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

The Ionization Constants of *n*-Butyric Acid in Isopropyl Alcohol–Water Mixtures from 0 to 40°

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

Introduction

The object of this investigation was to continue a study of the effect of change in solvent medium on the ionization of weak electrolytes by measurement of the ionization constants on *n*-butyric acid in 5, 10, and 20 weight per cent. isopropyl alcohol–water solutions. The first precise measurements of this type, using cells without liquid junction for a number of compounds in aqueous organic solvent mixtures, were made by Harned and co-workers.[2] In this Laboratory, the work has been extended by the same method to include acetic acid in methyl and ethyl alcohol–water mixtures[3] and propionic acid in isopropyl alcohol–water mixtures.[4]

In this investigation, the ionization constants were determined from electromotive force measurements on cells of the type H_2/HBu (m_1), NaBu (m_2), NaCl (m_3), X % Isopropyl Alcohol/AgCl-Ag, in which m_1, m_2, and m_3 are weight molalities. The ionization constant is given by

$$-\log K = (E - E^0)F/2.3026RT + \log m_{HBu}m_{Cl^-}/m_{Bu^-} + \log \gamma_{HBu}\gamma_{Cl^-}/\gamma_{Bu^-},$$

where K is the thermodynamic ionization constant; E is the observed cell voltage corrected to a hydrogen pressure of one atmosphere; E^0 is the molal electrode potential of the silver–silver chloride electrode in the solvent used[5]; $m_{HBu} = m_1 - m_{H^+}$; $m_{Bu^-} = m_2 + m_{H^+}$; $m_{Cl^-} = m_3$; and γ is an activity coefficient. An apparent ionization constant K' is obtained by omission of the activity coefficient term in the original expression.

$$-\log K' = -\log K - \log \gamma_{HBu}\gamma_{Cl^-}/\gamma_{Bu^-}$$

When $-\log K'$ is plotted against ionic strength ($m_2 + m_3 + m_{H^+}$) and extrapolated to infinite dilution, the intercept is $-\log K$. In the first extrapolation, m_{H^+} is neglected to give an approximate value of K; from this value m_{H^+} is calculated, and the process is repeated until the result is not changed by an additional step.

Experimental

The preparation of materials and the experimental techniques employed are briefly described below.

Water.—Conductivity water was used in the preparation of the cell solutions.

Isopropyl Alcohol.—Commercial 99% isopropyl alcohol was refluxed over unslaked lime for five hours and slowly distilled through a one-meter packed column. The middle portion, constant boiling at 82.3° at one atmosphere was reserved for use.

***n*-Butyric Acid.**—Eastman Kodak Co. "White Label" *n*-butyric acid was partially frozen three times in the absence of moist air and then distilled at a pressure of 7 mm. The freezing point, −6.0°, was not appreciably changed by this procedure. Titration of the final product with sodium hydroxide standardized against Bureau of Standards benzoic acid indicated 99.72% butyric acid. This factor was applied in the preparation of solutions.

Sodium Carbonate.—Reagent grade sodium carbonate was recrystallized twice, dried, and heated to 280° for one hour to convert any bicarbonate to carbonate.

Sodium Chloride.—Reagent grade sodium chloride was dissolved and reprecipitated by addition of hydrogen chloride prepared by reaction of reagent grade sodium chloride and sulfuric acid. The precipitate was slowly heated to 700°.

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

Solutions.—Stock solutions about 0.2 molal in butyric acid, sodium butyrate, and sodium chloride were prepared in each solvent by weighing the appropriate amounts of purified *n*-butyric acid, sodium carbonate, sodium chloride, isopropyl alcohol and water. Cell solutions were obtained by weight-dilutions of the stock solutions with the solvent mixtures, which were prepared by weight in eight liter quantities. The ionic strength of the cell solutions varied from approximately 0.01 to 0.1 molal.

Procedure of Measurements.—The apparatus and techniques were those described by Moore and Felsing.[5] All of the silver–silver chloride electrodes prepared by thermal decomposition of a mixture of 10% $AgClO_3$ and 90% Ag_2O. The voltages of triplicate cells were measured for each solution at 5° intervals in a low temperature series from 0 to 25° and a high temperature series, with new samples of solution, from 25 to 40°, providing six measurements on each solution at 25°. Constant voltages were attained in from one to seven hours after the flow of hydrogen was begun, the longest times being required in the 20% solutions. After a change of temperature, equilibrium was usually reached in one hour. The average difference between the voltages of like cells and between high and low temperature values was less than 0.1 millivolt, except that in the 20% alcohol the two series differed by an average of 0.13 millivolt. Because of the long time required to reach constant voltage in the 20% alcohol, a presaturator containing solvent only was used in addition to the ones containing cell solutions to minimize changes in concentration due to evaporation.

Results

The graphs[6] in Fig. 1 are representative of the extrapolations in each of the three solvents. One approximate value of K was found to be sufficient. Plots of $-\log K'$ *versus* ionic strength appear to be straight lines, with the buffer ratio (m_1/m_2) equal to 0.9177, 0.7034, and 0.5711 in the 5, 10, and 20% alcohol, respectively. Another series of measurements in 20% alcohol with a ratio of 0.9702 yielded curved lines in the dilute region, which introduced considerable uncertainty in the

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[1] Special Assistant, Research Institute, The University of Texas.

[2] Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corporation, New York, N. Y., 1942.

[3] Patterson with Felsing, THIS JOURNAL, **64**, 1480 (1942).

[4] Moore with Felsing, *ibid.*, **69**, 2420 (1947).

[5] Moore with Felsing, *ibid.*, **69**, 1076 (1947).

[6] The complete experimental data are available from the American Documentation Institute, 1719 N Street, N. W., Washington, D. C., as Document 2529, photoprints $1.60 or microfilm 50¢.

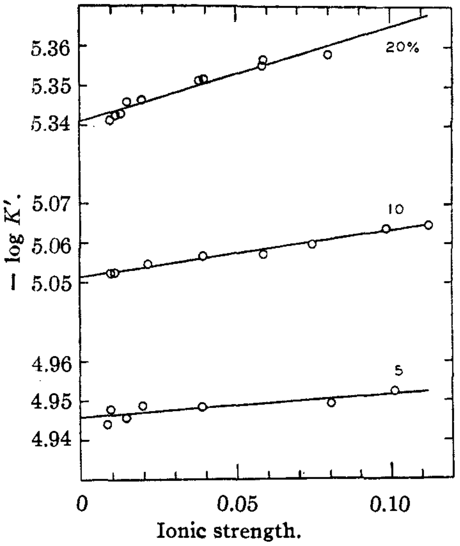

Fig. 1.—Evaluation of the ionization constants at 25°.

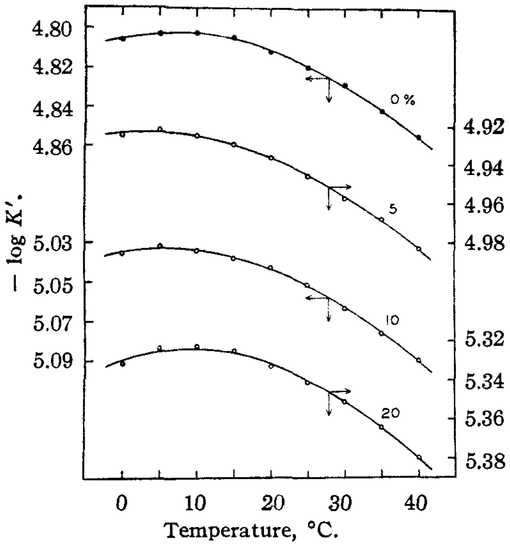

Fig. 2.—Temperature variation of the ionization constants: —●—, Harned and Sutherland; —O—, this investigation.

extrapolations. The values reported here were obtained with the higher ratio, in which case this difficulty did not appear. Final values of − log K were calculated by the method of least squares, and the corresponding K values are recorded in Table I. The average deviation of the experimental points from the best straight lines was 0.0012 pK units in the 5 and 20% alcohol, 0.0006 pK units in the 10% solutions. A deviation of 0.001 unit corresponds to 0.06 millivolt.

TABLE I

THE IONIZATION CONSTANTS OF *n*-BUTYRIC ACID IN ISOPROPYL ALCOHOL–WATER MIXTURES

t, °C.	$K \times 10^5$			
	0%	5%	10%	20%
0	1.563	1.190	0.922	0.466
5	1.574	1.197	.929	.475
10	1.576	1.189	.925	.476
15	1.569	1.177	.916	.473
20	1.542	1.157	.907	.465
25	1.515	1.133	.888	.456
30	1.484	1.104	.864	.446
35	1.439	1.077	.839	.432
40	1.395	1.040	.813	.417

The values of the ionization constant in water (*i. e.*, the values found in the 0% column of Table I) are those of Harned and Sutherland.[7]

The relation of the ionization constants to temperature is shown graphically in Fig. 2 and may be expressed by the empirical equation $-\log K = A/T + CT - D$, for which the constants in the three solvent mixtures are listed in Table II. Δ is the average difference between the observed and calculated values of − log K.

TABLE II

CONSTANTS OF THE EQUATION: $-\text{LOG } K = A/T + CT - D$

X, %	A	C	D	Δ
5	1048.516	0.0137527	2.67192	0.0006
10	1217.523	.0156246	3.69027	.0006
20	1459.369	.0183250	5.01868	.0011

From this equation, the following expressions are derived for the standard thermodynamic quantities of the ionization reaction.

$$\Delta F_i^0 = A' - D'T + C'T^2$$
$$\Delta H_i^0 = A' - C'T^2$$
$$\Delta C_{pi}^0 = -2C'T$$
$$\Delta S_i^0 = -2C'T + D'$$

where A', C', and D' are 2.3026 R times A, C, and D.

At each temperature a graph of "− log K" *versus* the reciprocal of the dielectric constant of the solvent is nearly a straight line, as predicted by the Born equation,[8] while a non-linear relation was found at the lower dielectric constants of dioxane–water mixtures.[9] Also, − log K is essentially a linear function of the mole fraction of isopropyl alcohol or water.

It has been observed that graphs of − log K *versus* temperature have the same shape for many weak electrolytes in aqueous solution and hence may be brought into coincidence by translation of the coördinate axes.[2] Propionic[4] and *n*-butyric acids appear to exhibit this similarity in each of the isopropyl alcohol–water mixtures investigated, although the temperatures of maximum ionization of the two acids are such that the data do not overlap throughout the entire range of measurements.

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[7] Harned and Sutherland, THIS JOURNAL, **56**, 2039 (1934).

[8] Born, *Z. Physik*, **1**, 45 (1920).

[9] Lynch and LaMer, THIS JOURNAL, **60**, 1252 (1938).

205, granted by the Research Institute of the University of Texas.

Summary

1. The ionization constants of *n*-butyric acid in 5, 10 and 20 weight per cent. isopropyl alcohol have been determined from 0 to 40° by use of cells without liquid junction.

2. The ionization constants and standard thermodynamic quantities have been expressed as functions of temperature.

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Some New Compounds Related to Amidone

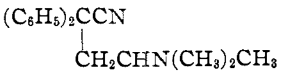
BY JOHN H. GARDNER, NELSON R. EASTON[1] AND JOSEPH R. STEVENS

The availability of the two isomeric nitriles prepared as intermediates in the synthesis of the Amidones[2] aroused interest in their application for the synthesis of other compounds of possible value. A number of these substances have now been prepared.

4-Dimethylamino-2,2-diphenylpentanenitrile (I), the higher melting of the two isomeric nitriles, was hydrolyzed with 72% sulfuric acid to the corresponding acid (II). This was isolated first as the bisulfate, from which the free acid was prepared. For the preparation of esters, the bisulfate was treated with thionyl chloride and the crude product brought into reaction with the alcohol. In this way, methyl, ethyl and β-dimethylaminoethyl 4-dimethylamino-2,2-diphenylpentanoates were prepared. These esters were isolated as the hydrochlorides.

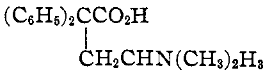
On attempting to prepare the corresponding isopropyl ester, the only product isolated in sufficient quantity and purity for identification was a neutral substance which was indicated by analysis to be 1,5-dimethyl-3,3-diphenyl-2-pyrrolidone (III).

The same compound was formed when the free acid was used instead of the bisulfate. It is probable that the pyrrolidone was one of the products formed in the reaction of the acid (II) with thionyl chloride as a similar compound was obtained when 4 - dimethylamino - 2,2 - diphenyl - 3 - methylbutanoic acid (IV) was allowed to react with thionyl chloride, without the addition of an alcohol. Similar compounds were obtained by Blicke and Zambito[3] by hydrolysis of the imides resulting from the action of alcoholic hydrogen chloride on acids closely related to II and IV.



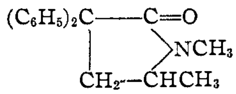
$(C_6H_5)_2CCN$ | $CH_2CHN(CH_3)_2CH_3$

I

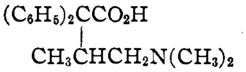


$(C_6H_5)_2CCO_2H$ | $CH_2CHN(CH_3)_2H_3$

II



III



$(C_6H_5)_2CCO_2H$ | $CH_3CHCH_2N(CH_3)_2$

IV

Isopropyl 4-dimethylamino-2,2-diphenylpentanoate was prepared by the reaction of the silver salt of the acid with isopropyl iodide. It was isolated as the hydrochloride.

The isomeric acid (IV) was prepared in a similar manner from the corresponding nitrile. Attempts to prepare esters by way of the acid chloride gave only 1,4-dimethyl-3,3-diphenyl-2-pyrrolidone. Ethyl 4-dimethylamino-2,2-diphenyl-3-methylbutanoate was prepared by the reaction of the silver salt of the acid with ethyl iodide. The ester was characterized as the hydrochloride.

In working up the residues from the isolation of 6 - dimethylamino - 4,4 - diphenyl - 5 - methyl-3-hexanone (Isoamidone II) oxalate,[2d] an oxygen-free base was isolated in substantial amounts. This has been identified as 1-dimethylamino-3,3-diphenyl-2-methylpropane (V) through its formation by the decyanation of 4-dimethylamino-2,2-diphenyl-3-methylbutanenitrile (VI) with sodium and isopropyl alcohol.

$(CH_3)_2NCH_2CH(CH_3)CH(C_6H_5)_2$

V

$(CH_3)_2NCH_2CH(CH_3)C(C_6H_5)_2CN$

VI

Experimental

4-Dimethylamino-2,2-diphenylpentanoic Acid Bisulfate.—A solution of 200 g. of 4-dimethylamino-2,2-diphenylpentanenitrile in a mixture of 240 ml. of concentrated sulfuric acid and 140 ml. of water was heated at 145–150° for about five hours. It was cooled and the crystals which formed were filtered out and washed with absolute alcohol. The yield was 278.5 g., m. p. 221–223° after crystallization from methanol.

Anal. Calcd. for $C_{19}H_{23}NO_2 \cdot H_2SO_4$. C, 57.70; H, 6.37; N, 3.54; S, 8.11. Found: C, 57.85; H, 6.56; N, 3.63; S, 8.27.

4-Dimethylamino-2,2-diphenylpentanoic Acid.—The acid bisulfate was dissolved in sufficient hot 5% sodium hydroxide to give a solution alkaline to phenolphthalein. This was treated with Nuchar W and filtered. The filtrate was acidified with 30% acetic acid, chilled and filtered. The yield of crude acid, m. p. 203–203.5°, was 88%. Crystallization from alcohol and drying at 100° under 2 mm. pressure raised the m. p. to 204–205°.

Anal. Calcd. for $C_{19}H_{23}NO_2$: C, 76.73; H, 7.79; N, 4.71. Found: C, 76.80; H, 7.78; N, 4.75.

4-Dimethylamino-2,2-diphenylpentanoyl Chloride Sulfate.—To 50 g. of the acid bisulfate, 75 ml. of thionyl

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[1] Present address, Lehigh University, Bethlehem, Pa.

[2] (a) O. P. B. Report PB 981, p. 96; (b) E. M. Schultz, C. M. Robb and J. M. Sprague, THIS JOURNAL, **69**, 188 (1947); W. R. Brode and M. W. Hill, *ibid.*, **69**, 724 (1947); N. R. Easton, J. H. Gardner, M. L. Evanick and J. R. Stevens, *ibid.*, **70**, 76 (1948).

[3] F. F. Blicke and A. J. Zambito, abstracts of papers presented at the meeting of the American Chemical Society, Atlantic City, N. J., April, 1947, p. 3K.