[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Ionization Constant of *n*-Butyric Acid from 0 to 60°[1]

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The ionization constants of formic, acetic and propionic acids at temperatures ranging from 0 to 60° have been determined recently by Harned and Embree,[2] and Harned and Ehlers[3] from the measurements of the electromotive forces of cells without liquid junction. A similar determination of the ionization constant of *n*-butyric acid from measurements of the cells

$$H_2 \mid HA(m_1), NaA(m_2), NaCl(m_3) \mid AgCl \mid Ag$$

is the subject of the present communication.

Experimental Results

Although the technique employed by Harned and Ehlers was followed as far as possible, certain details in the preparation of the solutions required modification. In the previous work, in order to eliminate air from the solutions, they were boiled *in vacuo*. In the present instance, this procedure was found to be clumsy since an appreciable amount of butyric acid was removed in the distillate, and for this reason each cell solution would require analysis. It was found to be more convenient to prepare an air-free stock solution containing approximately 0.05 *N* butyric acid, sodium chloride and sodium butyrate and keep this in an atmosphere of nitrogen.

For this purpose, an air-free and nitrogen-swept solution of carbonate-free sodium hydroxide of approximately 0.1 *N* concentration was prepared. It was analyzed by weight titration against hydrochloric acid which had been standardized by gravimetric analysis. Its strength was known to within ±0.05%. A butyric acid solution was prepared from the highest grade Eastman *n*-butyric acid. This had been purified by partially crystallizing and discarding the unfrozen liquid. This process was repeated twice. An approximately 0.2 *N* solution of the acid was prepared, rendered air-free and then backed by nitrogen. It was standardized against the sodium hydroxide solution by titration. Its strength was known to within ±0.1%.

(1) This investigation contains the material of an essay presented to the Graduate School of Yale University by Mr. Sutherland in partial fulfilment of the requirements for the degree of Master of Science, 1934.

(2) Harned and Embree, THIS JOURNAL, **56**, 1042 (1934).

(3) Harned and Ehlers, *ibid.*, **54**, 1350 (1932); **55**, 652 (1933); **55**, 2379 (1933).

The stock solution was made in portions of four liters each and a new stock solution was prepared for each series of electromotive force measurements. Approximately 0.2 mole of sodium chloride was weighed and introduced into a four-liter nitrogen filled flask which was weighed. Approximately 2 liters of the 0.1 *N* sodium hydroxide solution was then introduced and the flask and contents again weighed. Finally, two liters of the 0.2 *N* butyric acid solution was introduced and the final weighing was made. From these observations, an accurately known solution containing the three constituents each at approximately 0.05 *M* was obtained. All other solutions were made by dilution of this one with known weights of water.

The cell measurements were carried out with electrodes prepared in the same manner as those used by Harned and Ehlers. Three series of measurements were made through the temperature ranges of 0 to 15°, 20 to 40° and 40 to 60°, respectively. These are given in Table I. Each result recorded is the mean of the readings of three cells. The reproducibility was of the order of ±0.1 mv.

Calculation and Properties of the Ionization Constant.—The equation for the electromotive force, E, of a cell takes the form

$$\frac{2.3026\,F}{RT}(E - E_0) + \log \frac{m_{HA}m_{Cl}}{m_A} = \log \frac{\gamma_H\gamma_{Cl}\gamma_{HA}}{\gamma_H\gamma_A} - \log K = -\log K' \quad (1)$$

E_0 is the normal potential of the cell, K, the ionization constant of *n*-butyric acid and the "γ's" and "m's" are the activity coefficients and molalities of the molecules and ions denoted by subscripts. HA refers to the *n*-butyric acid and A to the butyrate ion. The left side of this equation which we denote $-\log K'$ equals $-\log K$ at infinite dilution since the term containing the "γ's" vanishes. Values of $-\log K'$ were computed as described by Harned and Ehlers and plotted against μ, the ionic strength. Such a plot for the higher temperatures is shown in Fig. 1. The plots are straight lines with small slopes and the extrapolation can be made fairly readily. The diameter of the circles representing the points corresponds to 0.1 mv. error in electro-

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS

H_2(1 atm.) | HA(m_1), NaA(m_2), NaCl(m_3) | AgCl | Ag

HA = $CH_3CH_2CH_2COOH$

Series I. 0 to 15°

m_1	m_2	m_3	E_0	E_5	E_{10}	E_{15}
0.04040	0.04594	0.04343	0.57463	0.57826	0.58179	0.58533
.03575	.04064	.03842	.57735	.58106	.58467	.58830
.02866	.03258	.03080	.58237	.58623	.58989	.59357
.02381	.02707	.02559	.58665	.59057	.59431	.59817
.01808	.02056	.01943	.59287	.59693	.60084	.60467
.01374	.01563	.01477	.59927	.60345	.60746	.61139
.00935	.01063	.01005	.60829	.61260	.61675	.62086
.00564	.00641	.00606	.62021	.62468	.62907	.63339

Series II. 20 to 40°

m_1	m_2	m_3	E_{20}	E_{25}	E_{30}	E_{35}	E_{40}
0.05106	0.04895	0.05029	....	0.58399	0.58741	0.59079	0.59412
.04100	.03931	.04039	....	.58969	.59314	.59661	.59994
.02232	.02139	.02198	0.60136	.60513	.60869	.61245	.61612
.01756	.01683	.01730	.60731	.61105	.61494	.61874	.62247
.01515	.01453	.01493	.61116	.61501	.61879	.62264	.62648
.01273	.01220	.01254	.61517	.61922	.62319	.62715	.63118
.00717	.00687	.00706	.62964	.63387	.63807	.64224	.64652

Series III. 40 to 60°

m_1	m_2	m_3	E_{40}	E_{45}	E_{50}	E_{55}	E_{60}
0.03921	0.04459	0.04214	0.60302	0.60643	0.60989	0.61326	0.61658
.03656	.04158	.03929	.60490	.60833	.61183	.61520	.61860
.02784	.03166	.02992	.61217	.61578	.61933	.62286	.62636
.02381	.02707	.02558	.61644	.62008	.62368	.62729	.63083
.01650	.01876	.01773	.62623	.62999	.63372	.63746	.64114
.01327	.01509	.01426	.63209	.63595	.63976	.64357	.64737
.00854	.00971	.00917	.64402	.64804	.65210	.65615	.66015
.00597	.00679	.00642	.65357	.65778	.66196	.66611	.67027

motive force. The values of the ionization constants thus derived are compiled in Table II.

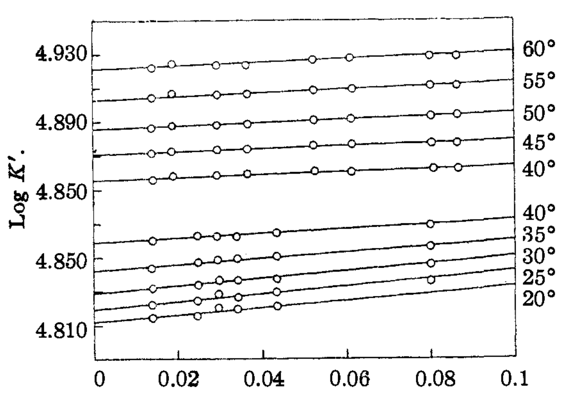

Fig. 1.—Graphs of $-\log K'$ against μ.

From these results, it is apparent that the ionization constant of *n*-butyric acid in aqueous solutions has a maximum value at 8°, a fact in accord with the general behavior of the acids of the fatty series. We have computed these results by the method recently suggested by Harned and Embree, who employed the function[4]

$$\log K/K_m = -p(t - \Theta)^2 \qquad (2)$$

TABLE II

IONIZATION CONSTANT AND HEAT OF IONIZATION OF *n*-BUTYRIC ACID

$\Theta = 8$; $K_m = 1.575 \times 10^{-5}$

t, °C.	$K \times 10^5$ (Obs.)	$K \times 10^5$ (Eq. 2)	ΔH (Eq. 3)	ΔC_p
0	1.563	1.563	+ 273	−32
5	1.574	1.573	+ 106	−35
8	...	1.575	0	−36
10	1.576	1.574	− 73	−37
15	1.569	1.566	− 266	−40
20	1.542	1.549	− 472	−42
25	1.515	1.523	− 691	−46
30	1.484	1.489	− 926	−48
35	1.439	1.448	−1174	−51
40	1.395	1.400	−1437	−54
45	1.347	1.345	−1714	−57
50	1.302	1.285	...	..
55	1.252	1.221	...	..
60	1.199	1.153	...	..

(4) Harned and Embree, THIS JOURNAL, 56, 1050 (1934).

where K_m is the maximum value of the ionization constant and Θ the corresponding temperature in degrees centigrade. t is the temperature in degrees centigrade and p is a universal constant for all weak electrolytes and has value of 5×10^{-5} in the neighborhood of the maximum. In order to evaluate the constants K_m and Θ, the graphical method suggested by them was adopted. Log $K + pt^2$ was plotted against t, Θ was derived from the slope and K_m evaluated. The result is shown in Fig. 2. It should be mentioned that the values at 50, 55 and 60° deviate considerably from the straight line, a behavior similar to that found by Harned and Embree for the other members of this series.[5] In the third column of Table II are given the values computed by this equation and it is seen that from 0 to 45° the result is excellent. In the fourth column of this table the values of ΔH, computed by the equation of Harned and Embree

$$\Delta H = 2.3 \times 10^{-4} RT^2 (t - \Theta) \qquad (3)$$

are given, and in the fifth column the values of ΔC_p computed by differentiation of (3) with respect to T are given. These latter values are obviously only approximate.

Since the previous determinations of this constant by conductance and electromotive measurements vary considerably from each other and were only obtained in the neighborhood of room temperature, we shall omit a discussion or comparison. The recent result of 1.55×10^{-5} at 18° obtained by Larsson and Adell[6] from electromotive force measurements with a quinhydrone electrode and in cells with liquid junctions compares well with the value, 1.56×10^{-5}, computed at 18° by equation (2).

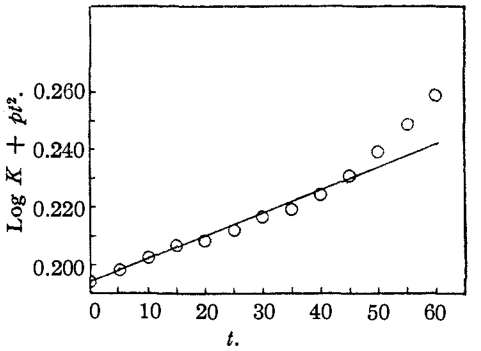

Fig. 2.—Plot of the Harned and Embree function.

One fact of importance is confirmed by our results. The maximum values of the ionization constants, K_m, of formic, acetic, propionic and n-butyric acids have been found to be 1.77×10^{-4}, 1.76×10^{-5}, 1.34×10^{-5} and 1.57×10^{-5}, respectively. It is interesting to note that the values decrease from formic to propionic acid but that the situation is complicated since n-butyric acid has a considerably higher dissociation constant than propionic acid.

Summary

1. From measurements of suitable cells, the ionization constant of n-butyric acid has been determined from 0 to 60° at 5° intervals.

2. The ionization constant at any temperature between 0 and 45° may be computed accurately by equation (2). The maximum value of the ionization constant, K_m, is 1.575×10^{-5} at 8°.

3. The heat of ionization of the reaction, ΔH, and the difference in specific heats of reactants and resultants of the ionization reaction have also been computed.

NEW HAVEN, CONN. RECEIVED JULY 27, 1934

(5) A part of this discrepancy may be due to the omission by Harned and Ehlers of a refinement in their calculation of E_0. They used the function, $\log \gamma = -u\sqrt{m} + \beta m$, for the law of Debye and Hückel, where strictly speaking, $\log \gamma = -u\sqrt{c} + \beta c$ should be used. Such an effect is small and only influences the result at the higher temperatures.

(6) Larsson and Adell, *Z. physik. Chem.*, **156**, 352 (1931).