[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY]

The Conductance of Aluminum Chloride in Nitrobenzene on Addition of Various Oxygen Bases at 25°[1,2]

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A comparison is made between aluminum chloride and bromide as electrolytes in nitrobenzene. Conductance data are presented for solutions of aluminum chloride in nitrobenzene on addition of dimethyl ether, methanol, acetone and acetic anhydride. The aluminum chloride etherate system is rather more complex than is the aluminum bromide etherate system in nitrobenzene, while the methanol, acetone and acetic anhydride complexes of the chloride behave much the same as the bromide complexes. In all cases the two to one addition compounds are better electrolytes than either the one to one complexes or the original solutions.

I. Introduction

In studying the properties of various addition compounds of the aluminum halides, the bromide was chosen first because of its greater solubility in a wider variety of solvents and because of greater ease of handling the pure anhydrous salt. With the development of similar techniques of preparation of pure samples of anhydrous aluminum chloride, it was decided to investigate these addition compounds of the chloride. The relative merits of the two salts as catalysts appear to depend upon the nature and conditions of the reaction, and relative solubilities of the salts. Thus a comparison of the tendency to form these addition compounds and their electrolytic properties may have some bearing upon the differences in catalytic activity under given conditions.

In this paper are presented dilution data for aluminum chloride in nitrobenzene, molecular weight data for aluminum chloride and bromide in nitrobenzene, as well as conductance data for solutions of aluminum chloride on addition of dimethyl ether, methanol, acetone and acetic anhydride.

II. Experimental

Materials.—Nitrobenzene[3] was purified according to procedures described previously.[4] The solvent had a specific conductance of 1–2 × 10^{-10} mho. and its melting point was reproducible to 0.001° on the Beckmann scale. It was stored in a large flask over activated alumina from which it was withdrawn through a fine fritted filter as needed. Dimethyl ether (Matheson product) was dried over aluminum oxide as described earlier.[4] Methanol, Baker C.P. product, was carefully dried over barium oxide and distilled as indicated in a previous paper.[5] Acetone, Baker C.P. product, was dried and distilled as described previously.[5] Acetic anhydride was purified by distillation through an efficient column, the boiling point serving as the criterion of purity. Anhydrous aluminum chloride was prepared by reaction of very pure aluminum[6] with chlorine in vapor phase in a manner similar to that described previously for the preparation of aluminum bromide.[7] After several sublimations the salt was collected in a long manifold to which numerous large fragile ampules were attached. The salt was collected in these ampules which were then sealed off under vacuum for use as needed.

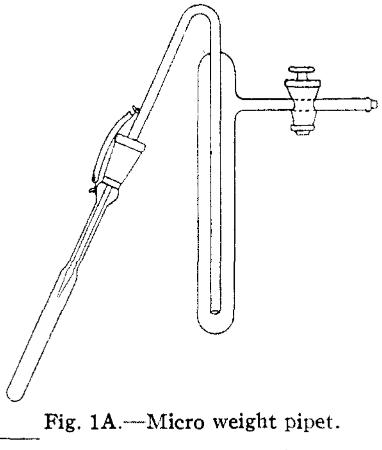

Fig. 1A.—Micro weight pipet.

Apparatus and Procedure.—All resistance measurements were carried out at 25 ± 0.01° with the Jones bridge employing the customary erlenmeyer type conductance cells. Dimethyl ether was measured by volume and introduced into the cell as described previously.[4] Liquid complexing agents were introduced by means of a micro weight pipet as shown in Fig. 1A. Nitrobenzene solutions of aluminum chloride were prepared in a separate flask with appropriate stopcocks, ground glass joints and delivery tubes to avoid contamination of atmospheric moisture. Transfer of the solution to the evacuated conductance cell was accomplished by dry nitrogen pressure.

III. Results

Conductance of aluminum chloride in nitrobenzene at 25° has been determined for concentrations as low as 3 × 10^{-4} molal. Two series of data are presented in Table I and are shown graphically in Fig. 1. Concentrations are expressed in moles of salt per 1,000 grams of solvent *m* and the Λ values are calculated on the basis of this concentration scale.

TABLE I

THE CONDUCTANCE OF ALUMINUM CHLORIDE IN NITROBENZENE AT 25°

Series I		Series II	
Λ molal	$m \times 10^3$	Λ molal	$m \times 10^3$
2.05	284.0	2.10	184.9
2.22	124.2	2.24	100.2
2.29	78.9	2.29	60.9
2.35	46.4	2.40	32.4
3.00	10.4	2.64	17.7
3.61	5.54	4.66	3.36
6.35	1.58	8.70	0.784
10.80	0.506		
14.90	.306		

Dimethyl Ether.—The conductance of aluminum chloride in nitrobenzene on addition of di-

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(1) This paper is based on a portion of a thesis presented by Harry E. Crawford in partial fulfillment of the requirements for the degree of Doctor of Philosophy in The Johns Hopkins University.

(2) For tables supplementary to this article order Document 3042 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

(3) Kindly donated by Calco Chemicals Division, American Cyanamid Co.

(4) Van Dyke and Kraus, THIS JOURNAL, **71**, 2694 (1949).

(5) Van Dyke, *ibid.*, **73**, 398 (1951).

(6) Kindly donated by The Aluminum Company of America.

(7) Jacober and Kraus, THIS JOURNAL, **71**, 2405 (1949).

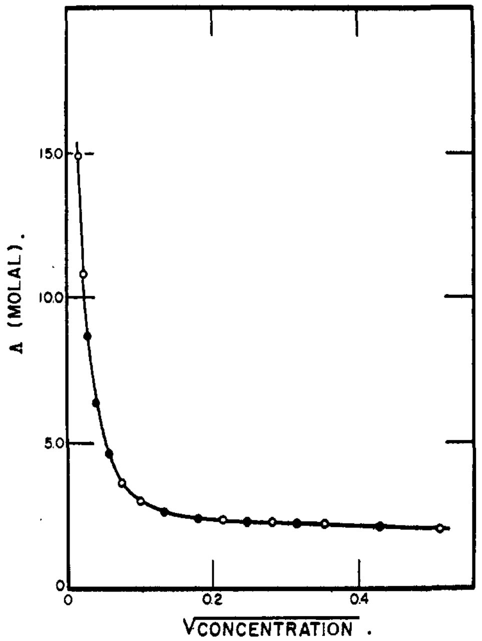

Fig. 1.—The conductance of aluminum chloride in nitrobenzene at 25°.

methyl ether has been determined for five concentrations of salt m(molality) = 0.2820, 0.2362, 0.1375, 0.1150 and 0.0750. These data are shown graphically in Fig. 2 and numerical values for two of the solutions are given in Table II. The solubility data of Van Dyke and Kraus[4] for dimethyl ether in nitrobenzene together with the observed vapor pressures recorded in the second column of Table II were used to determine the free ether content in these solutions.

TABLE II

CONDUCTANCE OF ALUMINUM CHLORIDE IN NITROBENZENE ON ADDITION OF DIMETHYL ETHER AT 25°

$\kappa \times 10^4$	V.p., cm.	Mmoles ether uncombined	Mmoles ether combined	Molar ratio ether/$AlCl_3$
A. Mmoles $AlCl_3$ = 8.465, m = 0.1150				
2.553	0.045	0.0000	0.000	0.0000
2.025	.045	.0000	1.946	.2299
1.430	.045	.0000	3.909	.4610
0.8897	.045	.0000	5.881	.6945
.6420	.045	.0000	6.873	.8120
.5273	.045	.0000	7.530	.8895
.4203	.045	.0000	8.201	.9685
.3931	.045	.0000	8.433	.9960
.4740	.440	.4410	8.648	1.022
.7724	2.050	2.080	8.990	1.062
.9850	3.630	3.677	9.373	1.107
1.362	5.060	5.118	9.942	1.175
1.646	6.615	6.700	10.336	1.221
1.901	8.070	8.250	10.787	1.274
2.275	11.570	12.000	10.968	1.350
2.565	14.330	14.975	11.935	1.409
B. Mmoles $AlCl_3$ = 19.623, m = 0.2362				
5.020	0.045	0.0000	0.000	0.0000
4.077	.045	.0000	4.011	.2045
3.119	.045	.0000	7.974	.4063
2.210	.045	.0000	11.819	.6023
1.314	.045	.0000	15.715	.8005
0.6338	.045	.0000	19.603	.9993
0.9115	.063	.7970	19.790	1.008
1.327	1.755	2.186	20.380	1.038
2.550	3.940	4.858	21.687	1.105
2.979	6.330	7.820	22.773	1.160
3.925	8.660	10.855	23.668	1.205
5.481	15.655	20.105	26.193	1.335
6.480	20.080	26.100	28.198	1.436

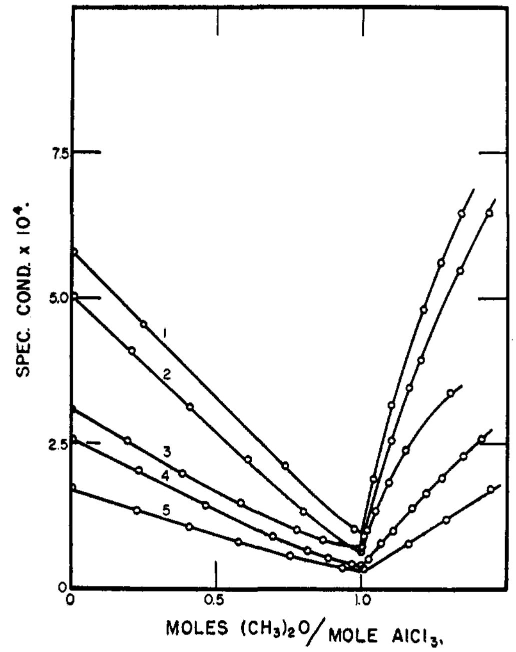

Fig. 2.—Conductance of aluminum chloride in nitrobenzene on addition of dimethyl ether at 25°: (1) 0.2820 molal, (2) 0.2362 molal, (3) 0.1375 molal, (4) 0.1150 molal, (5) 0.0750 molal.

Methanol.—The conductance of aluminum chloride on addition of methanol has been measured for four concentrations of salt m = 0.2521, 0.1782, 0.1182, 0.0275. These results are shown graphically in Fig. 3, while numerical data are given in Table III for one of these solutions.

TABLE III

CONDUCTANCE OF ALUMINUM CHLORIDE IN NITROBENZENE ON ADDITION OF METHANOL AT 25°

Mmoles $AlCl_3$ = 13.521, m = 0.1782

$\kappa \times 10^4$	Molar ratio $CH_3OH/AlCl_3$
3.915	0.0000
3.838	.1251
3.680	.3050
3.476	.4981
3.230	.6902
3.160	.7580
3.100	.8500
3.165	.9201
3.500	.9793
7.450	1.140
14.700	1.451
17.520	1.651
19.100	1.850

TABLE IV

CONDUCTANCE OF ALUMINUM CHLORIDE IN NITROBENZENE ON ADDITION OF ACETONE AT 25°

Mmoles $AlCl_3$ = 5.200, m = 0.1352

$\kappa \times 10^4$	Molar ratio $(CH_3)_2CO/AlCl_3$
3.001	0.0000
2.900	.1800
2.752	.5000
2.300	.8783
2.195	1.000
2.223	1.100
2.425	1.159
3.580	1.260
11.590	1.526
16.623	1.735
18.600	1.960
19.050	2.163
19.225	2.365

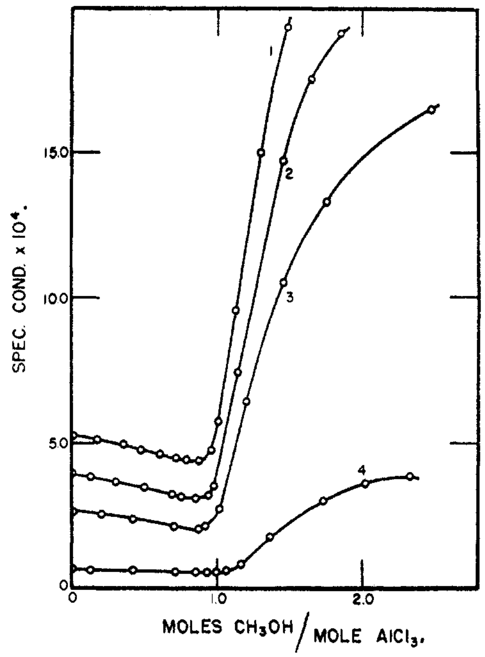

Fig. 3.—Conductance of aluminum chloride in nitrobenzene at 25° in presence of methanol: (1) 0.2521 molal, (2) 0.1782 molal, (3) 0.1182 molal, (4) 0.0275 molal.

Acetone has been studied as a complexing agent in two different solutions. Conductance data for one of these solutions are presented in Table IV and shown graphically in Fig. 4, curve 2.

Acetic anhydride was studied as a complexing agent for two different concentrations of salt. Conductance data for one of these solutions are presented in Table V and are shown graphically in Fig. 4, curve 4.

TABLE V

CONDUCTANCE OF ALUMINUM CHLORIDE IN NITROBENZENE ON ADDITION OF ACETIC ANHYDRIDE AT 25°

Mmoles $AlCl_3$ = 2.010, m = 0.1695

$\kappa \times 10^4$	Molar ratio $(CH_3CO)_2O/AlCl_3$
3.750	0.0000
4.600	.0384
5.505	.1119
6.500	.2223
7.300	.3280
7.815	.4750
7.715	.5801
6.745	.7881
5.960	.9655
5.655	1.038
5.405	1.109
5.300	1.315

IV. Discussion

According to Fig. 1, aluminum chloride behaves as a normal weak electrolyte in nitrobenzene. On comparing these data with those obtained for aluminum bromide[7,4] these are two points of interest. First, with aluminum bromide the molal conductance passes through a maximum at a concentration of 0.15 molal, whereas the curve for the chloride is nearly linear throughout this region. Secondly, the slope of the curve in the dilute region ($<10^{-3}$ molal) is much greater for the chloride than for the bromide. For the lowest concentrations reported for both salts (3×10^{-4} molal) the molal conductance for the bromide is approximately 7.0, while that of the chloride is nearly 15.0. The limiting conductances of chloride and bromide ions in nitrobenzene are 22.2 and 21.6, respectively. Since the solvent forms stable 1:1 addition compounds with these salts it seems reasonable to assume that the conductances of the positive ionic species do not differ greatly. The only apparent conclusion would be that the dissociation constant for the chloride is, roughly, twice as large as that for the bromide for these concentrations.

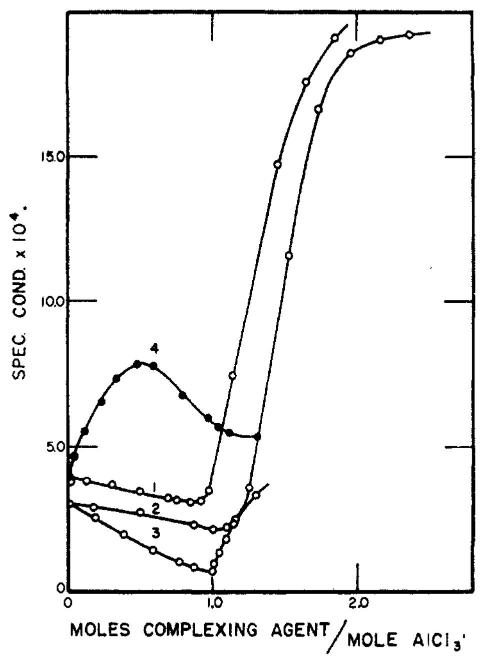

Fig. 4.—Comparison plot for various complexing agents in nitrobenzene at 25°: (1) 0.1782 molal $AlCl_3$ on addition of methanol; (2) 0.1352 molal $AlCl_3$ on addition of acetone; (3) 0.1375 molal $AlCl_3$ on addition of dimethyl ether; (4) 0.1695 molal $AlCl_3$ on addition of acetic anhydride.

In the light of the differences in conductance curves for these two salts in nitrobenzene apparent molecular weight data have been determined by the freezing point method. As may be seen in Table VI both salts are monomeric in nitrobenzene. The experimental values of the molecular weights agree with the calculated values of the monomer to within ±1% which is just within the limit of experimental error.

TABLE VI

MOLECULAR WEIGHTS OF ALUMINUM CHLORIDE AND BROMIDE IN NITROBENZENE

Aluminum chloride		Aluminum bromide	
App. mol. wt.	Molality	App. mol. wt.	Molality
131.6	0.2523	267.8	0.3405
134.0	.1828	268.1	.2120
133.6	.1445	264.3	.1671
132.5	.1200	265.4	.1111
133.9	.0860		
133.8	.0595		

1. **Dimethyl Ether.**—The conductance curves obtained for dimethyl ether as complexing agent are similar in form to those obtained with aluminum bromide as solute. The concentration range covered is considerably smaller due to the lower solubility of aluminum chloride in nitrobenzene. As shown in Fig. 2, the conductance decreases linearly on addition of ether until the molar ratio of ether to salt approaches unity. Slight deviations from linearity appear in the curves near the minimum point. Beyond this point the conductance increases rapidly but not exactly linearly as was observed with aluminum bromide solutions. In this region free ether was found in equilibrium with combined ether, but the system was not susceptible to a simple analysis. Analysis of the equilibrium data indicates that there are probably several equilibria occurring simultaneously. For all the solutions the relationship $C_{\text{dietherate}}/C_{\text{monoetherate}} = KC^{x}_{\text{ether where } 2 > x > 1}$ was observed. The complexity of this system probably accounts for the deviation from linearity of the curves just before a molar ratio of 1.0. As will be seen later the absence of a sharp break in the conductance curve at this point becomes more pronounced in the case of methanol as complexing agent. It seems clear that the principal reactions are those obtained with aluminum bromide and dimethyl ether.[4] Rather interesting is the fact that for corresponding concentrations the specific conductance of aluminum bromide is more than twice that of aluminum chloride in nitrobenzene but the monoetherates for the same concentrations are nearly equal.

2. **Methanol.**—The results for methanol as complexing agent are presented in Fig. 3. These curves are similar in every respect to those obtained on addition of methanol to solutions of aluminum bromide. The conductance decrease appears linear but the magnitude of the decrease is not large compared to that observed on addition of dimethyl ether. While the concentration of free methanol has not been determined, it appears probable that an equilibrium involving some free methanol occurs. For molar ratios of 2.0 and beyond a milky suspension was observed in contrast to the crystalline complex obtained with aluminum bromide.

3. **Acetone.**—A typical curve for acetone as complexing agent is shown in Fig. 4, curve 2. The general form of the curve is remarkably similar to that of the methanol curve. With acetone, the conductance does not begin to increase rapidly until the mole ratio value becomes close to 1.2. This behavior is markedly different from that observed on addition of acetone to aluminum bromide solutions. It seems reasonable to suggest that the reaction between acetone and aluminum chloride is not quantitative at any point on the curve. Comparison of curves 1 and 2 of Fig. 4 suggests that the diacetonate is equally as strong an electrolyte as the 2:1 methanol complex and probably is somewhat stronger. No evidence of precipitation was observed on addition of acetone beyond a molar ratio of 2.0. A further comparison of curves 1, 2 and 3 of Fig. 4 indicates that the two to one complexes of aluminum chloride with methanol and acetone are much stronger electrolytes than is the dietherate in nitrobenzene.

4. **Acetic Anhydride.**—On addition of acetic anhydride to a nitrobenzene solution of aluminum chloride the conductance increases, passes through a maximum at a molar ratio of 0.5 and then decreases to a value at a molar ratio of 1.0 which is just slightly higher than that of the original solution. A typical curve is shown in Fig. 4, curve 4. As was observed with addition of acetic anhydride to solutions of aluminum bromide, the yellow color of the solvent–halide complex vanishes at the conductance maximum for a ratio value of 0.5. The odor of acetyl chloride was observed as the conductance decreases from the maximum value to a molar ratio of 1.0. It is probable that the reactions are similar to those suggested previously for the bromide solutions.[5] These results are particularly interesting in view of the fact that two moles of aluminum chloride per mole of anhydride are required in a keto-acid synthesis in nitrobenzene solution.

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