANIA]

Conductivity Studies in Methanol[1,2]

BY E. CHARLES EVERS AND ANDREW G. KNOX

The conductance of dilute solutions of a number of quaternary ammonium and other 1–1 salts was investigated in methanol. Limiting equivalent conductances and ion–ion pair equilibrium constants have been evaluated using the methods of Kraus and Fuoss and of Shedlovsky; the merits of the two methods are considered and the results are discussed in the light of what is known regarding these ions in other solvents. Limiting ionic conductances have been evaluated by the method of Kraus and Fowler and compared with values obtained by Hartley from transport data. Methanol has been purified to the point where its specific conductance has ranged between 2 and 7 × 10^{-9} mho.

Introduction

The following investigation was undertaken to secure accurate data on the conductivity of dilute solutions of 1–1 salts in methanol, particularly those of the quaternary ammonium type which have been given thorough investigation in water and in various non-aqueous solvents largely by Kraus and his co-workers.[3]

The most reliable data in methanol previously reported appear to have been obtained by Hartley and his co-workers.[4] These investigators examined a large number of salts of the alkali and alkaline earth metals as well as several salts of the tetramethylammonium and tetraethylammonium types. We have checked the conductivity of several of these salts and have obtained particularly good agreement with their data for potassium chloride.

The conductance data were analyzed using the extrapolation methods of Fuoss and Kraus[5] and of Shedlovsky.[6] Both methods lead substantially to the same values for the limiting equivalent conductance, Λ_0; but in methanol the value of the dissociation constant for the ion-ion pair equilibrium K, computed by the method of Fuoss, is generally twice that obtained by the Shedlovsky method. As these authors have pointed out recently[7] such a difference is to be expected in a solvent of fairly high dielectric constant.

Limiting equivalent ionic conductances have been computed by the method first suggested by Fowler and Kraus[8] which consists of halving the conductance of a salt whose anion and cation conductances are assumed equal; *n*-octadecyltrimethylammonium *n*-octadecylsulfate was employed as the standard electrolyte in this study.

Finally, we have been able to purify methanol to a point where its specific conductance has ranged between 2 and 7 × 10^{-9} mho; consequently, the conductance of the solvent usually was negligible and this has largely eliminated uncertainties associated with the application of a correction for solvent conductance.

Experimental

1. **Salts.**—Spectroscopically pure potassium chloride was kindly supplied us by Dr. K. Krieger of this Laboratory.

Sodium chloride was Mallinckrodt Analytical Reagent Grade salt which was further purified by precipitation from solution with hydrogen chloride, only the middle third portion being retained. The product was recrystallized from conductivity water.

Potassium picrate was prepared by mixing stoichiometric amounts of picric acid with alcoholic potassium hydroxide. The salt was recrystallized from water and from 50% ethanol.

Potassium *n*-octadecylsulfate prepared by Dr. W. E. Thompson was obtained from Dr. C. A. Kraus. It was re-

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(1) Taken from the Thesis of Andrew G. Knox submitted in partial fulfillment of the requirements for the Ph.D. degree, June, 1950.

(2) Presented before the Meeting of the American Chemical Society, Division of Physical and Inorganic Chemistry, in Detroit, Michigan, April, 1950.

(3) C. A. Kraus, *Ann. N. Y. Acad. Sci.*, **51**, 789 (1949).

(4) (a) J. E. Frazer and H. Hartley, *Proc. Roy. Soc.* (*London*), **A109**, 351 (1925); (b) H. Hartley, A. Unmack and D. M. Murray-Rust, *ibid.*, **A127**, 228 (1930); (c) A. Unmack, E. Bullock, D. M. Murray-Rust and H. Hartley, *ibid.*, **A132**, 427 (1932); (d) E. D. Copley and H. Hartley, *J. Chem. Soc.*, 2488 (1930); (e) T. H. Mead, O. L. Hughes and H. Hartley, *ibid.*, 1207 (1933).

(5) R. M. Fuoss, THIS JOURNAL, **57**, 488 (1935); R. M. Fuoss and C. A. Kraus, *ibid.*, **55**, 476 (1933).

(6) T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

(7) R. M. Fuoss and T. Shedlovsky, THIS JOURNAL, **71**, 1496 (1949).

(8) D. L. Fowler and C. A. Kraus, *ibid.*, **62**, 2237 (1940).

crystallized from methanol, m.p. 180–181° (liquid crystals to 225°) (cor.).

n-Octadecyltrimethylammonium *n*-octadecylsulfate was prepared by the metathesis of *n*-octadecyltrimethylammonium nitrate with potassium *n*-octadecylsulfate in anhydrous isopropyl alcohol. After filtering off potassium nitrate the solution was concentrated and cooled to Dry Ice temperature to precipitate the product. The salt was leached with hexane, then recrystallized successively from anhydrous methanol, isopropyl alcohol and a 90% methanol–10% hexane mixture, m.p. 153.5–156.5° (cor.). The *n*-octadecyltrimethylammonium nitrate had been prepared from the iodide (supplied us by Dr. H. Daggett) by metathesis with silver nitrate in methanol solution. The nitrate was precipitated from solution at Dry Ice temperature and recrystallized from acetone.

n-Octadecyltrimethylammonium picrate was prepared by reacting the hydroxide with picric acid in methanol solution. It was recrystallized from methanol, m.p. 132–133° (cor.). The hydroxide was prepared from the iodide by reaction with moist silver oxide in methanol solution.

The symmetrical quaternary ammonium picrates were prepared by treating the corresponding hydroxides (prepared from the iodides) with picric acid in aqueous solution. The quaternary ammonium iodides were prepared by refluxing the trialkyl amines with the corresponding alkyl iodides; silver oxide was used to convert the iodides to hydroxides. Solvents used in their purification and the m.p.'s of the several salts were: tetramethylammonium picrate, 60% ethanol, m.p. 320° (cor.); tetraethylammonium picrate, ethanol and water, m.p. 254° (cor.); tetra-*n*-propylammonium picrate, 80% ethanol–20% ethyl acetate mixture, m.p. 114–115° (cor.); tetra-*n*-butylammonium picrate, 50% ethanol, m.p. 89° (cor.). The tetraethyl and tetra-*n*-butyl salts were prepared by Mr. M. H. Gruber.

Tetraisoamylammonium picrate was prepared as outlined above for the normal salts. The iodide was prepared by refluxing triisoamylamine and isoamyl iodide for 24 hours in ethanol; it was purified by the method of Kraus and Fuoss.[9] The picrate was recrystallized from ethanol, m.p. 85.5–86.5° (cor.).

Tri-*n*-butylammonium picrate was obtained by mixing tri-*n*-butylamine with picric acid in a water–ethanol mixture. The salt was recrystallized from ethanol, m.p. 104–105° (cor.).

2. **Methanol.**—Solvent having a specific conductance of 2–7 $\times 10^{-9}$ mho was obtained by treating it successively with magnesium metal, then silver nitrate,[9a] agitating it over activated alumina and finally distilling and storing it in an atmosphere of nitrogen. The treatment in detail follows: approximately 4.5 liters of synthetic methanol (Carbide and Carbon Chemicals Corporation) were refluxed over 50 g. of magnesium metal for 24 hours, care being taken to exclude atmospheric moisture. The middle fraction from distillation (4 l.) was refluxed for 24 hours with silver nitrate, then distilled with exclusion of atmospheric moisture and carbon dioxide. The middle fraction (3.5 l.) was rolled for 24 hours over activated alumina (Eimer and Amend Company, 8–14 mesh, heated to 450°). It was next filtered through sintered glass with the application of nitrogen pressure and collected in a still pot in an atmosphere of purified nitrogen. Final distillation was made in an atmosphere of nitrogen in an all-glass system. The rate of take-off was controlled by means of a ground-in glass needle valve, sealed with mercury, which was placed between the fractionating column and condenser. The conductance of the distillate was carefully checked as distillation proceeded by means of a small cell of approximately 50-cc. capacity (cell constant, 0.06054) which was sealed into the system between the condenser and receiving flask. The cell was fitted at its lower end with an automatic syphon which discharged the contents of the cell on filling. By means of this device it was possible to judge at what point to commence the collection of alcohol having a sufficiently low conductance. Ordinarily, collection was commenced when the specific conductance was 7 $\times 10^{-9}$ mho; invariably the conductance improved as distillation proceeded, reaching approximately 1.5 $\times 10^{-9}$ toward the end. On the average, a total of 500 cc. was discarded in this operation. Electrodes (cell constant, 0.0853) were also sealed in the storage flask in order to check accurately the conductance of the methanol employed in conductance measurements; consequently a very accurate correction could be made for solvent conductance when necessary. It may be pointed out that in order to store methanol for any period of time it is essential to properly condition the pyrex glass vessel. A suitable procedure was to steam the glass well, then treat with hot methanol vapor before the apparatus was assembled. Using this procedure we have been able to store methanol whose conductance was 5 $\times 10^{-9}$ for several weeks without material change.

3. **Apparatus and Procedure.**—The weight dilution method as described by Mead, Fuoss and Kraus[10] was employed in making conductivity measurements. Suitable means were provided to transfer solvent into the cell and carry out dilutions under an atmosphere of nitrogen in order to avoid contacting the solvent with air. Solutions were made up by weight and corrected to vacuum. In calculating concentrations on the volume basis it was assumed that the density of the solutions were the same as the density of the pure solvent. The following constants for the solvent at 25° were employed in calculations: dielectric constant, 32.63[11]; viscosity, 5.44 and 10^{-3} poise[12]; density, 0.7864 g./cc.[4] Values of fundamental constants were taken from Birge.[13]

Resistances were measured with a Leeds and Northrup Company Jones-type a.c. bridge at frequencies of 1, 2, 3 and 4 thousand cycles per sec.; polarization effects were corrected for by extrapolating a plot of resistance against the reciprocal of the frequency to infinite frequency. Since the electrodes were lightly platinized, polarization corrections amounted to no more than 0.03% in the more dilute solutions and to no more than 0.3% in the more concentrated solutions.

Two cells of the Erlenmeyer type were employed[5]; the cell constants were 0.12440 and 0.12869. These constants were determined by comparing them with a cell of the pipet type whose constant (0.25227) was evaluated by comparing it with a larger cell (cell constant = 14.543) employed as the standard. The standard cell was calibrated using the accepted values for the specific conductance of a 0.01 demal solution of potassium chloride as given by Jones and Bradshaw.[14]

Conductivity measurements were carried out in an oil-filled thermostat at 25 ± 0.01° with control to 0.002°. The temperature of the bath was established with a platinum resistance thermometer calibrated by the Bureau of Standards.

It was often noted that in the most dilute solutions (below approximately 0.0001 *N*) the resistance would decrease slightly with time (as much as 0.1%) even though temperature equilibrium had been established. But on shaking the cell gently, so as to change the liquid between the electrodes, the resistance returned consistently to a reproducible value, no matter how long between readings or its value before shaking. Accordingly, the resistances recorded are those obtained immediately after shaking. This effect may have been caused by desorption of electrolyte from the platinized electrodes.

It may be pointed out that in general a check of the m.p. is not sufficient evidence for establishing the purity of the salts employed in this study in so far as their conductance is concerned. Consequently, a salt was acceptable as pure only when the values of the conductance between two successive recrystallizations agreed within less than 0.1%.

Results

Values of the equivalent conductance, Λ, and the concentration in gram equivalents per liter, *C*, are presented in Table I. The results of two independent series of determinations are recorded for most salts.

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[9] C. A. Kraus and R. M. Fuoss, THIS JOURNAL, **55**, 21 (1933).

[9a] Suggested by Dr. H. Daggett.

[10] D. J. Mead, R. M. Fuoss and C. A. Kraus, *Trans. Faraday Soc.*, **32**, 594 (1936).

[11] P. S. Albright and L. J. Gostling, THIS JOURNAL, **68**, 1061 (1946); T. T. Jones and R. M. Davies, *Phil. Mag.*, **28**, 307 (1939).

[12] H. Hartley and H. R. Raikes, *J. Chem. Soc.*, 524 (1925); A. E. Dunstan and F. B. Thole, *ibid.*, 1556 (1909).

[13] R. T. Birge, *Rev. Mod. Phys.*, **13**, 233 (1941).

[14] G. Jones and B. C. Bradshaw, THIS JOURNAL, **55**, 1780 (1933)

TABLE I

CONDUCTANCE OF SOME SALTS IN METHANOL AT 25°

$C \times 10^4$	Λ
a. Tri-*n*-butylammonium picrate	
11.923	79.34
4.9195	82.97
3.1648	84.24
2.2500	85.04
1.2656	86.13
0.81000	86.73
9.5666	80.46
5.1711	82.91
2.9929	84.45
2.1433	85.21
1.2232	86.21
0.85082	86.69
b. Tetraisoamylammonium picrate	
8.6730	75.21
3.7714	77.78
2.2922	78.86
1.7345	79.37
1.1194	80.02
0.80802	80.42
0.62821	80.67
7.9355	75.49
4.4058	77.35
2.6276	78.54
1.8063	79.22
1.0527	80.06
0.74788	80.47
c. Sodium chloride	
39.930	82.94
22.363	86.19
17.247	87.42
10.311	89.55
7.1770	90.77
5.1393	91.73
3.4633	92.74
2.4056	93.51
1.7240	94.09
1.2837	94.52
0.82247	95.07
0.59121	95.41
0.42837	95.71
45.901	82.18
23.435	85.99
13.772	88.44
8.3405	90.33
5.8226	91.39
3.7752	92.51
2.7556	93.19
1.4246	94.30
0.91566	94.86
0.58890	95.31
d. Tetra-*n*-butylammonium picrate	
42.719	70.11
15.864	76.09
10.278	78.01
7.6784	79.12
4.8400	80.60
3.5006	81.44
2.4149	82.27
1.8171	82.80
1.3526	83.30
31.652	72.13
15.880	75.98
7.2469	79.26
4.4986	80.71
2.9653	81.73
1.3853	83.15
1.0343	83.56
e. *n*-Octadecyltrimethylammonium picrate	
14.600	72.10
5.6930	75.89
3.9046	77.01
2.6374	77.96
1.5901	78.93
1.1278	79.48
12.341	72.81
5.3824	76.13
3.6328	77.27
2.7922	77.88
1.9796	78.57
1.4019	79.14
f. Tetramethylammonium picrate	
23.775	101.50
6.3252	108.57
3.6864	110.38
2.9002	111.02
1.4738	112.53
1.0060	113.17
0.77387	113.53
0.67191	113.71
21.632	102.08
5.4382	109.11
3.6214	110.42
2.6929	111.23
1.7503	112.15
1.3042	112.70
g. Tetraethylammonium picrate	
59.552	86.82
31.742	91.77
22.392	94.14
16.484	95.97
10.362	98.30
7.1182	99.89
5.0445	101.13
3.7908	102.03
3.1898	102.49
2.4211	103.20
1.5351	104.11
1.1990	104.51
0.94206	104.87
17.581	95.54
11.512	97.77
5.7936	100.56
3.6941	101.98
2.9173	102.62
1.5625	103.92
1.1004	104.50
h. *n*-Octadecyltrimethylammonium *n*-octadecylsulfate	
13.337	57.29
6.5690	59.22
4.9684	60.51
3.7018	61.26
2.2983	62.25
1.5006	62.95
1.0262	63.48
0.79370	63.77
0.66651	63.94
12.688	58.39
6.7704	59.62
4.6959	60.68
3.3893	61.48
2.1815	62.36
1.4376	63.06
i. Potassium *n*-octadecyl sulfate	
8.0146	75.68
3.9800	77.83
2.3043	79.14
1.7213	79.70
1.3456	80.13
1.0816	80.45
6.1355	76.62
3.8573	77.94
2.5921	78.92
1.9825	79.46
1.6410	79.80
1.3179	80.13
j. Tetra-*n*-propylammonium picrate	
12.766	83.81
6.4821	86.48
4.0885	87.88
2.9241	88.71
2.3932	89.15
1.5055	90.01
1.0363	90.57
0.76773	90.94
16.810	82.43
6.5485	86.43
4.2973	87.74
3.2616	88.45
2.0079	89.50
1.3317	90.20
0.97970	90.61
k. Potassium chloride	
40.743	89.25
25.040	92.40
17.347	94.35
11.909	96.08
8.0372	97.67
5.3361	99.02
4.0160	99.85
2.8090	100.70
2.0592	101.34
1.4982	101.89
1.0181	102.44
0.77405	102.74
51.495	87.64
36.096	90.11
25.110	92.34
15.241	94.97
9.4679	96.99
7.0331	98.08
4.4944	99.45
3.4114	100.14
2.6147	100.75
1.6900	101.60
1.2034	102.11
0.84291	102.60
0.65756	102.88
l. Potassium picrate	
26.926	84.92
20.967	86.57
7.0824	91.95
5.0086	93.23
3.0976	94.59
2.0786	95.95
1.6538	96.43
0.91776	96.86

Discussion

Up to a concentration of approximately 0.001 N the data for the salts here reported were found to follow the square root law; at higher concentrations the curves bend upward slightly. Square root plots for potassium chloride, sodium chloride and tetramethylammonium picrate are shown in Fig. 1, where the data obtained by Hartley and coworkers[4a,4e] are included for comparison. The radii of the circles representing experimental points are equivalent to 0.05 Λ unit or approximately 0.05% on the ordinate; it will be noted that in the

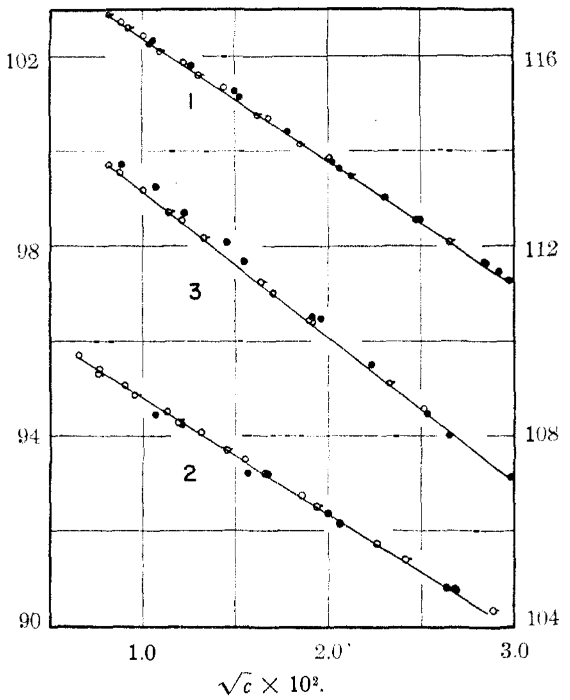

Fig. 1.—Conductances in methanol: Curve 1, potassium chloride, left ordinate: O run 1, O- run 2; ● Frazer and Hartley, ref. (4a). Curve 2, sodium chloride, left ordinate: O run 1, O- run 2; ● Frazer and Hartley, ref. (4a). Curve 3, tetramethylammonium chloride, right ordinate: O run 1, O- run 2; ● Mead, Hughes and Hartley, ref. (4e).

present investigation the maximum deviation of the points from the straight line relation in no case exceeds 0.05%, and the mean deviation is much lower; this is representative of all data presented in this paper. Hartley's data for potassium chloride are seen to agree exceedingly well with our results.[14a] In the case of sodium chloride, two of Hartley's data in the more dilute end lie approximately 0.25% below our curve, but the remaining data are within 0.05%. But in the case of tetramethylammonium picrate, Hartley's data lie well above our values in the dilute end and approach our results as the concentration is increased. A straight line could be drawn through Hartley's data, but this would yield a line having a greater slope. Hartley also studied tetraethylammonium picrate but we have not presented a plot for this salt since his data lie as much as 0.6% above our values in the dilute region.

1. **Analysis of Data.**—The straight line relation referred to above actually represents a region of inflection in the conductivity curves. The dielectric constant of methanol (32.6) is sufficiently low so that ion association causes a positive deviation from Onsager's theoretical slope. For most salts in methanol the slope of the square root plot is approximately 20% greater than theory (Table II), although a few salts, notably those of the monotomic ions, come very close to theory. Since an extrapolation of these plots would obviously yield high values for the limiting equivalent conductance, we are forced to employ extrapolation functions which correct for the deviation from theory caused by ion association.

TABLE II

LIMITING EQUIVALENT CONDUCTANCES AND DISSOCIATION CONSTANTS FOR SOME ELECTROLYTES IN METHANOL

Salt	Δ	Λ_0	$K_S \times 10^4$	$K_F \times 10^4$
a. Quaternary ammonium picrates				
$(CH_3)_4NPi$	21.0	115.94	340	460
$(C_2H_5)_4NPi$	20.2	107.43	380	500
$(n\text{-}C_3H_7)_4NPi$	15.7	93.09	380	550
$(n\text{-}C_4H_9)_4NPi$	14.4	86.10	380	580
$(i\text{-}C_5H_{11})_4NPi$	14.0	82.52	390	560
b. Salts for ionic conductances				
$(C_{18}H_{37})(CH_3)_3NC_{18}H_{37})SO_4$	28.1	65.73	270	410
$(C_{18}H_{37})(CH_3)_3NPi$	21.8	82.13	230	280
$K(C_{18}H_{37})SO_4$	23.1	83.04	240	300
KPi	20.0	99.31	360	480
c. Other salts				
$(n\text{-}C_4H_9)_3NHPi$	25.6	89.00	250	315
KCl	8.8	104.93	680	1210
NaCl	3.5	97.25	830	2200

Fuoss[5] and Shedlovsky[6] have proposed functions which enable us to compute the limiting conductance, Λ_0, and the dissociation constant, K, from the conductivity data itself. The two methods lead to identical values for Λ_0, but in solvents of moderately high dielectric constant such as methanol, where ion association is not marked, the values of K differ appreciably. The reason for this difference lies in the fact that different equations are employed to represent the conductance of those ions which are free, *i.e.*, the hypothetical conductance of the completely dissociated electrolyte in the solvent under consideration. The Fuoss analysis is based on Onsager's limiting law whereas Shedlovsky uses a modified form of this equation which approaches the limiting slope from above. In the latter respect the modified equation follows the general behavior pattern of strong electrolytes in water, which normally approach the limiting slope from above. Because of this, Fuoss and Shedlovsky[7] have reasoned that free ions should exhibit a similar behavior in solvents of lower dielectric constant and have concluded that the extrapolation function based on the Shedlovsky equation is to be preferred, especially when the dissociation constant is greater than approximately 10^{-3}. Unfortunately, as a result of ion association, it is seemingly impossible in non-aqueous solvents to decide by direct experiment which equation best represents the conductivity of the free ions. Accordingly, we have analyzed our data by both methods with the results shown in Table II where K_F is the constant according to Fuoss and K_S is the constant derived from the Shedlovsky treatment; Δ is the per cent. deviation of the empirical inflection slope from the theoretical limiting slope on the square root plot.

The difference to be encountered on using the two methods of extrapolation for data in methanol is clearly illustrated by the results in Table II; graphically, the Shedlovsky treatment yields

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[14a] This agreement is somewhat fortuitous since Hartley used Kohlrausch's values for the conductance of KCl in water as standard which lie approximately 0.1% above those of Jones and Bradshaw.

straight lines having the steeper slopes and hence the lower values of K.

It is not the purpose of this paper to present a detailed discussion of the two methods as applied to data in several solvents, but it may be pointed out that many examples are available which may be treated more conveniently by one method than by the other. In methanol both methods have given linear plots to sufficiently high concentrations so that an unambiguous extrapolation may be carried out to infinite dilution. In doubtful cases, however, it is strongly recommended that both methods of analyses be applied; taken together, the two treatments enable a less arbitrary choice of the limiting intercept.

2. **Dissociation Constants.**—As may be seen from Table II, the dissociation constants for ion–ion pair equilibria in methanol are uniformly high. Of particular interest are the constants for the symmetrical quaternary ammonium picrates listed in Part a of the table. In the case of K_F there is a uniform increase in the constant with increasing cation size. This behavior is expected in light of Bjerrum's[15] theory which calls for an increase in dissociation with increasing ion size. Values of K_S on the other hand are practically constant, which does not permit of such a satisfying physical interpretation. On going from the tetra-*n*-butyl- to the tetraisoamylammonium salt, K_F is seen to decrease slightly whereas K_S increases slightly. Although the two methods give roughly similar results it is seen that somewhat different conclusions may be arrived at if the results are subject to detailed consideration.

It is of interest to note that replacing a methyl group in the symmetrical tetramethylammonium salt by an octadecyl group produces a small but significant decrease in the constant. Such a result is unexpected and points to specific interactions which doubtless involve the solvent. In ethylene chloride,[16,17] for example, substitution of bulkier octadecyl groups for methyl groups causes a progressive increase in the constant. Also of interest is the fact that substitution of a butyl group by hydrogen in the symmetrical tetrabutylammonium salt causes only a slight lowering of the dissociation constant. This behavior parallels that found in pyridine,[3] a basic solvent, and is explained by the bonding of solvent with the hydrogen of the cation. In a non-basic solvent, such as nitrobenzene,[3] where there is no opportunity for such bonding, the presence of hydrogen on the cation results in a very marked enhancement of ion pair formation.

On combining our values of K_S for potassium salts with those derived from Hartley's data,[4] we have sufficient information to obtain some notion of the effect of the constitution of the negative ion on ion–ion pair equilibria. In order of decreasing interaction we have the following values for K_S: potassium octadecylsulfate, 240; potassium nitrate, 275; potassium picrate, 360; potassium chloride, 680; potassium bromide, 760; potassium thiocyanate, 780; potassium iodide, 1000. Potassium thiocyanate excepted, it is seen that the polyatomic anions interact more strongly with the potassium ion than do monoatomic ions; furthermore, the constant increases regularly with increasing size of the halide ion. The octadecylsulfate and nitrate ions behave effectively as small ions; in this respect the nitrate ion in methanol behaves much as it does in water where deviations from Onsager's limiting slope for the conductance of potassium nitrate has been interpreted as being due to incomplete dissociation.[18]

3. **Limiting Ionic Conductances.**—Since transference data are lacking in non-aqueous solvents generally, limiting ionic conductances have been estimated either by applying Walden's rule or by halving the conductance of some 1–1 electrolyte whose cation and anion conductances are assumed equal. Using the latter method, Kraus and his coworkers[3,8] have taken the conductances of the tetra-*n*-butylammonium and triphenylborofluoride ions as being equal and have employed the conductance of these ions as standards in computing ion conductances in a number of solvents. As a further check on the method, Thompson and Kraus[19] investigated the possibility of employing *n*-octadecyltrimethylammonium *n*-octadecylsulfate as a standard electrolyte. In ethylene chloride they found that the conductance of the *n*-octadecyltrimethylammonium ion obtained by using the borofluoride as standard was 23.6 units as compared with 22.6 obtained on halving the conductances of the double long chain salt. Although these results indicated that either salt was suitable as a standard, it was concluded that tetra-*n*-butylammonium triphenylborofluoride was the better standard in as much as it was probable that the *n*-octadecylsulfate ion might have a somewhat lower conductance than the *n*-octadecyltrimethylammonium ion.

In methanol, an opportunity is afforded for directly comparing ionic conductances as derived by the above method with those obtained through the use of transport data. Nonhebel and Hartley[20] have obtained transport data for the hydrogen ion (transport no. = 0.735 at 0.001 N) by measuring the e.m.f. of hydrogen chloride cells with and without liquid junction; combined with conductance measurements, this gave a value for the hydrogen ion of $\Lambda_0^+ = 142.2$.

Since tetra-*n*-butylammonium triphenylborofluoride is not stable in methanol[21] we have derived ionic conductances using *n*-octadecyltrimethylammonium *n*-octadecylsulfate as the standard electrolyte with the results given in Table III. The Λ_0 value for the standard was found to be 65.73, resulting in a value of 32.9 per ion. Our data proved to be mutually consistent by comparing the experimental value of Λ_0 for potassium picrate with that calculated by combining potassium and picrate ionic conductances derived from the experimental

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[15] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, p. 42.

[16] H. L. Pickering and C. A. Kraus, THIS JOURNAL, **71**, 3288 (1940).

[17] C. R. Witschonke and C. A. Kraus, *ibid.*, **69**, 2472 (1947).

[18] Reference 15, p. 146.

[19] W. E. Thompson and C. A. Kraus, THIS JOURNAL, **69**, 1016 (1947).

[20] G. Nonhebel and H. Hartley, *Phil. Mag.*, **50**, 729 (1925).

[21] H. Daggett, private communication.

values of Λ_0 for potassium *n*-octadecylsulfate (83.04) and *n*-octadecyltrimethylammonium picrate (82.13). Thus, Λ_0^+ for potassium (50.2) plus that for the picrate ion (49.2) gave 99.4, as compared with the experimental value of 99.31.

Table III

Ionic Conductance in Methanol

Cation	Λ_0^+	Anion	Λ_0^-
Octd. Me_3N	32.9	Octd. SO_4	32.9
K	50.2	Pi	49.2
Na	42.5	Cl	54.7
Me_4N	66.7		
Et_4N	58.2		
n-Pr_4N	43.9		
n-Bu_4N	36.9		
i-Am_4N	33.3		
n-Bu_3NH	39.9		

Of the values in Table III those for potassium chloride can be best compared with Hartley's results, since his value of Λ_0 for potassium chloride is exactly the same as that obtained in this investigation. Consequently, any differences in the ionic conductances of the potassium ion can be attributed solely to differences in the two methods. Hartley obtained 53.8 for the potassium ion as compared with 50.2 by Kraus' method, a difference of 3.6 units or 7%. Since hydrogen is a fast ion, any errors in determining its mobility would be magnified percentage-wise in calculating the conductance of slower ions. Thus, if the conductance of the hydrogen ion were 2.5% lower, the same value would be obtained for potassium as given here. Furthermore, if Thompson's observations[19] extend to methanol, the results with the long chain salt are apt to be somewhat low. In view of these factors it may be concluded that the Kraus method cannot be greatly in error and is particularly useful for comparing results in several solvents. In this connection it may be pointed out that calculation of the Walden product, $\Lambda_0^+\eta$, for the tetra-*n*-butylammonium ion in acetone, ethylene dichloride, pyridine and nitrobenzene has yielded the values, 0.204, 0.206, 0.212 and 0.212, respectively (based on tetra-*n*-butylammonium triphenylborofluoride). In methanol, using Hartley's ionic conductances, we obtained 0.222, whereas with the long chain salt as standard we obtain 0.202. This suggests that Hartley's value may be slightly high.

As yet we do not have data on enough substituted ammonium ions to gain much information regarding the effect of structure on their relative mobilities. However, in the series of quaternary ammonium salts here reported the tetramethylammonium ion shows a proportionately greater resistance per carbon atom than do the larger members of the series; as the size increases the resistance per carbon atom decreases slightly. On the same basis, the resistance of the tri-*n*-butylammonium ion is too high; its resistance lies between that of the tetra-*n*-propyl- and tetra-*n*-butylammonium ions. These results closely parallel those found in other solvents.[3]

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[Contribution from the Chemistry Division of the Argonne National Laboratory]

Spectrophotometry of Neptunium in Perchloric Acid Solutions[1]

By R. Sjoblom and J. C. Hindman

As a preliminary to the investigation of various problems in the solution chemistry of neptunium, details of the absorption spectra of the neptunium(III), (IV), (V) and (VI) ions in various perchloric acid concentrations have been investigated. The analytical usefulness of the various absorption bands has been tested in one molar perchloric acid solution. The spectrum of neptunium(VI) has been found to contain a vibrational fine structure similar to that found for the U(VI) and Pu(VI) ions. As in the case of the plutonium and uranium ions this fine structure is interpreted as arising from symmetrical metal-oxygen vibrations in ions of the type NpO_2^{++}. The vibrational frequency of the Np(VI) ion is 715 cm.$^{-1}$ in one molar perchloric acid, 709 cm.$^{-1}$ in ten molar perchloric acid and 704 cm.$^{-1}$ at *p*H 2.7 (in one molar sodium perchlorate). Evidence is also cited for a vibrational fine structure in the spectrum of Np(V). In this case a vibrational frequency of 753 cm.$^{-1}$ is found in one molar perchloric acid. No evidence has been obtained that would indicate any extensive degree of complex formation between Np^{+3} (hydrated) or Np^{+4} (hydrated) and perchlorate at total perchloric acid concentrations up to ten molar. On the basis of the spectral observations and the data on the disproportionation reaction $2Np(V) \rightleftarrows Np(IV) + Np(VI)$, which occurs at perchloric acid concentration above five molar it is concluded that the ions NpO_2^{++} and NpO_2^+ probably exist even in eight to ten molar acid although the possible existence of ions such as $NpOOH^{++}$ and $NpOOH^{+++}$ cannot be excluded.

Several publications have emphasized the application of absorption spectrum measurements in studies involving the solution behavior of the actinide elements, particularly of uranium[2] and plutonium.[3] Preliminary data on the characteristics of the absorption spectra of the different oxidation states of neptunium have appeared.[4] The purpose of the present investigation was three-

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[1] Presented in part before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Chicago Meeting, Sept. 1950.

[2] J. Sutton, Canadian Research Council Document, CRC-325, "Ionic Species in Uranyl Solutions," March 21, 1947.

[3] (a) G. E. Moore and K. A. Kraus, Paper No. 4.22, "The Transuranium Elements," Vol. 14B of the Plutonium Project Record of the National Nuclear Energy Series, McGraw-Hill Book Co., Inc., New York, 1949. (b) R. E. Connick, M. Kasha, W. H. McVey and G. E. Sheline, Paper No. 4.20, "The Transuranium Elements," Vol. 14B of the National Nuclear Energy Series, McGraw-Hill, New York, 1949. (c) J. C. Hindman, Papers 4.2, 4.4, 4.5 and 4.7, "The Transuranium Elements," Vol. 14B of the Plutonium Project Record of the National Nuclear Energy Series, McGraw-Hill, New York, 1949.

[4] J. C. Hindman, L. B. Magnusson and T. J. LaChapelle, This Journal, **71**, 687 (1949), paper No. 15.2, "The Transuranium Elements," Vol. 14B of the Plutonium Project Record of the National Nuclear Energy Series, McGraw-Hill, New York, 1949.