dibromide dissolves in nitrobenzene to give a solution whose conductance closely parallels that observed at a molar ratio of unity in the curves of Fig. 3. This fact provides strong evidence in support of eq. (4). A detailed explanation of the maxima in Fig. 3 will require further exploratory work.

In Fig. 4 are presented curves obtained with the various complexing agents for approximately the same concentration of aluminum bromide. When a second mole of ether, ester, ketone or alcohol is coördinated to aluminum bromide in nitrobenzene, a much better electrolyte is obtained than exists in the original solution or in the 1:1 addition compounds. When the second mole is coördinated, a strong ionic bond is formed presumably between the coördinated aluminum ion and a bromide ion. It is quite clear, however, from the order of magnitude of the conductances of these 2:1 addition compounds and the limiting value for bromide ion in nitrobenzene[6] that these compounds exist primarily as ion pairs for the concentrations considered here.

Ipatieff and Schmerling[3] report that these 2:1 addition complexes are not catalytically active for certain alkylation reactions in nitromethane. The results presented here give an interesting correlation between the catalytic activity in nitromethane and the electrolytic properties of the complexes in nitrobenzene. It is apparent from these studies that the nitrobenzene complex of aluminum bromide is much less stable than the 1:1 addition compounds with ether, alcohol, acetone, etc. These results appear to indicate that the catalytic activity of these various complexes may be more directly associated with the nature of the Al–halogen bond than with the electrophilic character of the aluminum halide molecule.

(6) Witschonke and Kraus, THIS JOURNAL, 69, 2472 (1947).

BALTIMORE, MARYLAND RECEIVED AUGUST 24, 1950

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

The Conductance of Aluminum Bromide in Benzonitrile on Addition of Various Basic Complexing Agents at 25°[1]

BY ROSS E. VAN DYKE AND THOMAS S. HARRISON[2]

In this paper the conductivities and relative stability of a number of addition compounds of aluminum bromide in benzonitrile are compared with observations made upon similar solutions in nitrobenzene as solvent.[3,4] Conductance data are presented for benzonitrile solutions of aluminum bromide on addition of methanol, trimethylamine and pyridine. Dimethyl ether and acetone apparently do not coördinate with aluminum bromide in this solvent. Data are also presented to show the effect of addition of benzonitrile to nitrobenzene solutions of aluminum bromide and for addition of pyridine to solutions of $AlBr_3 \cdot (CH_3)_3N$ in benzonitrile. These results yield some indications as to the relative stability of $(CH_3)_3N$, C_5H_5N and C_6H_5CN complexes of aluminum bromide.

I. Introduction

The conductance of aluminum bromide on addition of a wide variety of complexing agents in nitrobenzene has been determined recently.[3,4] Nitrobenzene forms a yellow complex $C_6H_5NO_2 \cdot AlBr_3$ which appears to be less stable than the ether, acetone or alcohol, etc., addition compounds. It was of considerable interest, therefore, to determine the relative stabilities and the conductance of a number of these addition compounds in a more basic solvent in which the extent of interaction of the salt with the solvent was greater than in the case of nitrobenzene. For this purpose benzonitrile was chosen. Benzonitrile has a vapor pressure of 0.060 cm. at 25° which renders it suitable for the techniques of handling gaseous complexing agents as used in the earlier studies and it is readily purified.

The conductance curve for aluminum bromide in benzonitrile has been determined for molalities as low as 3×10^{-3} and the nature and stability of the salt–solvent complex has been clarified. The conductance of aluminum bromide in benzonitrile on addition of varying quantities of trimethylamine, methanol and pyridine has been determined. In addition, the effect of addition of pyridine to a benzonitrile solution of the 1:1 trimethylamine complex of aluminum bromide is reported.

II. Experimental

(1) **Materials.**—Benzonitrile[5] was treated with anhydrous aluminum chloride from which it was rapidly distilled *in vacuo* at 40–50°. The distillate was washed with alkali, dried over calcium chloride and subjected to several vacuum distillations at 35°. This product was then fractionally crystallized several times and was dried finally over finely divided activated aluminum oxide. The solvent was stored in this manner and withdrawn through a sintered glass filter as needed. The solvent had a specific conductance of 2×10^{-8} mho and the index of refraction was found to be $n^{25.5}{}_D$ 1.52568. Aluminum bromide was prepared, purified and handled as described in earlier papers.[3] Nitrobenzene was purified according to previously described procedures.[3] Trimethylamine (Matheson Product) was found by analysis to be of 98.5% purity, assuming the impurity to be dimethylamine. The gas was dried over barium oxide as used. Ammonia from the laboratory stock cylinder was dried over sodium. Acetone (Baker C.P. Product) was preliminarily dried over barium oxide, followed by distillation from a fresh batch of barium oxide through an efficient column as needed. Methanol (Baker C.P. Product) was dried and handled in a manner similar to that for acetone. Pyridine (Barrett Co. research grade) was subjected to two fractionations followed by several fractional crystallizations. The final product was stored over activated aluminum oxide. Nitrogen was dried over silica gel and phosphoric anhydride.

(2) **Apparatus and Procedure.**—Resistances were measured on a Leeds and Northrup bridge of the Jones type, the cells being thermostated in oil at 25 ± 0.01°. The conductance cells were of varying design but were similar to

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

(2) *Grasselli Division, E. I. du Pont de Nemours & Company,* Wilmington, Del.

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

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

(5) Kindly donated by Socony-Vacuum Oil Company.

those described in earlier papers.[3] The techniques of handling the cells and of solution preparation have been described previously.[3] Gaseous complexing agents were measured by volume over mercury in a gas buret and were introduced into the cell containing the solution which was completely outgassed. Liquid complexing agents were introduced by means of a micro weight pipet from which small uniform droplets were obtained. These materials were added by removing the cap of the conductance cell in which a nitrogen atmosphere was maintained. The magnitude of the additions was determined with the usual 0.1 mg. precision.

(3) **Solubility of Trimethylamine in Benzonitrile.**—The solubility of trimethylamine was determined at 25° as a function of pressure. These results are presented in Table I where the pressure is recorded in the first column and the concentration of the solution in moles per 1000 g. of solvent in the second column. The pressures were read by means of a cathetometer and a closed end manometer. By interpolation from a plot of these data, the concentration of free amine in the benzonitrile solutions of aluminum bromide could be determined.

TABLE I

THE SOLUBILITY OF TRIMETHYLAMINE IN BENZONITRILE AT 25°

P, cm.	Molality
0.06	0.000
1.49	.0534
3.47	.1298
7.48	.2913
11.77	.4675
15.74	.6366
19.29	.8044

III. Results

(1) **Benzonitrile as Complexing Agent in Nitrobenzene.**—The conductance of aluminum bromide in nitrobenzene on addition of benzonitrile has been studied for several concentrations of salt. These data are all presented graphically in Fig. 1. Numerical data for two of these solutions are presented in Table II.

TABLE II

THE CONDUCTANCE OF ALUMINUM BROMIDE IN NITROBENZENE ON ADDITION OF BENZONITRILE AT 25°

A. Mmoles $AlBr_3$, 9.765; molality, 0.2115		B. Mmoles $AlBr_3$, 30.130, molality, 0.5409	
$\kappa \times 10^4$	Molar ratio $C_6H_5CN/AlBr_3$	$\kappa \times 10^4$	Molar ratio $C_6H_5CN/AlBr_3$
8.595	0.000	18.02	0.000
10.55	0.1337	22.47	0.2263
13.52	.3955	26.13	.5132
15.12	.5861	28.04	.7665
16.45	.7950	29.30	1.060
17.72	1.102	29.20	1.417
18.23	1.406		
18.42	1.668		
18.47	2.073		
18.44	2.420		

(2) **The conductance of aluminum bromide in benzonitrile** as a function of concentration has been determined at 25°. Concentrations are reported in moles of salt per 1000 g. of solvent *m* and the Λ values are calculated accordingly, $\Lambda_{\text{Molal}} = 1000\ \kappa/m$. Two series of data are presented in Table III.

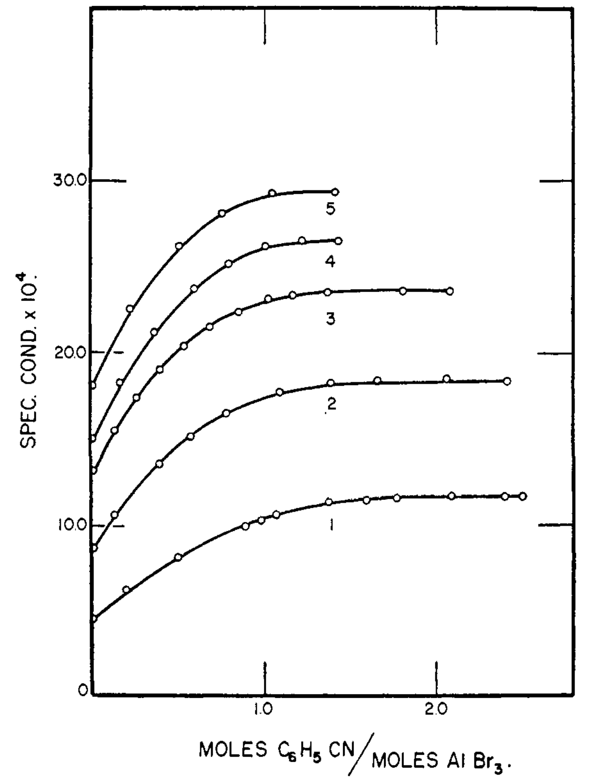


Fig. 1.—Conductance of aluminum bromide in nitrobenzene on addition of benzonitrile at 25°: (1), 0.1033 molal; (2), 0.2115 molal; (3), 0.3046 molal; (4), 0.4013 molal; (5), 0.5409 molal.

(3) **Trimethylamine.**—The conductance of aluminum bromide in benzonitrile on addition of trimethylamine was determined for three concentrations of salt, *m* = 0.1601, 0.1010 and 0.0772. These data are all presented graphically in Fig. 2;

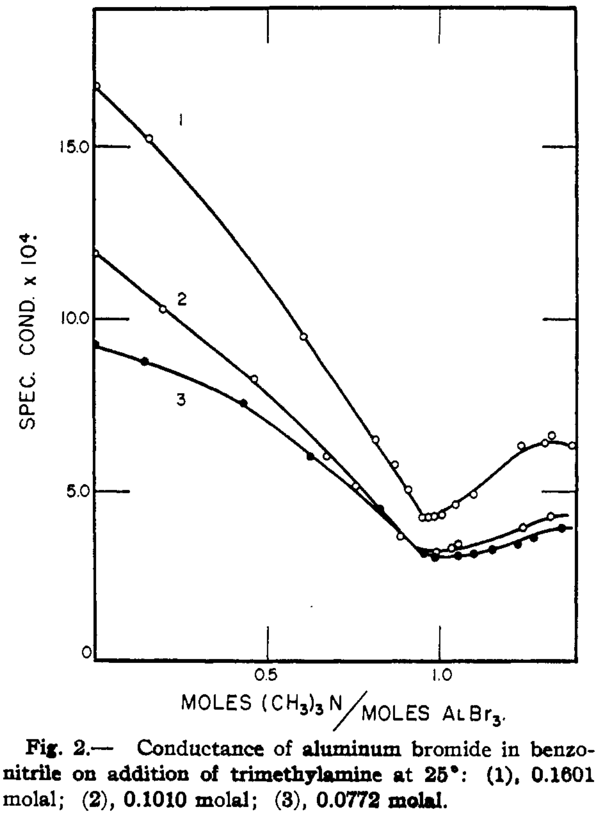


Fig. 2.— Conductance of aluminum bromide in benzonitrile on addition of trimethylamine at 25°: (1), 0.1601 molal; (2), 0.1010 molal; (3), 0.0772 molal.

TABLE III

THE CONDUCTANCE OF ALUMINUM BROMIDE IN BENZONITRILE AT 25°

A, Λ_{Mola}	$m \times 10^3$	B, Λ_{Molal}	$m \times 10^3$
10.30	138.3	9.70	170.3
12.99	38.3	13.42	38.4
15.32	10.4	15.56	13.3
15.59	3.49	17.52	3.35

numerical values for one of these solutions are given in Table IV.

TABLE IV

THE CONDUCTANCE OF ALUMINUM BROMIDE IN BENZONITRILE ON ADDITION OF TRIMETHYLAMINE

Mmoles $AlBr_3$, 9.660; *m* 0.1601

$\kappa \times 10^4$	Vapor press., cm.	Uncomb. amine, mmoles	Combined amine, mmoles	Combined amine/salt
16.75	0.05	0.000	0.000	0.000
15.20	.16	.302	1.500	0.1547
9.495	.21	.422	5.871	.6050
6.495	.21	.422	7.943	.8190
5.752	.18	.362	8.424	.8690
4.990	.23	.482	8.729	.9010
4.224	.25	.542	9.218	.9510
4.196	.37	.783	9.381	.9675
4.227	.57	1.205	9.538	.9835
4.248	.82	1.747	9.809	1.011
4.610	1.36	2.895	10.167	1.048
4.898	2.67	5.850	10.663	1.099
6.305	6.58	15.13	12.05	1.242
6.407	7.79	18.21	12.70	1.309
6.685	9.11	21.53	12.85	1.325
6.350	10.34	24.60	13.46	1.388

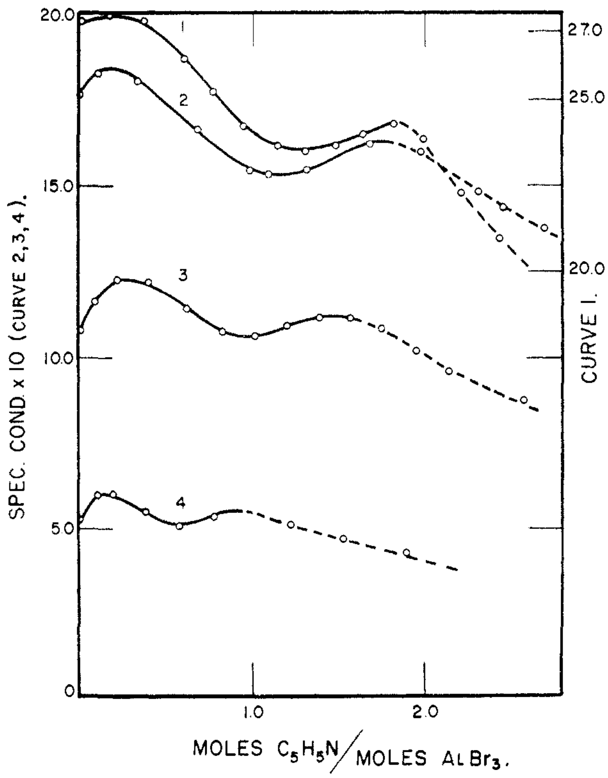


Fig. 3.—Conductance of aluminum bromide in benzonitrile on addition of pyridine at 25°: (1), 0.3330 molal; (2), 0.1720 molal; (3), 0.0932 molal; (4), 0.0633 molal.

(4) **Pyridine.**—The conductance of aluminum bromide in benzonitrile on addition of pyridine was studied at four concentrations of salt, *m* = 0.3330, 0.1720, 0.0932, 0.0633. These data are presented graphically in Fig. 3. Numerical data for two of these solutions are listed in Table V.

TABLE V

THE CONDUCTANCE OF ALUMINUM BROMIDE IN BENZONITRILE ON ADDITION OF PYRIDINE AT 25°

A. Mmoles $AlBr_3$, 10.600; molality, 0.1720		B. Mmoles $AlBr_3$, 1.827; molality, 0.0633	
$\kappa \times 10^4$	Ratio pyridine/$AlBr_3$	$\kappa \times 10^4$	Ratio pyridine/$AlBr_3$
17.67	0.000	5.275	0.000
18.27	.1118	5.975	.1087
18.05	.3440	6.002	.2008
16.64	.6840	5.495	.3898
15.49	.9940	5.045	.5785
15.37	1.104	5.298	.7815
15.47	1.329	5.092	1.225
16.22	1.689	4.690	1.528
15.96	1.983	4.306	1.886
14.85	2.313		
14.38	2.458		
13.72	2.703		
13.07	3.047		

(5) **Methanol.**—The conductance of aluminum bromide in benzonitrile on addition of methanol was studied at three concentrations of salt, *m* = 0.2963, 0.1890, 0.0465. Numerical data for one of these solutions are presented in Table VI and are shown graphically in Fig. 4, curve 1.

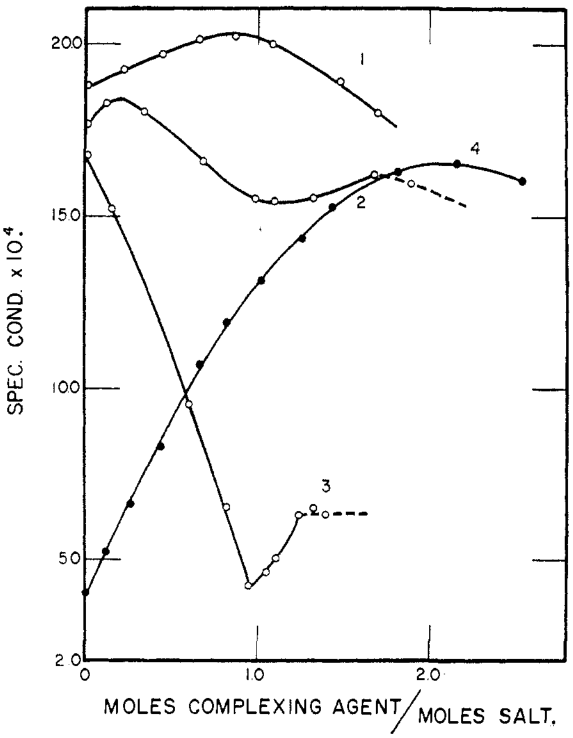


Fig. 4.—Comparison plot for various complexing agents in benzonitrile at 25°: (1), 0.1890 molal $AlBr_3$ on addition of methanol; (2), 0.1720 molal $AlBr_3$ on addition of pyridine; (3), 0.1601 molal $AlBr_3$ on addition of trimethylamine; (4), 0.2270 molal $AlBr_3 \cdot (CH_3)_3N$ on addition of pyridine.

TABLE VI

THE CONDUCTANCE OF ALUMINUM BROMIDE IN BENZONITRILE ON ADDITION OF METHANOL AT 25°

Mmoles $AlBr_3$, 7.958; molality = 0.1890

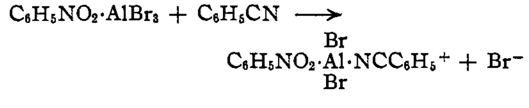
$\kappa \times 10^4$	Ratio $CH_3OH/AlBr_3$	$\kappa \times 10^4$	Ratio $CH_3OH/AlBr_3$
18.78	0.000	20.02	1.079
19.17	.2193	19.70	1.212
19.67	.4497	18.89	1.476
20.06	.6520	18.03	1.705
20.19	.8720	17.04	1.950

IV. Discussion

The extent to which benzonitrile reacts with aluminum bromide was determined by isolation of the reaction product. Upon removal of excess solvent from a concentrated solution by prolonged pumping at 40°, the weight of the white powdery product compared to the weight of the original sample of aluminum bromide indicated the formation of a 2:1 addition compound $AlBr_3\cdot 2C_6H_5CN$. With further pumping at a somewhat higher temperature the loss in weight of this complex indicated a ratio of approximately 1.5 moles of solvent per mole of salt. It is quite probable that complexes of higher order occur in solutions of the concentration range considered in this paper. Müller and Weisitsch[6] report a complex involving 4 moles of benzonitrile per mole of $AlBr_3$.

The values for the molal conductance in benzonitrile in Table III indicate that aluminum bromide is a rather strong electrolyte in this solvent. While the study has not been extended to dilutions sufficiently great to estimate a limiting conductance, a Λ *versus* $\sqrt{m}$ plot of the data is similar in form to that obtained for this salt in pyridine.[7]

Since aluminum bromide forms a 1:1 addition compound with nitrobenzene in which it is a weak electrolyte, it was decided to study the effect upon the conductance of addition of benzonitrile to such solutions. According to Fig. 1, the conductance increases upon addition of nitrile, the magnitude of the increase depending upon the aluminum bromide concentration as would be expected. In all cases the conductance reaches a nearly constant maximum value. In the more concentrated solutions this appears at a molar ratio close to unity, while for more dilute solutions the conductance becomes constant as the molar ratio approaches a value of 2.0. The intense yellow color of the nitrobenzene complex which is probably due to the resonating structure, was observed to vanish completely when the conductance reached this constant maximum value. While it is not possible to determine with any certainty the extent of interaction of the nitrile with the nitrobenzene complex, the initial reaction as presented in eq. (1) appears probable.

(1)


$$C_6H_5NO_2\cdot AlBr_3 + C_6H_5CN \longrightarrow C_6H_5NO_2\cdot\overset{Br}{\underset{Br}{Al}}\cdot NCC_6H_5^+ + Br^-$$

Any further interaction with benzonitrile would be that of substitution for the nitrobenzene or coordination of another mole of nitrile to the $C_6H_5NO_2\cdot AlBr_2\cdot C_6H_5CN^+$ ion. Of interest is the fact that the maximum values of the conductance reached in these solutions are approximately equal to the conductances of aluminum bromide in benzonitrile for similar concentrations. The data of Table VII present this comparison.

TABLE VII

Benzonitrile solutions		Nitrobenzene solutions + benzonitrile	
$\kappa \times 10^4$	Molality	$\kappa \times 10^4$	Molality
11.86	0.1010	11.63	0.1033
18.78	.1890	18.44	.2115
27.36	.3330	23.55	.3046

Trimethylamine.—The results for trimethylamine as complexing agent are shown in Fig. 2. The solutions studied are more dilute than those studied in nitrobenzene because of the limited solubility of the amine complexes in benzonitrile. The conductance of the solutions decreases rapidly along a smooth curve to a molar ratio close to 1.0. In this region there appears a small concentration of free amine. In the vicinity of unit molar ratio the conductance changes are small and then begin to increase somewhat with further additions of amine. This increase is accompanied by a rapid increase in free amine concentration. When the molar ratio of amine to salt reaches a value of about 1.3, the amine complex precipitates as a finely divided crystalline material. The general form of the curve is similar to that observed on addition of trimethylamine to aluminum bromide in nitrobenzene. It is of interest to record the fact that while dimethyl ether forms a quite stable 1:1 addition compound with aluminum bromide in nitrobenzene, there appears to be no interaction between these molecules in benzonitrile. When the complex $AlBr_3\cdot(CH_3)_3N$ is prepared by reaction of these materials directly and dissolved in benzonitrile, the specific conductance of the solution for corresponding concentrations lies very close to the values at the minima in Fig. 2. This would indicate that formation of this complex is the principal reaction taking place upon addition of amine up to a molar ratio of unity. Thereafter, it appears that there is strong competition between the amine and the solvent molecules for coördination positions.

Pyridine.—As shown in Fig. 3, when pyridine is added to solutions of aluminum bromide in benzonitrile the conductance increases at first, passes through a maximum, then decreases to a minimum and passes through a second maximum which is followed by precipitation of a pyridine complex which is indicated by the broken line portion of the curves. The changes in conductance on addition of pyridine are not large either for concentrated or more dilute solutions. Of considerable interest is the shift in position of the minimum from a molar ratio close to unity for the concentrated solutions represented by curves 1 and 2 to a ratio value of approximately 0.6 for the dilute solution (curve 4). The gradual changes in direction of the conductance curves suggest an equilibrium among several species of pyridine addition compounds. Further, the results indicate that the strength of

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[6] Müller and Weisitsch, *Z. anorg. Chem.*, **208**, 304 (1932).

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

the pyridine complexes as electrolytes in benzonitrile is not much different from that of the salt–solvent complex. The composition of the precipitated complex appeared to vary somewhat in accordance with the shift in the position of the conductance minimum and the point at which precipitation took place. Further clarification of this system will require additional investigation.

When pyridine is added to a solution of the trimethylamine complex $AlBr_3 \cdot (CH_3)_3N$ in benzonitrile, the reaction appears to be more straightforward. In Fig. 4 curve 4, are plotted data for a 0.2270 molal solution of the amine complex in benzonitrile on addition of pyridine. The conductance increases rapidly on addition of pyridine without any noticeable break at the 1:1 mole ratio and approaches a maximum at a ratio value of 2.0. Upon further additions of pyridine the conductance decreases with precipitation of a pyridine complex. An aluminum analysis on the dried precipitate yielded a value of 563 for the molecular weight which rather clearly indicates that the complex was $AlBr_3 \cdot (CH_3)_3N \cdot 3C_5H_5N$.

Methanol.—In Curve 1, Fig. 4 are presented conductance data for addition of methanol to a solution of aluminum bromide in benzonitrile. The conductance increases somewhat, passes through a maximum at a point close to a molar ratio of 1.0 and then decreases with apparent evolution of small amounts of hydrogen bromide on addition of further quantities of methanol. The magnitude of the conductance increase to the maximum varies with initial concentration of salt but the position of the maximum does not appear to vary. The increase in conductance on addition of methanol may be due to direct addition to the salt–solvent complex rather than a reaction involving competition with the complexed solvent molecule. It was observed that acetone as well as dimethyl ether does not coördinate in this solvent. On the other hand, ammonia forms stable complexes in this solvent as expected, but the limited solubility of these complexes renders the determination of the form of the curve very difficult.

The curves of Fig. 4 present a comparison of typical curves for approximately equivalent concentrations of salt in benzonitrile upon addition of methanol, pyridine and trimethylamine. The form of the amine curve is quite similar to that obtained for addition of ether or amine to aluminum bromide in nitrobenzene in which the reactions appear to be straightforward addition reactions. With pyridine, reaction is probably complete, but the competition of the solvent molecules presents a very complex picture which is difficult to analyze by this method. With methanol the complex $AlBr_3 \cdot (C_6H_5CN)_x \cdot CH_3OH$ (where $x \geqslant 2$) is probably formed with subsequent evolution of hydrogen bromide.

BALTIMORE, MARYLAND RECEIVED AUGUST 24, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

The Ionization Constants of β-Alanine in Water and Isopropyl Alcohol–Water Mixtures

BY MARGIE MAY[1] WITH W. A. FELSING

From electromotive force measurements on cells without liquid junction, the acid ionization constants of β-alanine have been determined in 0, 5, 10 and 20 weight per cent. isopropyl alcohol in water from 0 to 40°. The basic ionization constants were determined in water by the same method. The ionization constants have been expressed as functions of temperature by equations of the form $-\log K = A/T + CT - D$.

The effect of solvent medium on the ionization of propionic[2,3] and *n*-butyric[4] acids has been determined in this Laboratory by measurements in several alcohol–water solutions from 0 to 40°.

In this investigation the study was extended to the ampholyte, β-alanine, in water and 5, 10 and 20 weight per cent. isopropyl alcohol–water mixtures. The acidic and basic dissociations may be written $HA^+ \rightleftarrows A^{\pm} + H^+$ and $AOH^- \rightleftarrows A^{\pm} + OH^-$, where $A^{\pm}$ represents the dipolar ion structure of the electrically neutral molecule. The corresponding ionization constants K_A and K_B were determined from electromotive force measurements on cells without liquid junction, which is the precise method developed by Harned and co-workers.[5]

From cells of the type

$$H_2 \left| \begin{array}{l} \beta\text{-alanine } (m_1) \\ \beta\text{-alanine hydrochloride } (m_2) \\ X\ \%\text{ isopropyl alcohol} \end{array} \right| \text{AgCl–Ag}$$

the thermodynamic ionization constant K_A is given by

$$-\log K_A = (E - E^0)F/2.3026RT + \log m_{HA^+}(m_{Cl^-}/m_{A^{\pm}}) + \log \gamma_{HA^+}(\gamma_{Cl^-}/\gamma_{A^{\pm}}) \quad (1)$$

where E is the cell voltage corrected to a hydrogen pressure of one atmosphere; E^0 is the molal potential of the silver–silver chloride electrode in the solvent used[6,7]; m is weight molality; and γ is an activity coefficient. The activity coefficient term in Eq. (1) may be approximated in two ways, the first of which employs the Debye–Hückel limiting law expression for $\gamma_{HA^+} \cdot \gamma_{Cl^-}$, which is, after substitution of the proper constants

$$\log \gamma_{HA^+} \cdot \gamma_{Cl^-} = -2(1.844 \times 10^{-6})(DT)^{-3/2} \sqrt{\mu d_0} \quad (2)$$

or $-2S_{(f)}\sqrt{\mu d_0}$, where D is the dielectric constant of the solvent, d_0 is its density and μ is ionic

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(1) Holder of the Magnolia Petroleum Company fellowship for 1949–1950.

(2) Patterson with Felsing, THIS JOURNAL, 64, 1480 (1942).

(3) Moore with Felsing, *ibid.*, 69, 2420 (1947).

(4) Felsing and May, *ibid.*, 70, 2904 (1948).

(5) Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Second Edition, Reinhold Publishing Corp., New York, N. Y., 1950.

(6) Harned and Ehlers, THIS JOURNAL, 54, 1350 (1932).

(7) Moore with Felsing, *ibid.*, 69, 1076 (1947).