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).

strength. A quantity $-\log K_A'$ is now defined by

$$-\log K_A' = (E - E^0)F/2.3026RT + \log m_{HA^+}(m_{Cl^-}/m_{A^\pm}) - 2\,S_{(f)}\sqrt{\mu d_0} \quad (3)$$

From the cell expression and the ionization reaction it is apparent that $m_{HA^+} = m_2 - m_{H^+}$; $m_{A^\pm} = m_1 + m_{H^+}$; $m_{Cl^-} = \mu = m_2$. An estimate of m_{H^+} is given by

$$-\log m_{H^+} \cong (E - E^0)F/2.3026RT + \log m_2 - 2S_{(f)}\sqrt{\mu d_0} \quad (4)$$

and substituted into Eq. (3) for a series of cell solutions prepared by dilution of a single stock solution. Extrapolation of $-\log K_A'$ *vs.* μ to $\mu = 0$ then yields a preliminary value of $-\log K_A$, which is used to recalculate m_{H^+}. Then a new series of $-\log K_A'$ values is plotted and extrapolated as before, the process being repeated until an additional step will not change the intercept.

As an alternate method[6] of extrapolation, the experimentally determined activity coefficients of an electrolyte of similar ionic type may be substituted for $\gamma_{HA^+}.\gamma_{Cl^-}$. The use of two curves is of practical advantage in making the graphical extrapolations.

To determine K_B, cells of the type

$$\mathrm{H_2}\left|\begin{array}{l}\beta\text{-alanine }(m_1)\\ \text{sodium salt of }\beta\text{-alanine }(m_2)\\ \text{sodium chloride }(m_3)\end{array}\right|\mathrm{AgCl{-}Ag}$$

are used.

$$-\log K_B = -\log K_w - (E - E^0)F/2.3026RT - \log m_{A^\pm}(m_{Cl^-}/m_{AOH^-}) - \log \gamma_{A^\pm}\cdot\gamma_{Cl^-}/\gamma_{AOH^-} \quad (5)$$

K_w is the ion product of water. The last term in Eq. (5), containing the activity coefficient of a neutral molecule and the ratio of those of univalent ions, is approximately linear in μ and vanishes at $\mu = 0$. Hence, no attempt is made to evaluate it, and $-\log K_B'$ is defined by

$$-\log K_B' = -\log K_w - (E - E^0)F/2.3026RT - \log m_{A^\pm}(m_{Cl^-}/m_{AOH^-}) \quad (6)$$

where

$$m_{A^\pm} = m_1 + m_{OH^-};\ m_{AOH^-} = m_2 - m_{OH^-};\ m_{Cl^-} = m_3;\ \mu = m_2 + m_3$$

The first estimation of m_{OH^-} and the steps of the graphical procedure are made in a manner analogous to that described for K_A. Two graphs were sufficient in all cases.

It should be possible to determine K_w in the alcohol–water mixtures from cells represented by

$$\mathrm{H_2}\left|\begin{array}{l}\mathrm{NaOH}\\ \mathrm{NaCl}\\ X\ \%\ \text{isopropyl alcohol}\end{array}\right|\mathrm{AgCl{-}Ag}$$

since this has been done successfully in water and in dioxane–water mixtures.[5]

Experimental

β-Alanine.—β-Alanine from the Eastman Kodak Company was recrystallized from an ethyl alcohol–water solution and dried several days in a vacuum desiccator over solid potassium hydroxide. On the basis of loss in weight at 105°, which reached a limiting value of 0.10% in 4.5 hours, the amino acid was assumed to be 99.90% pure. A Kjeldahl analysis indicated 15.5% nitrogen; the theoretical value is 15.72.

Hydrochloric Acid.—Concentrated reagent grade hydrochloric acid was used in the preparation of solutions.

Hydrogen.—Electrolytic hydrogen was passed through sulfuric acid–dichromate solution, 5 *N* NaOH, water, "Drierite" and over-heated copper turnings.

Isopropyl Alcohol.—Ninety-nine per cent. isopropyl alcohol was refluxed over unslaked lime and distilled twice through a one-meter packed column. The middle portion, normal b.p. 82.5°, was reserved for use.

Sodium Chloride.—Concentrated hydrochloric acid was added to a solution of reagent grade sodium chloride. The resulting precipitate was dried and heated at 650° for 2 hours.

Sodium Hydroxide.—A 50% solution prepared from reagent grade sodium hydroxide which contained not more than 0.01% chloride was filtered through sintered glass and used immediately in the preparation of solutions.

Water.—Conductivity water produced in a special glass still was used in the preparation of the solutions.

Solutions.—Hydrochloric acid, 0.15 to 0.2 *N*, was standardized gravimetrically. Sodium hydroxide solutions, 0.1 to 0.2 *N*, were standardized by weight titration with the standard hydrochloric acid to the methyl red end-point. Results of this titration procedure were confirmed by use of Bureau of Standards benzoic acid.

Stock solutions in the various solvents were prepared by weight from the appropriate materials and were stored in a refrigerator to prevent bacterial decomposition. The cell solutions were made by weight dilutions of the stock solutions with the solvent mixtures.

Precautions were taken to exclude carbon dioxide in the preparation and handling of the basic solutions.

Electromotive Force Measurements.—The apparatus and techniques were essentially those described previously.[7] The silver–silver chloride electrodes were prepared by thermal decomposition of a mixture of 10% silver chlorate and 90% silver oxide.

A single series of measurements was made on each cell solution at 0, 5, 15, 25, 35 and 40°. Cells containing the acid solutions reached constant voltages at 0° in 1 to 2 hours and in less time after a change of temperature. Duplicate cells seldom differed by more than 0.05 mv.

In the basic solutions the time required to attain constant voltages and the constancy of these values was comparable to that in the acid solutions, but the average reproducibility of like cells was 0.16, 0.08, 0.17 and 0.13 mv. in the 1B, 2B, 3B and 4B series, respectively. The 3B and 4B measurements were made on triplicate cells.

Results are reported here for K_B in water only. Many attempts to measure K_w in isopropyl alcohol–water solutions by means of cells of the third type described were unsuccessful because of lack of reproducibility, differences of 0.5 to 1 mv. in like cells being frequently found. In some check measurements on this type of cell in water the agreement was quite good, indicating that the difficulty was due to the presence of the alcohol.

Results[8]

Evaluation of K_A and K_B.—In all four solvents the graphs of $-\log K_A'$ *vs.* μ are typical of those found for other amino acids.[5] In each case m_1 was approximately equal to m_2. Figure 1 illustrates the two extrapolation methods which were described. In the alcohol–water solutions it was found more convenient to plot an empirical function obtained by addition of a term $k\mu$ (k is an arbitrary constant) to the value of $-\log K_A'$ based on the Debye–Hückel expression than to use experimental activity coefficients. The purpose of this new function, represented by the solid circles in Fig. 2, is only to aid in location of the intercept. The circles representing $-\log K_A'$ have a radius of 0.001 *pK* unit, corresponding to 0.06 mv.

From Fig. 3 it is apparent that the uncertainty

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[8] For tables supplementary to this article order Document 2919 from American Documentation Institute, 1719 N Street, N. W., Washington, D. C., remitting $0.50 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $0.50 for photocopies (6 × 8 inches) readable without optical aid.

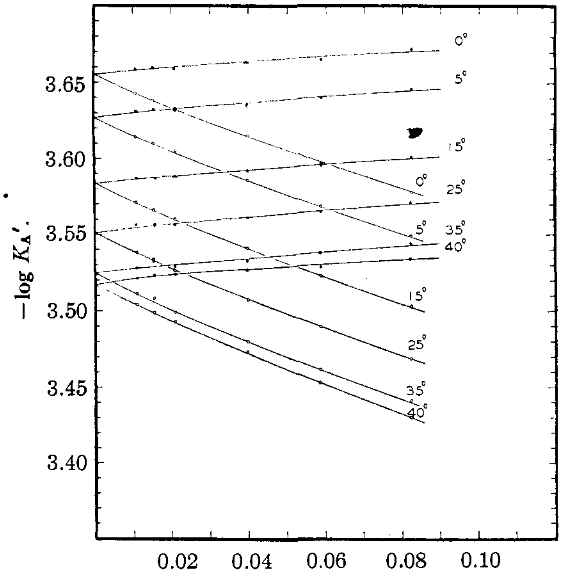

Fig. 1.—Evaluation of −log K_A in water: —O—, using limiting law; —●—, using $\gamma_{\pm}$ for HCl.

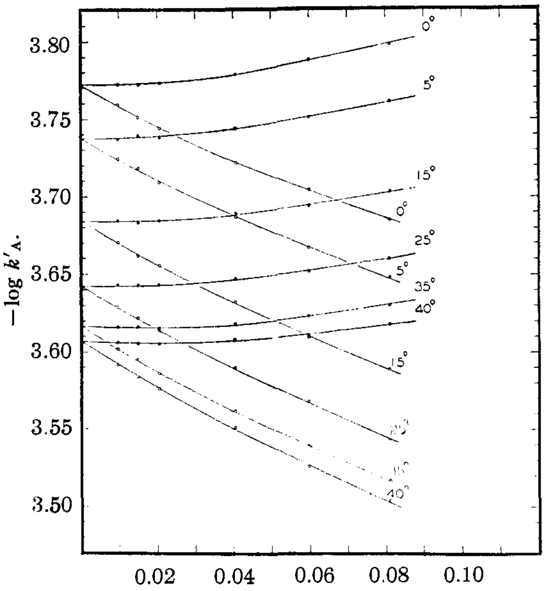

Fig. 2.—Evaluation of −log K_A in 10% isopropyl alcohol: —O—, −log K_A'; —●—, −log K_A' + 1.4μ.

in the values of K_B is greater because of scattering of points and curvature of the lines in the dilute region. For this reason, data were obtained from four stock solutions with different concentration ratios $m_1:m_2:m_3$, which were, in stock solution 1B, approximately 1:1:1; in 2B, 1:1.5:1.4; in 3B, 1:1.2:3.3; and in 4B, 1:2.0:4.1. It was hoped that increasing the relative concentration of chloride ion would decrease any error caused by the low solubility of silver oxide in the basic solutions or by the tendency of the silver ion to form complexes with the amino acid. In plots of −log K_B' the radius of the circles is 0.0025 *pK* unit.

The ionization constants corresponding to the

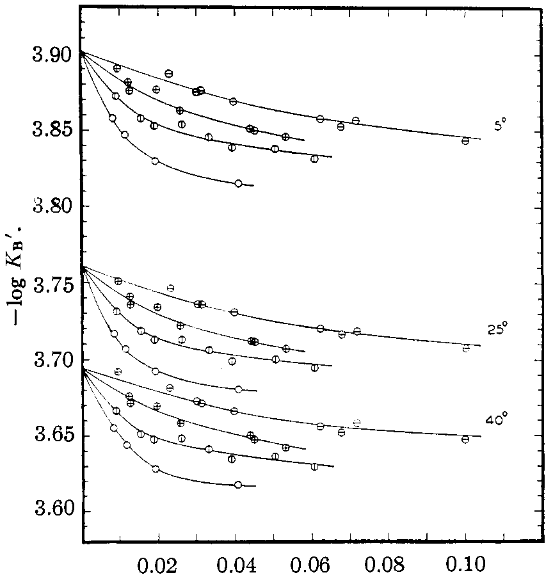

Fig. 3.—Evaluation of −log K_B in water: —O—, stock solution 1B; —⦶—, 2B; —⊖—, 3B; —⊕—, 4B.

extrapolated functions at each temperature are recorded in Table I.

Effect of Temperature.—Least squares equations of the form $-\log K = A/T + CT - D$ reproduce the data with an average deviation of ±0.0008 *pK* unit and a maximum of ±0.002 unit. These equations are shown by the solid lines in Fig. 4, the extrapolated values by the circles. The constants A, C and D are given in Table II.

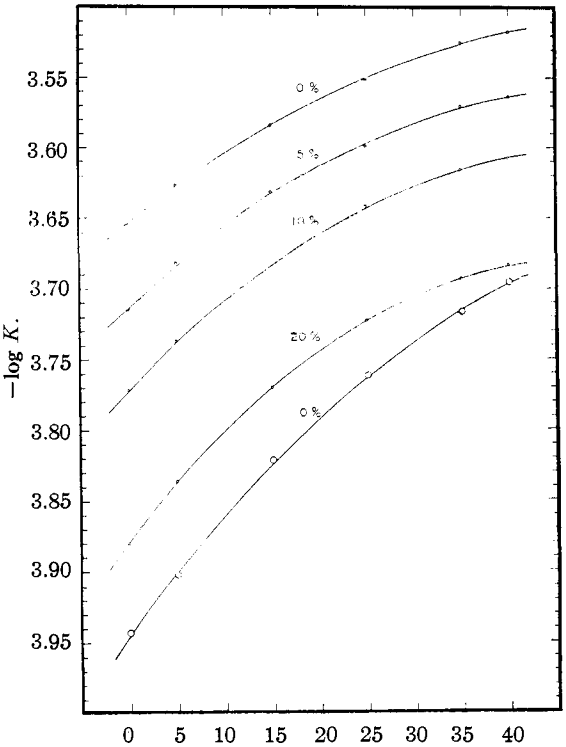

Fig. 4.—Effect of temperature on the ionization constants: —o—, −log K_A; —O—, −log K_B.

TABLE I

THE IONIZATION CONSTANTS OF β-ALANINE IN 0, 5, 10 AND 20% ISOPROPYL ALCOHOL

Alcohol, %	0°	5°	15°	25°	35°	40°
			$K_A \times 10^4$			
0	2.21	2.36	2.61	2.81	2.99	3.04
5	1.93	2.08	2.33	2.52	2.69	2.73
10	1.69	1.83	2.07	2.28	2.42	2.48
20	1.32	1.46	1.70	1.89	2.03	2.07
			$K_B \times 10^4$			
0	1.14	1.25	1.51	1.73	1.92	2.02

From these equations the standard thermodynamic quantities ΔF_i^0, ΔH_i^0, ΔCp_i^0 and ΔS_i^0 for the ionization reactions may be calculated.[3]

TABLE II

CONSTANTS OF THE EQUATION $-\log K = A/T + CT - D$

Alcohol, %	A	C	D
		$-\log K_A$	
0	1231.71	0.010957	3.8478
5	1594.69	.014887	6.1904
10	1753.58	.016375	7.1209
20	2351.54	.022608	10.9051
		$-\log K_B$	
0	1881.78	.015784	7.2558

Effect of Solvent.—Graphs of $-\log K_A$ *versus* the mole fraction isopropyl alcohol and *versus* the reciprocal of the dielectric constant consist of families of smooth curves with greater curvature than those for propionic[2] and *n*-butyric[3] acids in the same solvents.

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[CONTRIBUTION FROM THE LABORATORY OF C. A. WAMSER]

Equilibria in the System Boron Trifluoride–Water at 25°

BY CHRISTIAN A. WAMSER

The system BF_3–H_2O is investigated from dilute solutions to the dihydrate, $BF_3 \cdot 2H_2O$. Evidence of the formation and hydrolysis of HBF_3OH in the reaction of BF_3 with H_2O is afforded by conductance measurements, and suggests a mechanism for the experimentally observed slow formation of HBF_4. The rate constant for the net reaction of BF_3 and H_2O is given by: k (in liters mole^{-1} min.$^{-1}$) = 0.064 + 7.35[H$^+$] at 25°. The hydrolysis constant of HBF_3OH, evaluated from kinetic considerations, is 0.011 at 25°. Mixtures of BF_3–H_2O at equilibrium contain the species: HBF_4, HBF_3OH, $HBF_2(OH)_2$, $HBF(OH)_3$(?) and $B(OH)_3$. Determination of the equilibrium composition from dilute solutions to the dihydrate is made possible by special analytical methods. The dihydrate consists essentially of pure $H_3O^+BF_3OH^-$ at 25°. The relative strengths of the fluoboric acids are estimated from conductance data.

It has long been known that fluoboric and boric acids are produced when boron trifluoride reacts with water

$$4BF_3 + 3H_2O = 3HBF_4 + B(OH)_3$$

In an attempt to interpret the titratable acidities of aqueous solutions of boron trifluoride, and to account for the presence of fluoride ion at the titration end-point, Gasselin[1] has expressed the reaction as

$$2BF_3 + 3H_2O \longrightarrow HBF_4 + B(OH)_3 + 2HF$$

However, both of the above equations have always been recognized as oversimplifications, since aqueous solutions of boron trifluoride do not contain the fluoride ions of hydrofluoric acid but behave as if an easily hydrolyzed form of fluoboric acid were present.[2]

No studies of kinetics or equilibria in the system boron trifluoride–water are reported in the literature,[3] and only recent investigations[4,5,6] have suggested the nature of the species that may be present and the analytical methods that might be applicable.

Nature of the Present Investigation.—The present investigation is concerned with the system boron trifluoride–water over the concentration range extending from dilute solutions to the dihydrate, $BF_3 \cdot 2H_2O$. The range of stability of the dihydrate, generally conceded to exist as the pure compound $H_3O^+BF_3OH^-$ at or below its melting point, is extended to 25° on the basis of conductance and analytical data. Evidence of the formation and hydrolysis of HBF_3OH when BF_3 reacts with water is afforded by conductance measurements, and suggests a mechanism for the experimentally observed (slow) formation of HBF_4 on the basis of the reaction $HBF_3OH + HF \rightarrow HBF_4 + H_2O$. Determination of the equilibrium composition of BF_3–H_2O mixtures is made possible by application of specially developed analytical techniques and methods. Electrometric titration of a solution of BF_3–H_2O at equilibrium confirms the analytical interpretation of the relative concentrations of the various species. The hydrolysis constant of HBF_3OH cannot be evaluated from analytical or conductance data and is hence approached from kinetic considerations. Finally, certain conclusions dependent upon this hydrolysis constant, such as the relative strengths of the fluoboric acids and their concentrations, are considered.

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