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

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

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Conductance curves for nitrobenzene solutions of aluminum chloride on addition of pyridine, benzonitrile, trimethylamine and ammonia are compared with curves obtained from similar studies with aluminum bromide solutions. The curves obtained with pyridine, trimethylamine and ammonia are themselves similar but differ considerably from the curves obtained with bromide solutions. The conductance curves are explained on the basis of competitive reactions forming various aluminum chloride addition compounds and are substantiated in the case of pyridine complexes by molecular weight measurements.

I. Introduction

In studying the compounds ammonia,[3] pyridine[4] and benzonitrile[5] as complexing agents in nitrobenzene solutions of aluminum bromide, marked differences in the type of conductance curves were observed as compared with those obtained with oxygen bases as complexing agents.[6]

As shown in the preceding paper[7] these oxygen bases as complexing agents with aluminum chloride yield conductance curves similar in form to those obtained with the bromide. It is of interest, therefore, to compare the curves for aluminum chloride on addition of the nitrogen bases with those obtained for the oxygen bases as well as those obtained on addition of nitrogen bases to aluminum bromide solutions.

In this paper are reported conductance data for aluminum chloride solutions on addition of pyridine, benzonitrile, trimethylamine and ammonia. In addition, molecular weight data are presented for aluminum chloride solutions containing varying amounts of pyridine.

II. Experimental

Materials.—Nitrobenzene[8] was purified and handled in accordance with previously described procedures.[3] Aluminum chloride was prepared by reaction of the elements, purified and collected in fragile ampules as described in the preceding paper.[7] Benzonitrile[9] was purified in accordance with the procedure described previously.[5] Pyridine, Barrett Company Product, was purified by distillation from barium oxide followed by several fractional crystallizations and a final distillation. The material was stored over activated aluminum oxide from which it was withdrawn through a sintered glass frit as needed. Trimethylamine, Matheson Product of 98.5% purity, was dried over barium oxide. Ammonia from a laboratory stock cylinder was dried over sodium before use.

Apparatus and Procedure.—Resistance measurements were made with a Leeds and Northrup bridge of the Jones type using the customary erlenmeyer type cells. The procedure for cleaning and handling the cells and for preparation of the solutions has been adequately described in an earlier paper.[3] The methods employed in introducing liquid and gaseous complexing agents have been described previously.[6] Molecular weights were determined by the Beckmann method using a magnetic stirrer.

III. Results

1. **Pyridine.**—The conductance of aluminum chloride in nitrobenzene on addition of pyridine has been determined for three different solutions of concentration *m* (molality) = 0.1638, 0.1550,

TABLE I

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

$\kappa \times 10^4$	Molar ratio $C_5H_5N/AlCl_3$	$\kappa \times 10^4$	Molar ratio $C_5H_5N/AlCl_3$
A. Nitrobenzene of Questionable Purity, mmoles $AlCl_3$ = 3.165, *m* = 0.1638		B. Pure Nitrobenzene, mmoles $AlCl_3$ = 2.840, *m* = 0.1550	
3.650	0.0000	3.430	0.0000
4.650	.0650	4.411	.0461
4.795	.0961	5.450	.0952
4.610	.2020	6.512	.1410
4.450	.3061	7.701	.1863
4.075	.5155	8.990	.2340
3.835	.8255	10.080	.3491
3.840	.9301	10.431	.4600
3.935	.9755	10.562	.9202
4.350	1.015	10.690	1.039
5.750	1.120	12.092	1.270
7.625	1.222	14.391	1.500
11.110	1.430	17.900	1.965
15.580	1.740	17.991	2.145
18.085	2.043	17.800	2.321
17.790	2.521	17.352	2.750
		16.751	3.430
C. Pure Nitrobenzene, mmoles $AlCl_3$ = 2.940, *m* = 0.0750		D. Benzonitrile as Solvent, mmoles $AlCl_3$ = 1.020, *m* = 0.0914	
1.715	0.0000	14.180	0.0000
2.750	.0892	15.811	.1421
4.010	.1793	17.310	.2782
4.780	.2901	17.202	.5350
4.970	.4921	16.524	.6691
5.040	.6042	15.602	.8031
5.100	.6941	15.020	.9333
5.150	.8054	15.211	1.073
5.200	.9090	15.902	1.200
5.230	1.000	17.103	1.458
5.401	1.071	18.160	1.717
5.605	1.131	18.361	1.972
6.245	1.241	18.000	2.743
7.990	1.531		
9.490	1.816		
9.900	1.969		
9.981	2.075		
9.752	2.600		

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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 requirement for the degree of Doctor of Philosophy in The Johns Hopkins University.

[2] For tables supplementary to this article order Document 3043 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] Van Dyke and Kraus, THIS JOURNAL, **71**, 2694 (1949).

[4] Van Dyke and Harrison, *ibid.*, **73**, 575 (1951).

[5] Van Dyke and Harrison, *ibid.*, **73**, 402 (1951).

[6] Van Dyke, *ibid.*, **73**, 398 (1951).

[7] Van Dyke and Crawford, *ibid.*, **73**, 2018 (1951).

[8] Kindly donated by Calco Chemicals Division, American Cyanamid Company.

[9] Kindly donated by Socony Vacuum Oil Company.

0.0750. In the first of these solutions the results were somewhat erratic and not reproducible. The data are included in Table I A for comparison with the reproducible results. The results are shown graphically in Fig. 1. Data are also included in Table I D for a benzonitrile solution of aluminum chloride on addition of pyridine.

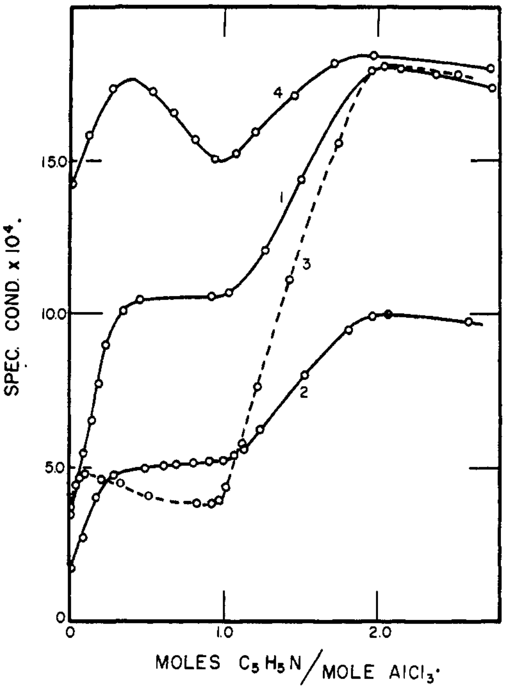

Fig. 1.—Conductance of aluminum chloride in several solvents on addition of pyridine at 25°: (1) 0.1550 molal in pure nitrobenzene; (2) 0.0750 molal in pure nitrobenzene; (3) 0.1638 molal in impure nitrobenzene; (4) 0.0914 molal in benzonitrile.

2. **Benzonitrile.**—Conductance data for benzonitrile as complexing agent for one solution are given in Table II and are shown graphically in Fig. 3, Curve 1.

Table II

Conductance of Aluminum Chloride in Nitrobenzene on Addition of Benzonitrile at 25°

$\kappa \times 10^4$	Molar ratio $C_6H_5CN/AlCl_3$	$\kappa \times 10^4$	Molar ratio $C_6H_5CN/AlCl_3$
Mmoles $AlCl_3$ = 13.390, m = 0.1925			
4.200	0.0000	11.910	1.049
4.755	.0601	12.522	1.162
5.345	.1271	14.621	1.560
6.750	.2962	15.750	1.837
8.155	.4801	16.000	1.949
10.100	.7600	16.353	2.235
11.591	.9901	16.610	2.820

3. **Trimethylamine and Ammonia.**—The conductance of aluminum chloride in nitrobenzene on addition of trimethylamine has been determined for two concentrations of salt m = 0.2750 and 0.0848. Data for one of these solutions are given in Table III A and are shown graphically in Fig. 3, Curve 4. Studies with ammonia as complexing agent have been made at two different concentrations m ≐ 0.1637 and 0.736. Conductance data for one of these solutions are listed in Table III B and are presented graphically in Fig. 3, Curve 2.

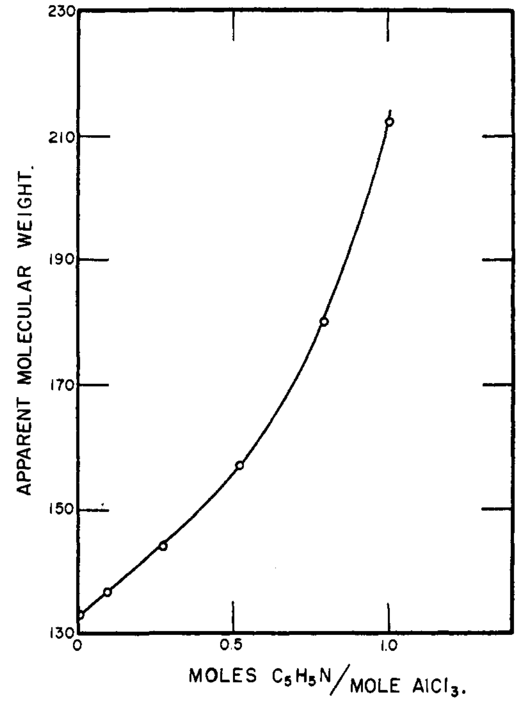

Fig. 2.—Apparent molecular weight of aluminum chloride in nitrobenzene on addition of pyridine.

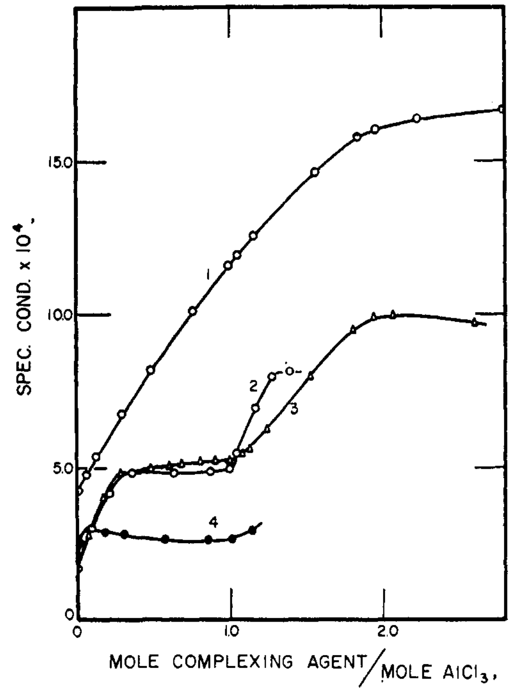

Fig. 3.—Comparison plot for various complexing agents in nitrobenzene at 25°: (1) 0.1925 molal $AlCl_3$ on addition of benzonitrile; (2) 0.0736 molal $AlCl_3$ on addition of ammonia; (3) 0.0750 molal $AlCl_3$ on addition of pyridine; (4) 0.0848 molal $AlCl_3$ on addition of trimethylamine.

IV. Discussion

1. **Pyridine.**—The initial studies with pyridine as complexing agent appear to have been carried

TABLE III

CONDUCTANCE OF ALUMINUM CHLORIDE IN NITROBENZENE IN PRESENCE OF TRIMETHYLAMINE AND AMMONIA AT 25°

$\kappa \times 10^4$	Molar ratio $(CH_3)_3N/AlCl_3$	$\kappa \times 10^4$	Molar ratio $NH_3/AlCl_3$
A. Trimethylamine, mmoles $AlCl_3$ = 3.430, m = 0.0848		B. Ammonia, mmoles $AlCl_3$ = 4.100, m = 0.0736	
1.929	0.0000	1.680	0.0000
2.500	.0251	2.985	.1021
2.875	.1810	4.110	.2102
2.781	.3082	4.810	.3621
2.618	.5801	4.840	.6401
2.595	.8601	4.830	.8712
2.616	1.020	4.975	1.001
2.958	1.151	5.455	1.045
		6.925	1.170
		7.975	1.275
		8.100	1.400

out with nitrobenzene of questionable purity. These results are extremely interesting when compared with data obtained using solvent of apparently greater purity. Results obtained using the solvent of uncertain purity are presented graphically in Fig. 1, Curve 3. The conductance increases slightly on addition of pyridine accompanied by precipitation of a white complex which was shown by analysis to be a 1:1 addition compound $AlCl_3 \cdot C_5H_5N$. With further addition of pyridine the conductance passes through a maximum and decreases somewhat until a molar ratio of 1.0 is reached. At this point the system is again homogeneous and the conductance increases approximately linearly with further addition of pyridine to a ratio value of 2.0. Beyond this point the conductance levels off with no further apparent interaction. A sample of this solvent batch was found to yield a non-reproducible melting point. However, the specific conductance of the solvent was up to the standards previously reported (*e.g.* 1–2 × 10^{-10} mho).

On addition of pyridine to solutions of aluminum chloride using a new freshly purified batch of solvent results as shown in curves 1 and 2 were obtained. The conductance increased sharply at first and then levelled off at a molar ratio of about 0.3. The conductance continued nearly constant up to a molar ratio of unity after which the usual linear increase occurred. Precipitation was not observed at any point. On comparing curves 1 and 3 of Fig. 1 for similar concentrations of aluminum chloride it will be seen that the conductances at a ratio value of two are nearly equivalent. This fact suggests that at this point the molecular species in the two solutions were probably the same. It seems clear from the form of these curves that two competing reactions take place similar to those observed on addition of pyridine to aluminum bromide solutions. In all cases the yellow color of the $C_6H_5NO_2 \cdot AlCl_3$ complex was observed to vanish at a pyridine–salt ratio of 1.0. In all probability the initial increase in conductance is due to formation to some extent of a stronger electrolyte involving coördination of pyridine to the salt–solvent complex to form the complex $C_6H_5NO_2 \cdot AlCl_3 \cdot C_5H_5N$. This reaction is in competition with the reaction producing the one to one addition compound $C_5H_5N:AlCl_3$ which presumably does not differ greatly in electrolytic strength from the salt–solvent complex. As the conductance increases beyond a molar ratio of 1.0, both these complexes are converted to the two to one addition compound $AlCl_3 \cdot 2C_5H_5N$. It would appear that small amounts of impurity present in the initial batch of solvent were sufficient to disrupt the homogeneity of the system with precipitation of some of the 1:1 addition compound.

Pyridine reacts vigorously with aluminum chloride and bromide to form stable complexes containing three moles of pyridine per mole of salt. Van Dyke and Harrison[4] have observed that when pyridine is added to nitrobenzene solutions of aluminum bromide the complex $AlBr_3 \cdot 3C_5H_5N$ precipitates when the molar ratio of pyridine to salt exceeds a value of 2.0. In the case of aluminum chloride solutions such precipitation was not observed. Furthermore, it was observed that the complex $AlCl_3 \cdot 3C_5H_5N$, prepared by direct combination of pyridine and aluminum chloride, was quite insoluble in nitrobenzene. In view of these results molecular weights were determined for aluminum chloride solutions on addition of varying amounts of pyridine. According to Table IV the experimental values for molar ratios of 1.0 and 2.0 are in excellent agreement with the calculated values of 212.44 and 291.50 for the 1:1 and 2:1 complexes. However, a wide discrepancy exists between the calculated and experimental values for a molar ratio of 3.0. It seems clear that the complex $AlCl_3 \cdot 3C_5H_5N$ cannot be prepared in nitrobenzene.

TABLE IV

APPARENT MOLECULAR WEIGHT OF ALUMINUM CHLORIDE IN NITROBENZENE ON ADDITION OF PYRIDINE

App. mol. wt.	Molar ratio $C_5H_5N/AlCl_3$
133.0	0.000
136.8	.0921
144.1	.2720
156.8	.5200
180.2	.7911
212.3	1.000
292.0	2.000
202.0	3.000

In Fig. 2 are plotted the data of Table IV for molar ratios as high as 1.0. For ratio values as high as 0.3 the curve appears linear. At this point a significant change of slope of the molecular weight curve occurs in agreement with the conductance studies in Fig. 1.

In Curve 4, Fig. 1, are presented the data obtained when pyridine is added to a benzonitrile solution of aluminum chloride. It is clear that the marked differences in behavior between the pyridine complexes of aluminum chloride and bromide, which exist in nitrobenzene, are not evident in benzonitrile solution. This becomes obvious when Curve 4 of Fig. 1 is compared with the results obtained on addition of pyridine to benzonitrile solutions of aluminum bromide.[5]

2. **Benzonitrile.**—The results for addition of benzonitrile to nitrobenzene solutions of alumi-

num chloride as shown in Curve 1, Fig. 3, are much the same as those obtained with solutions of aluminum bromide.[5] The lack of a marked change in slope or an inflection point in the curve near a molar ratio of 1.0 and the fact that the yellow color of the salt–solvent complex does not vanish until the molar ratio approaches a value of 2.0 indicates that effective competition occurs between reactions forming the complexes $C_6H_5CN{:}AlCl_3$ and $C_6H_5NO_2{\cdot}AlCl_3{\cdot}C_6H_5CN$.

3. **Trimethylamine.**—On addition of trimethylamine to solutions of aluminum chloride a curve similar to that obtained for pyridine is observed (Curve 4, Fig. 3). The only significant difference is that the initial rise in conductance on addition of amine is much less than was observed on addition of pyridine. Again a significant difference in the form of the curve is obtained as between nitrobenzene solutions of aluminum chloride and bromide.[3] It was found impossible to continue this study much beyond a molar ratio of unity due to apparent decomposition involving the solvent molecule. This situation has been observed with aluminum bromide solutions also.[3]

Ammonia.—A typical curve for ammonia as complexing agent in aluminum chloride solutions is shown in Curve 2, Fig. 3. The curve for ammonia is much the same as that obtained on addition of pyridine for molar ratios as high as 1.0. This is clearly shown by comparing Curves 2 and 3 of Fig. 3. Beyond the ratio of 1.0 the conductance on addition of ammonia increases much more rapidly than is the case with pyridine. At a ratio value in the neighborhood of 1.3 precipitation of the ammonia complex occurs. It seems clear that the reactions of ammonia with aluminum chloride in nitrobenzene are much the same as those with pyridine and trimethylamine. Curves 2, 3 and 4 of Fig. 3 for these three complexing agents are remarkably similar in form in contrast to the curves obtained with the same complexing agents and aluminum bromide solutions in which each of the three curves is significantly different.[3,4]

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Heat of Reaction of Americium Metal with 1.5 *M* Hydrochloric Acid and a Note on the Heats of Formation of La^{+3}(aq.) and Pr^{+3}(aq.)

BY H. R. LOHR[1] AND B. B. CUNNINGHAM

The measurements described in the content of this paper were made for the purpose of securing basic thermodynamic information concerning americium and some of its compounds. Such information is of twofold interest: as a part of the data required for the systematic comprehension of the chemistry of americium and as a basis for correlating the chemistry of americium with that of other actinide elements for which similar data are available. The heat of reaction of americium metal with 1.5 *M* HCl was found to be -162.3 ± 2.7 kcal. per mole at 25°. The heats of formation at the same temperature of Am^{+3}(aq.), AmO_2(c) and $AmCl_3$(c) are calculated to be -163.2 ± 2.7, -240.3 ± 3 and -251.3 ± 2.7 kcal. mole^{-1}, respectively. The *E* value for the couple $Am(c) = Am^{+3}(aq.) + 3e^-$, at unit concentration uncorrected for the activity coefficient of Am^{+3} is estimated to be 2.36 ± 0.04 v. The heats of formation of Am^{+3}(aq.) and $AmCl_3$(c) given above are about 21 kcal. more negative than those for the corresponding plutonium compounds, while the heat of formation of AmO_2(c) is about 11 kcal. more positive than that of PuO_2(c). The potential of the $Am(c) = Am^{+3}(aq.) + 3e^-$ couple is 0.30 v. more positive than that of the corresponding plutonium couple. Americium metal is substantially more electropositive than plutonium metal, and is closely similar to lanthanum or praseodymium in this respect. Preliminary measurements, carried out as an incidental part of the measurements on americium, suggest that the heats of formation of La^{+3}(aq.) and Pr^{+3}(aq.) are -167.0 ± 1.4 and -165.3 ± 0.9 kcal. mole^{-1}, respectively.

Introduction

The work described here represents a continuation of a systematic investigation of the basic thermodynamic properties of americium and its compounds. Estimates of the heat and free energy of the reaction

$$Am^{+3}(aq.) + H^+(aq.) = Am^{+4}(aq.) + {}^1/_2H_2(g) \quad (1)$$

at 298°K. have been reported elsewhere.[1a]

The objective of the present investigation was to determine the heat of formation of Am^{+3}(aq.).

Throughout this paper all heats of reaction, formation, etc., and all entropies are values at 298°K., unless designated otherwise, and all accepted values for heats of formation, vaporization, etc., used in our calculations are those given by the National Bureau of Standards "Selected Values of Chemical Thermodynamic Properties" unless some other source is credited. All values are expressed only to the nearest 0.1 kcal., consistent with our experimental accuracy. The activity coefficients of the aqueous tripositive and tetrapositive ions dealt with in this work are not known. Our calculated thermodynamic values involving such ions do not therefore include this customary correction. Strictly speaking, we are not justified in designating our calculated heats of formation as $\Delta H°$ values, and we have not done so.

Experimental

The americium for this work was prepared by the sequence of nuclear reactions[2]: $Pu^{239}(n,\gamma)Pu^{240}(n,\gamma)Pu^{241} \xrightarrow{\beta^-} Am^{241}$. Methods of concentration, purification, and isolation of americium produced in this way have been dis-

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(1) Argonne National Laboratory, Chicago, Illinois. Part of the work described here was included in a dissertation submitted to the Graduate Division of the University of California by H. R. Lohr in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(1a) L. Eyring, B. B. Cunningham and H. R. Lohr, reported at the Symposium on the Chemistry of the Actinide Elements, 118th National Meeting, American Chemical Society, Chicago, September 5, 1950.

(2) G. T. Seaborg, *Phys. Rev.*, **78**, 472 (1950).