Discussion

The information available at present would not permit one to distinguish between formulas such as $HCb_3(SO_4)_6 \cdot xH_2O$ and $H_8Cb_6O_3(SO_4)_{12} \cdot xH_2O$ or between $K_4Cb_3(OH)_3(SO_4)_6 \cdot 9H_2O$ and $K_8Cb_6O_3(SO_4)_{12} \cdot 21H_2O$. The latter compound is undoubtedly the same as that previously represented as $4K_2O \cdot Cb_2O_5 \cdot 2Cb_2O_3 \cdot 12H_2SO_4 \cdot 12H_2O$,[3] but no evidence has been found from this work to indicate a variation in composition as previously reported.

The numerous compounds of molybdenum, vanadium, columbium and tantalum which can be represented as containing six metal atoms[6] would lead one to favor a similar structure for the complex sulfates. The latter also bear an interesting resemblance to a complex chloride prepared by dry methods[7] which contained columbium in a lower oxidation state. This compound and its solutions were deep green in color and were reported to be remarkably stable with respect to oxidation, but could be oxidized and decolorized by strong oxidizing agents. Lack of accurate data on the oxidation number of the columbium has caused it to be variously represented as $Cb_6Cl_{14} \cdot 7H_2O$ (oxidation number 2.33) and $Cb_3OCl_7 \cdot 3H_2O$ (oxidation number 3) but the possibility of the columbium having an oxidation number of 3.333 or 3.67 should not be overlooked. In solution, only two of the fourteen chlorides are precipitated by silver nitrate, the other twelve apparently existing in a complex which may resemble that of the complex sulfate.

The various intense colors exhibited by solutions of columbium in lower oxidation states have been the cause of much speculation and have often been attributed to the formation of different complexes in different concentrations of sulfuric acid and to different hydrates of trivalent columbium.

While the acid concentration was found to affect these colors it should be noted that all three colors mentioned previously could be produced in approximately 45% acid by varying the average oxidation number of the columbium only. It is of further interest that a red compound containing columbium with an average oxidation number of 3.67 was isolated from the red solutions and a green substance (actually dichroic) containing columbium with an average oxidation number approximating 3.33 was obtained from the green solutions. Both these oxidation numbers are represented by simple ratios of tri- and pentavalent columbium.

Summary

A complex columbium sulfate having a ratio of two trivalent columbium atoms to one pentavalent atom and a SO_4:Cb ratio of 2.00 precipitated from 75% sulfuric acid during electrolytic reduction of pentavalent columbium.

Sodium, potassium and ammonium salts were prepared all containing columbium with an average oxidation number of 3.67 and having an SO_4:Cb ratio of 2.00. The monovalent ion content varied for different ions.

The crystal type of the potassium salt was found to be monoclinic and density measurements indicated $K_8Cb_6(OH)_6(SO_4)_{12} \cdot 18H_2O$ per unit cell.

A green (actually dichroic) complex sulfate containing columbium with an average oxidation number approximating 3.33 was prepared.

The complex sulfates described offer a possible means of separating tantalum from columbium.

Cambridge, Mass. Received July 10, 1948

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(6) Pauling, *Chem. Eng. News*, **25**, 2970 (1947).

(7) Harned, This Journal, **35**, 1078 (1913).

[Contribution from Metcalf Research Laboratory, Brown University]

Properties of Electrolytic Solutions. XL. Conductance of Aluminum Bromide in Several Solvents and of Methylaluminum Bromides in Methyl Bromide[1]

By William J. Jacober[2] and Charles A. Kraus

I. Introduction

The properties and, particularly, the conductance of uni-univalent salts in a number of non-aqueous solvents, as well as in water, have been measured with a reasonable degree of precision. Higher types of salts, however, have received but little attention and, except for aqueous solutions, little is known concerning their properties. In general, the salts of multivalent ions of the more electropositive elements are difficultly soluble in non-aqueous solvents. Salts of multiply charged ions of less electropositive elements are often soluble in non-aqueous solvents but they are ordinarily weak electrolytes. The properties of solutions of such salts are often greatly influenced by interaction with solvent molecules or with impurities that may be present.

It seemed worth while to study the conductance of aluminum bromide in nitrobenzene, pyridine and methyl bromide; the dielectric constants of these solvents are, nitrobenzene, 34.5 and pyridine 12.3 (at 25°) and methyl bromide 10.6 (at 0°) and 15.7 (at −78°). The dielectric

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(1) This paper is based on a portion of a thesis presented by William J. Jacober in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Graduate School of Brown University, October, 1942.

(2) University Fellow, Brown University, 1940–1941; Ethyl Corporation Fellow, 1941–1942.

constants of these solvents are sufficiently high to yield solutions of fairly high conductance with typical uni-univalent salts. They differ in type, however, and it is of interest to discover to what extent interaction between aluminum bromide and the solvent molecules affects the properties of its solutions in these solvents. Aluminum bromide is well suited for a study of this kind since it is quite soluble in a variety of solvents and it may be purified and manipulated with ease.

The conductance of aluminum bromide in nitrobenzene has been measured by Plotnikov and his co-workers[3] and Wertyporoch and Adamus.[4] Müller[5] measured the conductance of aluminum bromide in pyridine. The solvents used in these earlier investigations were not properly purified as is indicated by their high specific conductance and the erratic nature of the experimental results. With a salt such as aluminum bromide, the greatest care is required in the purification of solvents.

II. Materials, Apparatus and Procedure

1. **Materials.**—Nitrobenzene was purified according to the method of Witschonke[6] except that after initial treatment with hydrochloric acid and washing and drying, it was distilled from a solution of aluminum chloride (50 g. to 3 liters) after which it was again washed and dried. Thereafter it was distilled according to Witschonke's directions. The solvent had a specific conductance of 1×10^{-10}.

Pyridine was purified according to the method of Burgess[7]; its specific conductance was 1×10^{-10}.

Methyl bromide of 99% purity was condensed on 15 g. of aluminum bromide in a stainless steel tank. To remove the hydrogen bromide that was formed, the methyl bromide was passed through a 100-cm., packed, scrubbing tower maintained between 5 and 10°. The bromide forms a hydrate below 4°.[8] Approximately one millimole of acid was scrubbed out per mole of methyl bromide. After scrubbing, the methyl bromide was passed over calcium chloride and then condensed on calcium chloride in a stainless steel tank. After standing some time, the methyl bromide was condensed in a third tank containing activated alumina. After standing in this tank for a week or more, the material was ready for use. It had a specific conductance of $1\text{-}2 \times 10^{-10}$. Using the parallel arm bridge, the dielectric constant of methyl bromide was determined to be 10.6 at 0° and 15.7 at −78°.

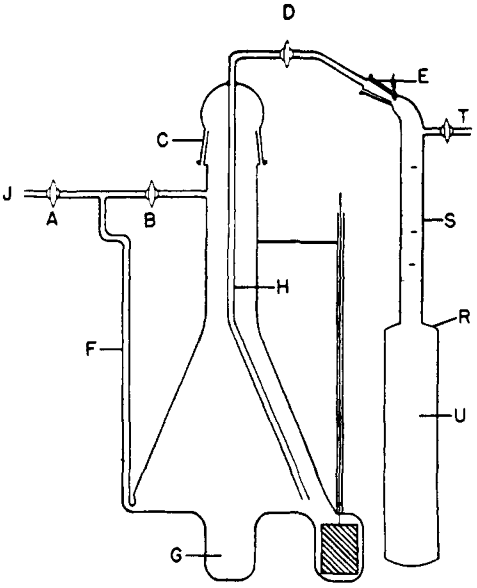

Fig. 1.—Conductance cell with attached dilution pipet.

Aluminum bromide was prepared by passing bromine vapor over fresh turnings of pure aluminum. Reaction set in at 500° and proceeded smoothly thereafter at 300°. A white product was obtained which was further purified by several distillations. The material was filled into weighed, fragile bulbs by a method similar to that used by Kraus and Nelson.[9] An atmosphere of pure, dry nitrogen was used in all operations.

Methylaluminum dibromide and dimethylaluminum bromide were prepared according to the method of Hnizda and Kraus.[10] The desired amount of dry, freshly cut aluminum was placed in a two-liter, round bottom flask equipped with a methyl bromide inlet, a product discharge line, thermometer and manometers, provision for heating and cooling and a safety trap. About 0.1% of aluminum bromide or the product of a previous reaction was placed on one spot of the aluminum and the reaction vessel was closed. Air was exhausted from the apparatus and methyl bromide was introduced at a pressure of 1.5 atmospheres, while the flask was heated to 100°. Once started, the reaction is autocatalytic and highly exothermic. Methyl bromide was added while the flask was cooled so as to maintain a suitable reaction rate at a temperature below 75° within the charge. When about 90% of the aluminum had reacted, a black coating appeared and reaction ceased. The water-white, oily liquid was decanted or vacuum-distilled into a suitable container in order to separate it from the metallic sludge. The material is highly reactive toward air, water or oxygen-bearing compounds; however, its reaction with air is not violent. The two methylaluminum bromides are formed in equimolar proportions; no evidence was found of the formation of trimethylaluminum.

Dimethylaluminum bromide is readily separated from the dibromide by adding an excess of sodium bromide which forms a non-volatile complex with it (dibromide); the monobromide may then be obtained in a pure state by distilling at 75° under a pressure of 50 mm. The product crystallizes in the form of white needles at Dry Ice temperatures.

The dibromide is obtained by fractionating off the monobromide under vacuum. The solid remaining in the still when 20% of the original mixture remained was practically pure methylaluminum dibromide, m.p. 79°.[11] The products were vacuum distilled into the filling tube and fragile bulbs were filled as in the case of aluminum bromide. All operations are carried out *in vacuo* or under oxygen-free nitrogen. *Anal.* Calcd. for: CH_3AlBr_2, % Br, required, 79.20; found, 81.18 ± 0.08; % Al, required, 13.36; found, 13.48 ± 0.18. $(CH_3)_2AlBr$, % Br, required, 58.36; found, 58.12 ± 0.74; % Al, required, 19.69; found, 19.58 ± 0.06.

2. **Apparatus and Procedure.**—The conductance of the solution was measured by means of a Jones bridge, that of solvents by means of a parallel arm bridge specially designed for measuring high resistances. With nitrobenzene and pyridine, the cells employed and the dilution procedure were similar to those described in earlier papers.[12] With methyl bromide, a modified cell was employed as illustrated in Fig. 1. The small chamber, *G*,

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[3] Plotnikov, *J. Russ. Phys. Chem. Soc.*, **34, I**, 466 (1902); Plotnikov, *Z. physik. Chem.*, **127**, 225 (1927).

[4] Wertyporoch and Adamus, *ibid.*, **168A**, 31 (1934).

[5] Müller, *Z. anorg. Chem.*, **156**, 56 (1926).

[6] Witschonke and Kraus, This Journal, **69**, 2472 (1947).

[7] Burgess and Kraus, *ibid.*, **70**, 706 (1948).

[8] Merrill, *J. prakt. Chem.*, **126**, 293 (1878).

[9] Kraus and Nelson, *ibid.*, **56**, 198 (1934).

[10] Hnizda and Kraus, *ibid.*, **60**, 2276 (1938).

[11] von Grosse and Mavitz, *J. Org. Chem.*, **5**, 106 (1940).

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

at the bottom of the cell is for the purpose of retaining the chips of the glass bulbs containing the salt. The methyl bromide introduced into the cell was condensed in a special pipet[13]; its volume was measured at 0° and it was then evaporated and condensed in the conductance cell. In making a dilution, about two-thirds of the solution (cooled to −70°) was withdrawn under nitrogen pressure into the receiver, U, where its volume was measured at 0°. A volume of solvent approximately equal to that withdrawn was then introduced into the cell.

III. Results

In Table I are presented values of the concentration in moles of solute per liter of pure solvent and the corresponding value of the molar conductance, Λ, for solutions of aluminum bromide in nitrobenzene at 25°. Measurements were also carried out with nitrobenzene that had not been treated with aluminum chloride; numerical data are omitted, but the results are shown graphically in curve 1 of Fig. 2.

In Table II are presented data for aluminum bromide in pyridine at 25°. Concentrations are given in moles of salt per liter of solvent and molar conductances are based on these concentrations.

In Table IIIA, B and C, are given data for aluminum bromide, methylaluminum dibromide and dimethylaluminum bromide, respectively, in methyl bromide at 0°. Concentrations are expressed in moles of solute per liter of solvent and molar conductances are based on these values. Measurements with these solutions were also carried out at −78° but numerical data are omitted; the results are shown graphically in Fig. 5. The density of methyl bromide was taken to be 1.7321.[13a]

TABLE I

CONDUCTANCE OF ALUMINUM BROMIDE IN NITROBENZENE AT 25°

$C \times 10^3$	38.11	16.33	6.416	1.143	0.338
Λ	3.36	3.28	3.14	3.57	6.94

TABLE II

CONDUCTANCE OF ALUMINUM BROMIDE IN PYRIDINE AT 25°

$C \times 10^3$	0.713	0.296	0.129	0.0372	0.0107
Λ	29.0	42.0	59.4	97.4	150.0

TABLE III

A. CONDUCTANCE OF ALUMINUM BROMIDE IN METHYL BROMIDE AT 0°

C	0.9024	0.4688	0.3270	0.3105
$\Lambda \times 10^2$	4.29	2.62	2.46	2.41

B. CONDUCTANCE OF CH_3AlBr_2 IN METHYL BROMIDE AT 0°

C	0.802	0.475	0.336
$\Lambda \times 10^2$	1.62	1.11	0.783

C. CONDUCTANCE OF $(CH_3)_2AlBr$ IN METHYL BROMIDE AT 0°

C	0.861	0.787	0.590	0.330
$\Lambda \times 10^2$	0.666	0.533	0.373	0.453

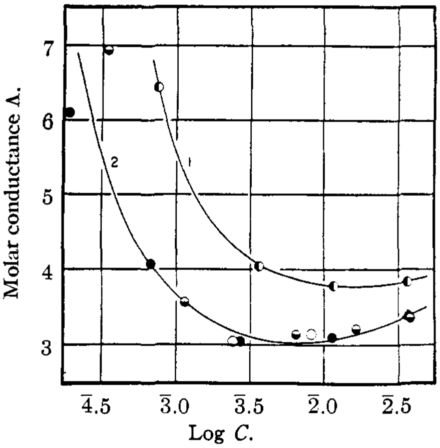

Fig. 2.—The conductance of aluminum bromide in nitrobenzene at 25°: 1, solvent untreated with aluminum chloride; 2, solvent treated with aluminum chloride.

IV. Discussion

1. **Nitrobenzene.**—The sensitivity of aluminum bromide to impurities is well illustrated in Fig. 2. Curve 2 relates to solutions in which the solvent was treated with aluminum chloride while curve 1 relates to solutions in untreated solvent. The solvent conductance in both cases was 1×10^{-10}. It is evident that in the untreated solvent, impurities were present which combined with aluminum bromide to render its solutions better conductors.

Aluminum bromide is a weak electrolyte in nitrobenzene. This is not unexpected in view of the weak complexing power of this solvent. According to Menshutkin,[14] one molecule of solvent combines with one of aluminum bromide. The solutions of aluminum bromide in nitrobenzene have a brilliant yellow color.

At lowest concentrations measured, the conductance showed a marked drift toward lower values. This may have been due to traces of moisture, although great care was exercised in eliminating it from the apparatus before use. Nevertheless, addition of small quantities of water caused a large decrease in conductance. The conductance of the bromide ion in nitrobenzene is 22.6[6]; aluminum bromide is, therefore, only weakly dissociated in this solvent.

The conductance of aluminum bromide passes through a minimum at about 6.5×10^{-3}. According to Van Dyke,[15] the conductance passes through a maximum at 0.15 molal.

2. **Pyridine.**—Müller[5] investigated the composition of solid phases in equilibrium with solutions of aluminum bromide in pyridine over the temperature range −3 to 80°. He found compounds containing from 12 to 3 molecules of pyridine per molecule of $AlBr_3$ over this temperature range. A preparation in this Laboratory

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[13] Kraus, THIS JOURNAL, **47**, 749 (1921).

[13a] Beilstein, Vol. I, p. 66.

[14] Menshutkin, *J. Russ. Phys.-Chem. Soc.*, **41**, 1053 (1910); *Chem. Abs.*, **4**, 1487 (1910).

[15] R. E. Van Dyke, Thesis, Brown University, June, 1947.

at 25° yielded a compound containing approximately five molecules of pyridine[16]; the compound had a pronounced odor of pyridine.

As was to be expected, in view of the strong complexing tendency between aluminum bromide and pyridine, its solutions in this solvent are excellent conductors as is evident from Fig. 3. While the limiting (molecular) conductance of the salt in pyridine has not been determined, it must lie not far from 180. The conductance of the bromide ions in pyridine is 51.3.[17]

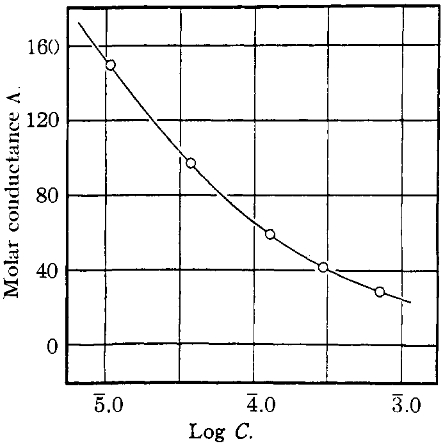

Fig. 3.—The conductance of aluminum bromide in pyridine at 25°.

It follows that aluminum bromide behaves like a strong 3-1 electrolyte in pyridine. This illustrates the importance of interaction between ions and solvent molecules; in nitrobenzene with a dielectric constant of 34.5, the salt is a very weak electrolyte, in pyridine with a dielectric constant of 12.3, it is a strong one.

3. Methyl Bromide.—We have no good evidence indicating the existence of complexes between aluminum bromide and methyl bromide. In accordance with this circumstance, the conductance of aluminum bromide in methyl bromide is very low. Thus, its molar conductance is of the order of 2 × 10^2, indicating an ionic dissociation of the order of 10^{-4}. The dielectric constant of the solvent at 0° is 10.7, not greatly below that of pyridine.

As may be seen from curve 1, Fig. 4, the conductance of aluminum bromide in methyl bromide passes through a minimum in the neighborhood of 0.02 molar. The conductance of methylaluminum dibromide is markedly lower than that of aluminum bromide, and that of the dimethyl derivative is even lower. All compounds give evidence of the existence of a minimum in their conductance curves but the minimum for different salts lies at different concentrations, being highest for the dimethyl derivative.

At −78° (Fig. 5), the conductance curves for

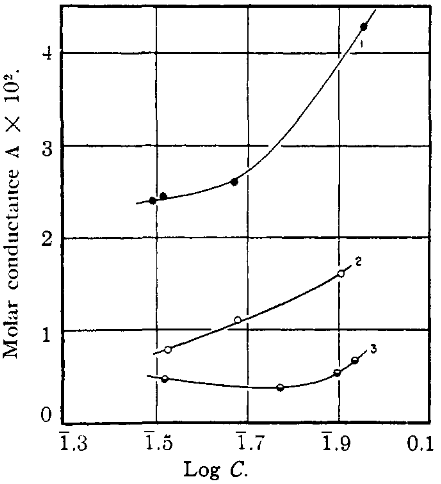

Fig. 4.—The conductance of $AlBr_3$ (1), CH_3AlBr_2 (2) and $(CH_3)_2AlBr$ (3) in methyl bromide at 0°.

the three salts show a marked change over that at 0°. Aluminum bromide shows a weak minimum at about 0.2 molar. The methyl derivatives show decreasing conductance with increasing concentration, approximately linear with respect to log C. There is no great change in the order of magnitude of conductance values between the two temperatures.

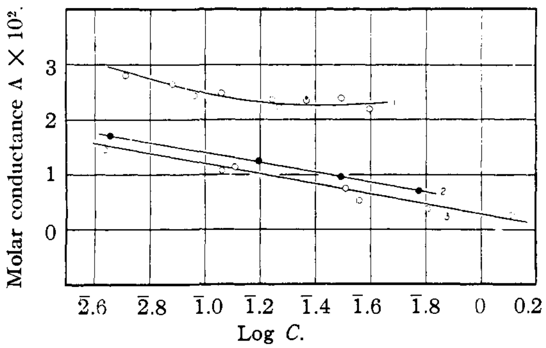

Fig. 5.—The conductance of $AlBr_3$ (1), CH_3AlBr_2 (2) and $(CH_3)_2AlBr$ (3) in methyl bromide at −78°.

V. Summary

1. The conductance of aluminum bromide has been measured in nitrobenzene and pyridine at 25° and in methyl bromide at 0°.
2. The conductance of aluminum bromide in nitrobenzene is greatly influenced (increased) by impurities that may be eliminated by treating the solvent with aluminum chloride.
3. Aluminum bromide is a weak electrolyte in nitrobenzene, a strong electrolyte in pyridine and a very weak electrolyte in methyl bromide.
4. The conductances of methylaluminum dibromide and dimethylaluminum bromide have been measured in methyl bromide at 0 and −78°. Both salts are markedly weaker electrolytes in this solvent than is aluminum bromide.

Providence, R. I. Received February 24, 1949

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[16] C. L. Morris, Thesis, Brown University, 1941.

[17] Luder and Kraus, This Journal, **69**, 2481 (1947).