[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Studies on the Chemistry of Halogens and of Polyhalides. III. Electrical Conductances of Some Polyhalogen Complexes in Acetonitrile at 25°[1,2]

BY ALEXANDER I. POPOV AND NORMAN E. SKELLY[3]

RECEIVED APRIL 26, 1954

The electrical conductance of the following salts has been determined in acetonitrile at 25°: $(CH_3)_4NIBr_2$, $(CH_3)_4NIBrCl$, $(CH_3)_4NBr_3$, $(CH_3)_4NCl$, $(CH_3)_4NBr$, $(CH_3)_4NI$ and $CsIBr_2$. The polyhalogen complexes behaved as strong electrolytes, while the tetramethylammonium halides show some association. The limiting conductances were determined from the Λ *vs.* $\sqrt{c}$ plots and the experimentally obtained slopes are compared with the ones derived from the Onsager equation. While considerable deviation occurs with the simple halides, the agreement was quite good in the case of polyhalogen complexes. The dissociation constants and the limiting conductances were calculated for the tetramethylammonium halides using the method of Fuoss and Kraus, and of Fuoss and Shedlovsky.

Introduction

Spectrophotometric studies on polyhalogen complexes in acetonitrile have indicated that these compounds undergo a ready dissociation into a polyhalide anion and a corresponding cation, according to the mechanism

$$MX_n \rightleftarrows M^+ + X_n^-$$

where M^+ may be a tetraalkylammonium ion, trialkylsulfonium, a metal ion, or a complex halide cation of the type PCl_4^+, PBr_4^+, *etc.*, while X_n^- may be ICl_2^-, IBr_2^-, I_3^-, ICl_4^-, etc.[1] However, since spectrophotometric studies do not yield information as to the extent of such dissociation, it was decided to investigate the electrical conductance of these complexes in acetonitrile. For the sake of comparison the conductances of simple tetramethylammonium halides were likewise determined.

Literature survey indicated that the studies on the electrical conductances of polyhalogen complexes are quite sparse. Kuz'menko and Fialkov[4] have reported that phosphorus hexabromoiodide and phosphorus hexachloroiodide form conducting solutions in acetonitrile. The conductance of tetramethylammonium triiodide and pentaiodide in nitromethane has been studied by Walden and Birr.[5] These investigators have also studied the conductances of a number of substituted ammonium salts in acetonitrile.[6] Their results showed good agreement with the Onsager theory in the case of fully substituted salts, and a lesser agreement for the partially substituted ones.

Of the simple tetramethylammonium halides only the iodide conductance in acetonitrile was reported by Walden.[7]

Experimental

Apparatus.—The conductivity measurements were made with a Campbell-Shackelton shielded ratio box, manufactured by the Leeds and Northrup Company. A 3-inch oscilloscope was used as a null point indicator. Over-all accuracy of the instrument was within 0.1% of the resistance measured.

Three cells of the Jones–Bollinger type[8] were used in this investigation so as to keep the measured resistance in the 1000–15,000 ohm region. All the measurements were made with unplatinized electrodes. The cell constants were determined with known potassium chloride solutions using the values given by Shedlovsky.[9] A slight Parker effect[10] was observed, which made it necessary to calibrate the cells with several solutions of potassium chloride at different dilutions and to construct a calibration curve for each cell. As determined with a 0.001 *N* potassium chloride the three cell constants were 1.822, 0.7219, and 0.1278. The change in cell constants for the extreme solutions did not exceed 0.5%. The cells were thermostated in an oil-bath, and the temperature was maintained at 25 ± 0.003°.

Reagents.—Tetramethylammonium halides were obtained from the Eastman Kodak Company. They were recrystallized from alcohol-water mixture. Gravimetric analysis for the halide ion indicated purity of better than 99.5%.

The tetramethylammonium polyhalides described in this investigation were prepared by the method of Chattaway and Hoyle.[11] The melting point of the tribromide was 118° as compared with the reported value of 118.5°,[11] that of the dibromoiodide was 192°, reported, 192°,[11] and the chlorobromoiodide melted at 205–206°, reported, 205°.[11] Iodometric titration in each case indicated approximately 99% purity.

Cesium dibromoiodide was prepared by the addition of a bromine solution in ethanol to a water–ethanol solution of cesium iodide, and the resulting solution was heated to approximately 70°. Upon cooling, red crystals of the product precipitated out. They were filtered, washed with ethanol and dried. Iodometric titration indicated only 97% purity. Repeated attempts to prepare a purer compound either by variation of the synthesis, or by recrystallization were fruitless.

Acetonitrile was purified by the method described by Wawzonek and Runner.[12] The purified solvent boiled at 81.5° at 750 mm. of pressure. The specific conductance of the solvent varied between $0.8\text{–}1.5 \times 10^{-7}$ ohm^{-1}cm.$^{-1}$.

Solutions.—Solutions down to 10^{-3} *M* concentration were prepared by dissolving weighed amounts of an appropriate salt in a known volume of the solvent. Solutions of lower concentration were prepared by diluting 10^{-3} *M* stock solutions. Fresh stock solutions were prepared for each set of measurements, which were made within 2–3 hours. All glassware was recalibrated at 25°. With the exception of the tetramethylammonium tribromide all of the solutions were stable for at least 24 hours.

The correction for the conductance of the solvent never exceeded 1–2% of the total conductance for the most dilute solutions.

Results and Discussion

The variations of equivalent conductance with the square root of concentration are given in Table

---

(1) Previous papers of this series are: (a) THIS JOURNAL, **74**, 4672 (1952); (b) *ibid.*, **74**, 6127 (1952).

(2) Abstracted in part from the Ph.D. thesis of Norman E. Skelly, State University of Iowa, 1955.

(3) Du Pont Postgraduate Fellow, 1953–1954.

(4) A. A. Kuz'menko and Ya. A. Fialkov, *Zhur. Obshchei Khim.*, **21**, 473 (1951).

(5) P. Walden and E. J. Birr, *Z. physik. Chem.*, **163**, 263 (1932–33).

(6) P. Walden and E. J. Birr, *ibid.*, **144**, 269 (1929).

(7) P. Walden, *ibid.*, **54**, 183 (1906); *Bull. Acad. Sci. Imper. St. Petersburg*, 438 (1913).

(8) G. Jones and G. M. Bollinger, THIS JOURNAL, **53**, 411 (1931).

(9) T. Shedlovsky, *ibid.*, **54**, 1411 (1932).

(10) H. C. Parker, *ibid.*, **45**, 1366, 2017 (1923).

(11) F. D. Chattaway and G. Hoyle, *J. Chem. Soc.*, **123**, 654 (1923).

(12) S. Wawzonek and M. E. Runner, *J. Electrochem. Soc.*, **99**, 457 (1952).

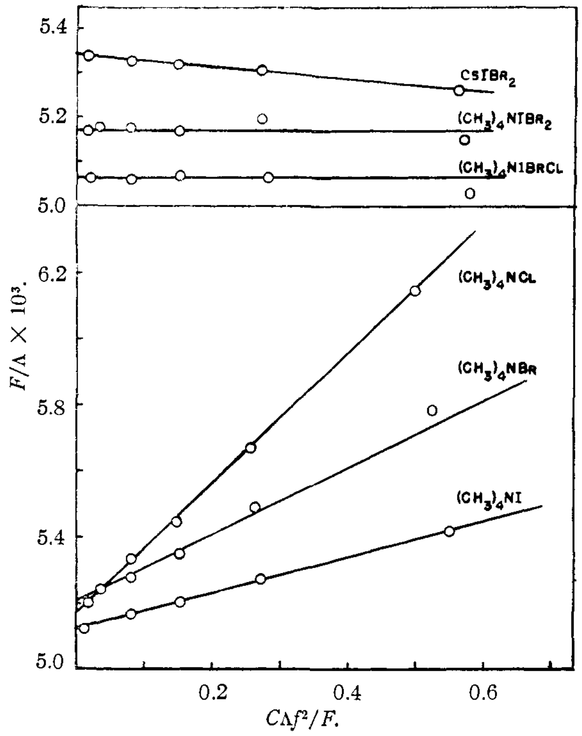

Fig. 1.—The Fuoss and Kraus plots for the polyhalogen complexes, and the simple halides in acetonitrile at 25°.

I. The values recorded represent the average of two independent runs, which agree to better than 0.2%. The calculated equivalent conductance was a linear function of the square root of the concentration for solutions $\leqslant 4 \times 10^{-3}$ *M*. The limiting conductance and the slope were obtained by the least square method, and the experimental slope was compared with the theoretical slope as calculated from the Onsager equation. Results are shown in Table II.

TABLE I

EQUIVALENT CONDUCTANCES IN ACETONITRILE AT 25°

Concn., *M*	$(CH_3)_4$-NCl	$(CH_3)_4$-NBr	$(CH_3)_4$-NI	$(CH_3)_4$-$NIBr_2$	$(CH_3)_4$-NIBrCl	$CsIBr_2$
0.00005	190.4	190.8	192.2	...		
.0001	188.5	189.2	190.0	189.6	193.7	183.7
.0002	184.8	185.9	188.2	187.5	191.7	181.9
.0005	179.5	181.5	185.3	184.8	189.3	179.5
.001	172.8	176.1	180.5	181.7	185.6	176.3
.002	162.2	167.3	173.9	176.0	180.9	172.0
.005	142.8	151.1	160.6	167.9	172.3	163.7
.01	...	...	...	159.9	163.5	156.2

TABLE II

COMPARISON OF CALCULATED AND ONSAGER SLOPES

Salt	Slope Exp.	Slope Onsager	Δ[a]	Λ_0 (extrap.)
$(CH_3)_4NCl$	743	367	102	195.8
$(CH_3)_4NBr$	696	367	90	196.9
$(CH_3)_4NI$	473	369	28	195.3[b]
$(CH_3)_4NIBr_2$	385	367	5	193.4
$(CH_3)_4NIBrCl$	367	370	−1	197.3
$(CH_3)_4NBr_3$	..	..	..	(201)
$CsIBr_2$	333	363	−8	186.9

[a] $\Delta = 100\,(S_{(obsd)} - S_{(calcd)})/S_{(calcd)}$. [b] The value given by Walden[7] is 205.

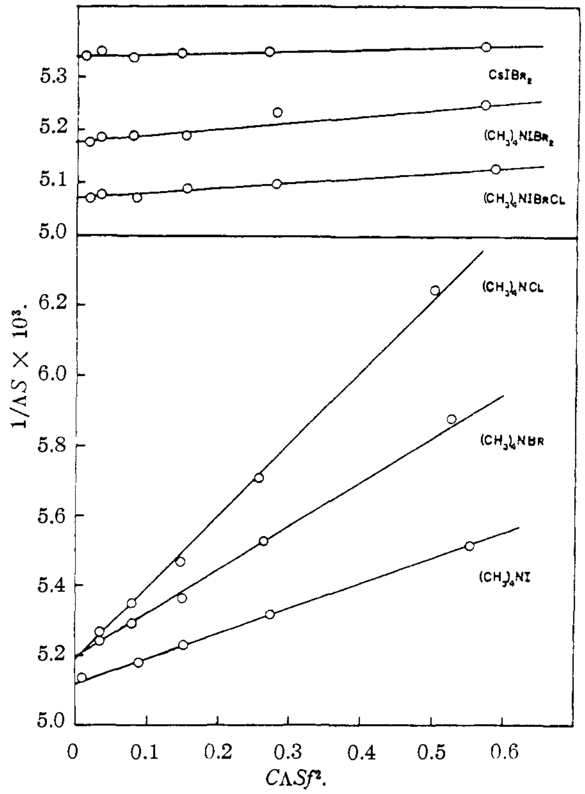

Fig. 2.—The Fuoss and Shedlovsky plots for the polyhalogen complexes and the simple halides in acetonitrile at 25°.

The Onsager equation for a 1–1 electrolyte in acetonitrile at 25° has the form: $\Lambda = \Lambda_0 - (229 + 0.716\ \Lambda_0)\sqrt{c}$. The solvent has a dielectric constant of 36.7 and its viscosity at the same temperature is 0.00344 poise.[13]

Since the tribromide was rather unstable in acetonitrile, only an approximate value for the limiting conductance was obtained by extrapolating the data obtained in a series of rapid measurements on freshly prepared solutions. No attempt was made, in this case, to determine the experimental slope.

It is well known that the polyhalogen ions dissociate in solution into a halogen or interhalogen molecule and a halide ion. However, recent studies of the dissociation of I_3^-, IBr_2^- and ICl_2^- in acetonitrile show that the dissociation constants are of the order of magnitude of 10^{-7}.[14] Therefore, the dissociation is too small to significantly influence the conductance of polyhalide salts at the concentrations used.

As seen from Table II the agreement between the experimental and the theoretical slopes for the tetramethylammonium dibromoiodide, the chlorobromoiodide, and the cesium dibromoiodide is very good, indicating that these complexes behave as strong electrolytes.

On the other hand, the simple tetramethylammonium halides have a much steeper slope than the one predicted by the Onsager equation, and are, therefore, somewhat associated in solution.

---

(13) S. Glasstone, "Introduction to Electrochemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1942, p. 90.

(14) (a) R. E. Buckles and J. Mills, THIS JOURNAL, **76**, 4845 (1954); (b) A. I. Popov and N. E. Skelly, to be published

The correct value of the limiting conductance and the extent of ionization of these salts, were calculated using the method of Fuoss and Kraus.[15] Since the dissociation constants were greater than 10^{-3} the results were recalculated using the method proposed by Fuoss and Shedlovsky.[16] Figs. 1 and 2, respectively, indicate the results obtained by the two methods and the respective dissociation constants are given in Table III.

TABLE III

CALCULATED LIMITING CONDUCTANCES AND DISSOCIATION CONSTANTS

Salt	Λ_0 (calcd.)	F. and K. method $K \times 10^2$	F. and S. method, $K \times 10^2$
$(CH_3)_4NCl$	193.1	1.30	1.29
$(CH_3)_4NBr$	192.7	4.58	2.41
$(CH_3)_4NI$	195.3	4.94	3.62
$(CH_3)_4NIBrCl$	197.2	..	..
$(CH_3)_4NIBr_2$	193.0	..	..
$CsIBr_2$	187.1	..	..

Thus the two treatments agree, in that the tetramethylammonium polyhalides behave as strong electrolytes in acetonitrile, while the tetramethylammonium halides are considerably associated. Cesium dibromoiodide likewise appears to be a strong electrolyte.

It is interesting to note that there is a large difference in the solubilities of the simple halides and of the polyhalides in acetonitrile. The polyhalogen complexes are easily dissolved in this solvent and may form solutions containing as much as 40 g. of the polyhalide per 100 ml. of solvent at 25°. On the other hand, the simple halides dissolve with great difficulty, the solubility of the tetramethylammonium chloride, bromide and iodide being 0.265, 0.170 and 0.183 g., respectively, per 100 ml. of solvent at the same temperature.[7b,17]

It seems from the above data that the polyhalide ions are considerably more solvated by acetonitrile than the simple halide ions. This is probably to be expected since it is well known that compounds capable of acting as Lewis bases strongly polarize interhalides, especially if the latter contain iodine. This increased solvation, then can likewise account for the fact that the polyhalides form stronger electrolytes in acetonitrile than the simple halides.

Acknowledgment.—This work was partially supported by a grant from the Research Corporation.

IOWA CITY, IOWA

---

[15] (a) R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 476 (1933); (b) R. M. Fuoss, *ibid.*, **57**, 488 (1935).

[16] R. M. Fuoss and T. Shedlovsky, *ibid.*, **71**, 1496 (1949).

[17] P. Walden, *Z. physik. Chem.*, **55**, 712 (1906).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF CALIFORNIA BERKELEY]

Complexing of Magnesium Ion by Fluoride Ion

BY ROBERT E. CONNICK AND MAAK-SANG TSAO

RECEIVED MAY 14, 1954

The complexing of magnesium ion by fluoride ion was measured by the "ferri"[1,2] method. The equilibrium quotient for complex formation at 25° and an ionic strength of 0.50 is 20. The heat and entropy changes are 4 ± 2 kcal. and 19 ± 7 e.u., respectively. Upper limits were set for fluoride complexing of calcium and barium ions. The available data on fluoride complexes of positive ions are consistent qualitatively with an ionic type of binding.

The fluoride complexing of a number of $+3$[1-7] and $+4$[2,8,9] ions has been studied recently, but of the $+2$ ions only beryllium[4,10] has been investigated quantitatively. To clarify the effects of charge and radius on the stability of such complexes it was desirable to have data on the other alkaline earth ions.

Experimental

The method was essentially that employed by Brosset and Orring[1] and Dodgen and Rollefson[2] in their studies of fluoride complexing of Al^{+3} and Th^{+4}, respectively. Complexing of the $+2$ cation is determined indirectly by studying its effect on the fluoride complexing of Fe^{+3}, as measured potentiometrically through the Fe^{++}-Fe^{+++} couple.

Two cells were used—a reference cell and a sample cell. Each cell consisted of a pair of half cells connected by an agar-agar bridge of 1.5 *M* sodium perchlorate. Each half cell contained 5.87×10^{-4} *M* ferric perchlorate, 2.315×10^{-4} *M* ferrous perchlorate and equal concentrations of perchloric acid. The sample half cells contained equal concentrations of alkaline earth perchlorate. To all half cells was added sufficient sodium perchlorate to give an ionic strength of 0.50.

Successive portions of sodium fluoride solution were added to one half cell of the reference and sample cells and the e.m.f. recorded. With no fluoride present the e.m.f.'s were less than 0.2 mv., usually less than 0.1 mv., and became constant within five minutes after addition of fluoride. Platinum electrodes were used. The solutions were stirred, and the cell and stirrer were coated with paraffin to prevent attack of the glass by hydrofluoric acid.

A magnesium perchlorate solution was prepared by dissolving analytical reagent grade magnesium oxide in perchloric acid. Barium and calcium perchlorate solutions were similarly prepared from $Ba(OH)_2$ and $CaCO_3$. Sodium perchlorate solutions were made by neutralization of perchloric acid with sodium carbonate. Pure iron wire was dissolved in excess perchloric acid and partially oxidized with hydrogen peroxide to give a mixed ferrous and ferric perchlorate solution. Distilled water was re-distilled from alkaline permanganate for use in all solutions.

---

[1] C. Brosset and J. Orring, *Svensk Kem. Tid.*, **55**, 101 (1943).

[2] H. W. Dodgen and G. K. Rollefson, THIS JOURNAL, **71**, 2600 (1949).

[3] A. S. Wilson and H. Taube, *ibid.*, **74**, 3509 (1952).

[4] H. W. Dodgen and L. M. Yates, presented at Fall Meeting of the American Chemical Society at Atlantic City, 1952.

[5] S. W. Mayer and S. D. Schwartz, THIS JOURNAL, **73**, 222 (1951).

[6] Z Z. Hugus, L. G. Hepler and J. W. Kury, unpublished work, this Laboratory.

[7] M. S. Tsao, Thesis, University of California, Berkeley, 1952.

[8] C. K. McLane, "National Nuclear Energy Series, Division IV—Plutonium Project Record," Vol. 14B, McGraw-Hill Book Co., Inc., New York, N. Y., 1949, p. 414.

[9] R. E. Connick and W. H. McVey, THIS JOURNAL, **71**, 3182 (1949).

[10] K. E. Kleiner, *J. Gen. Chem. (U.S.S.R.)*, **21**, 19 (1951), Consultants Bureau Translation.