[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY OF PROVIDENCE COLLEGE]

The Ionization of Lactic Acid in Aqueous Sodium Chloride Solutions from 0 to 37.5°

BY F. C. HICKEY, O.P.

The very accurate determinations of the ionization constant of lactic acid from 0 to 50° by Nims and Smith[1] from electromotive force measurements of buffered lactate cells without liquid junctions, and similar determinations over the same temperature range by Martin and Tartar[2] from conductance measurements suggested the study of salt action upon the ionization of lactic acid by the method developed by Harned and Owen.[3] Accordingly, unbuffered cells, without liquid junctions, of the type

$$H_2 \mid HLac\ (M),\ NaCl\ (m) \mid AgCl\text{–}Ag \qquad (1)$$

were employed. The electromotive forces of these cells were measured at 0, 12.5, 25, 37.5° and the lactic acid concentration was varied from 0.2 to 0.5 M and the salt concentration from 0.1 to 2 M. These data, when combined with the electromotive forces for the cell

$$H_2 \mid HCl\ (0.01) \mid AgCl\text{–}Ag \qquad (2)$$

obtained by Harned and Ehlers,[4] allow the computation of the ionization and the activity coefficients of the acid in salt solutions as well as the temperature variation of ionization at all salt concentrations.

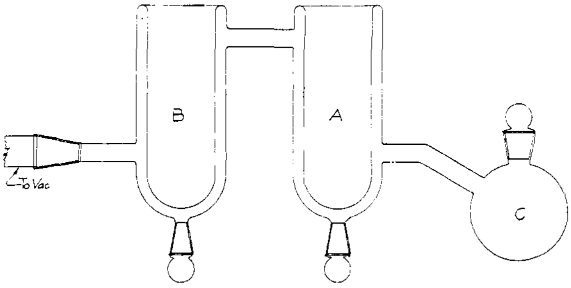

Fig. 1.

Experimental Results

The experimental procedure was essentially the same as that previously employed in the case of acetic acid,[5,6] except for the purification and analysis of the lactic acid. After several methods were attempted for the purification of the acid without success, a still was constructed according to the suggestion contained in a private communication from Dr. Norris D. Embree, of the Eastman Kodak Company. The apparatus (Fig. 1) consists of a distilling bulb provided with a ground glass stopper and sealed to a series of two dry-ice traps by large size glass tubing. The bottoms of these traps are also provided with interchangeable ground glass stoppers. The complete apparatus, permanently mounted in a steel cradle, is connected to the vacuum pump by a ground glass joint.

The lactic acid was first dehydrated in a vacuum desiccator over concentrated sulfuric acid for a day or more. About fifty cc. of the dehydrated acid was then introduced into the distilling bulb (C). Only the dry-ice trap (B) was cooled with dry-ice and acetone when the vacuum pump was started. As the pressure within the system was lowered, some residual water in the acid would, at times, cause foaming and splashing to some extent. This was controlled by regulating the pressure. The residual water, of course, passed directly through trap (A) and condensed in trap (B). When all the water had been eliminated, trap (A) was filled with the freezing mixture and the pressure reduced to the limit—below one micron. A water-bath was then placed around the distilling bulb and the temperature was maintained at about 60° by an electric hot plate. After six to ten hours, 10 to 20 g. of the frozen acid gathered in trap (A). It was collected directly in a weighing bottle by removing the freezing mixture and by allowing the acid to melt and drain from the bottom of the trap. During the withdrawal of the acid enough water was absorbed from the atmosphere to render impossible a quantitative estimate of its purity.

In the first series of experiments, a mercury vapor pump backed with a Hyvac pump was used. Because of the relatively long and narrow tubing of this apparatus, twelve to fifteen hours were required for the distillation of a single sample. Furthermore, the cells made up from this acid gave consistently high values of the electromotive force. When a single stage oil diffusion pump, backed by a Pressovac pump, was substituted for the original vacuum apparatus, the time required for a sample was reduced to about six hours and the acid gave electromotive forces which were consistent with the known values of the dissociation constant.

The purified lactic acid was diluted and analyzed by titration against standardized barium hydroxide solution, with phenolphthalein as an indicator. During the titration, a stream of carbon dioxide-free air was bubbled through the solution. At the first appearance of pink color, the titrating flask was placed on a hot plate and the solution brought to a boil. During this time the color faded. The color was then restored by a few added drops of base. The acid concentration was known with an accuracy of ±0.1%. Freshly distilled acid was used for each determination.

The purified sodium chloride was carefully dried at 450° in a muffle furnace and samples were weighed out directly on an analytical balance. The concentration of the salt,

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[1] Nims and Smith, *J. Biol. Chem.*, **113**, 145 (1936).
[2] Martin and Tartar, THIS JOURNAL, **59**, 2672 (1937).
[3] Harned and Owen, *ibid.*, **52**, 5079 (1930).
[4] Harned and Ehlers, *ibid.*, **55**, 2179 (1933).
[5] Harned and Ehlers, *ibid.*, **54**, 1350 (1932).
[6] Harned and Hickey, *ibid.*, **59**, 1284 (1937).

therefore, was known with greater accuracy than that of the acid.

Vacuum technique was employed. The hydrogen and silver–silver chloride electrodes were freshly prepared for each determination. Three cells were measured at each concentration and temperature. The temperature was regulated to ±0.02° and determined by calibrated thermometers. The electromotive forces were measured with an Eppley Feussner type potentiometer and the standard cell was calibrated by the Eppley Laboratory.

Measurements were made at 0, 12.5, 25 and 37.5° in order to coincide with the data of Nims and Smith and because of possible biological applications. The values of the dissociation constant of lactic acid were taken from Nims and Smith in order to keep the whole problem on an electromotive force basis. The observed electromotive forces are given in Table I.

TABLE I

ELECTROMOTIVE FORCES OF CELLS: $H_2|HLac\ (M),\ NaCl\ (m)|AgCl–Ag$

M	m	0	12.5	25	37.5
0.2029	0.1015	0.41790	0.41934	0.42049	0.42046
.2001	.2002	.40236	.40313	.40348	.40309
.1988	.2982	.39303	.39340	.39331	.39254
.2002	.5005	.38079	.38053	.38000	.37850
.2004	1.0020	.36183	.36100	.35967	.35789
.2001	2.0062	.34091	.33875	.33654	.33331
0.5005	0.1001	0.40497	0.40611	0.40660	0.40651
.5017	.2007	.38991	.39033	.39021	.38935
.5010	.3006	.38023	.38026	.37975	.37860
.5008	.5008	.36885	.36815	.36703	.36523
.5005	1.0011	.35004	.34860	.34679	.34427
.5012	2.0046	.33154	.32892	.32579	.32252

Calculation of the Ionization, k_A.—The method of calculation has been discussed in detail by Harned and Owen[3] and by Harned and Hickey.[6] Suffice it to say that directly from the electromotive force, the "apparent" hydrogen ion concentration, m'_H, defined by the equation

$$m'_H = m_H \frac{\gamma^2_{HCl}}{\gamma^{0\,2}_{HCl}} \quad (3)$$

can be calculated. γ_{HCl} is the activity coefficient of hydrochloric acid at zero molality in an aqueous solution of salt concentration m and lactic acid concentration M, while γ^0_{HCl} is the activity coefficient of hydrochloric acid at zero molality in an aqueous solution containing only sodium chloride at concentration m. From the "apparent" hydrogen ion concentration, an "apparent" dissociation, k', may be calculated by the equation

$$k'_A = \frac{m'^2_H}{M - m'_H} \quad (4)$$

In order to extrapolate k' to zero ionic strength, the Debye–Hückel equation was used in the form

$$\log k'_A - 2u\sqrt{\mu'}/(1 + A\sqrt{2\mu'}) = \left(\log k^0_A + 2 \log \gamma^0_A + 2 \log \frac{\gamma_A}{\gamma'_A}\right) - 2Bu' \quad (5)$$

in which μ' is the "apparent" ionic strength, $m + m'_H$. This is equation (8) of Harned and Hickey.[6] At zero ionic strength the right-hand side of equation (5) becomes $\log k^0_A$, the logarithm of the ionization of lactic acid at the specified concentration in pure water. The constant A of equation (5) is related to the apparent ionic diameter, a, and was determined by plotting the left side of equation (5) against the "apparent" ionic strength, using various values of a until a straight line was obtained. In all previous work, one value of a was used at all acid concentrations. In the present case, however, the same value of a could not be used for both acid concentrations. It was found, however, that when a was assigned values which yielded straight lines for each series, the lines were parallel. It was necessary, therefore, to assume that the value of a varies with the lactic acid concentration.

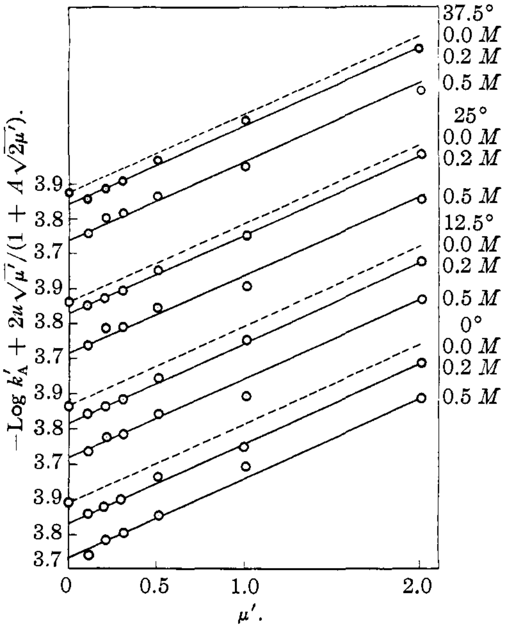

Fig. 2.—Plots of negative left side of eq. 5 *vs.* μ'.

It was found that when smoothed values of $-\log k'_A$, computed by means of equation (5) from points read from Fig. 2, were plotted against the "apparent" ionic strength, μ', the curves for the 0.2 and 0.5 M lactic acid intersected at approximately the same value of μ' at all tempera-

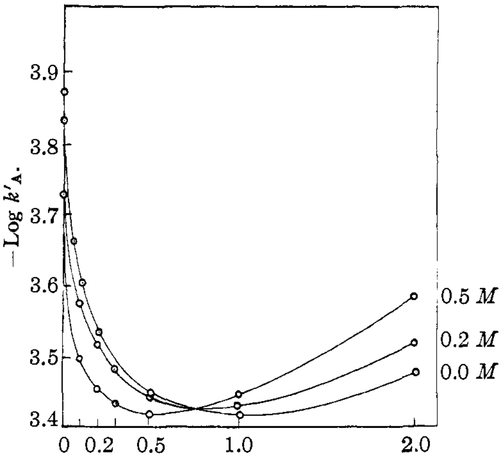

Fig. 3.—Plots of smoothed values of $-\log k'_A$ and $-\log k_A$ *vs.* μ' at 25°.

tures. The plot for 25° is given in Fig. 3 to which has been added the curve of $-\log k_A$ *vs.* μ, the upper curve on the left side. Where these curves coincide, there is no medium effect due to undissociated lactic acid molecules. This fact allows one to determine the proper value of the apparent ionic diameter to be used in calculating k_A which is the ionization of lactic acid at zero concentration in salt solutions of designated ionic strength. The numerical value of the apparent ionic diameter used in these calculations is 1.5 Å., an average of those determined at each temperature. k_A was then determined at each temperature and salt concentration by drawing a line, on a large scale plot, from $-\log K_A$ as reported by Nims and Smith,[1] and parallel to the lines obtained by plotting the left side of equation (5) against μ'. These lines (the dotted lines of Fig. 2) represent the values of $-\log k_A + 2u\sqrt{\mu}/(1 + A\sqrt{2\mu})$ which were read off the plots at convenient values of μ. From these, values of k_A were computed. From the relation $K_A = \gamma_A^2 k_A$, where K_A is the thermodynamic ionization constant, γ_A^2 or $\gamma_H\gamma_{Lac}/\gamma_{HLac}$ may be easily calculated.

The Ionization, k_A, and its Variation with Temperature in Sodium Chloride Solutions.—Harned and Embree[7] have shown that the ionization constants of weak uni-univalent electrolytes in aqueous solution may be expressed as functions of temperature by the equation

$$-\log K = -\log K_m + 5 \times 10^{-5}(t - \theta)^2 \qquad (6)$$

in which K_m is the maximum value of K and θ, the temperature at which K becomes a maximum. Nims and Smith[1] have shown that this equation applies also to the ionization constant of lactic acid. In applying it to lactic acid in salt solutions, not only does its validity in this case become apparent but the experimental values of k_A are reported in convenient form. Accordingly in Table II are listed the values of $-\log k_{Am}$ and θ for various concentrations of sodium chloride up to 2 *M*.

Table II

Constants of the Equation

$$-\log k_A = -\log k_{Am} + 5 \times 10^{-5}(t - \theta)^2$$

μ	$-\log k_{Am}$	θ
0.00	3.862	23.5[1]
.02	3.732	26
.03	3.707	26
.06	3.655	27
.11	3.597	27
.21	3.529	30
.51	3.438	32.5
1.01	3.401	37
2.01	3.461	39

Maximum deviation = 0.01
Average deviation = 0.0015

The values of k_A reported here involve the combined errors of several investigators whose data were used in the calculation. An approximate estimate indicates that k_A is known with an error of less than ±1% and therefore log k_A is known within ±0.005.

Acknowledgment.—The writer wishes to express his gratitude to Dr. Marion Eppley for his gift to the Chemistry Department of Providence College of the Eppley Feussner type potentiometer which made this work possible.

Summary

1. Accurate measurements of the electromotive forces of the cells

$$H_2 \mid HLac\ (M),\ NaCl\ (m) \mid AgCl\text{-}Ag$$

at 0.2 and 0.5 *M* lactic acid and at sodium chloride concentrations from 0.1 to 2 *M* have been made at 0, 12.5, 25 and 37.5°.

2. In applying the method of Harned and Owen[3] as modified by Harned and Hickey[6] for the calculation of the ionization in salt solutions, the apparent ionic diameter, *a*, of the Debye–Hückel theory was found to vary with the lactic acid concentration. A method for determining its value at infinite dilution of lactic acid is suggested.

3. Values of the ionization of lactic acid or

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(7) Harned and Embree, This Journal, **56**, 1050 (1934).

$m_H^2/M - m_H$ in salt solutions up to 2 M and from 0 to 37.5° have been computed.

4. The ionization, k_A, was found to vary with the temperature in accordance with the equation of Harned and Embree.[7]

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Measurement of the Conductance of Electrolytes. IX.[1] The Use of the Cathode-Ray Oscillograph as a Detector

BY GRINNELL JONES, KAROL J. MYSELS[2] AND WALTER JUDA

A telephone has been almost universally used as the detector in making measurements of the conductance of solutions of electrolytes since Kohlrausch developed his alternating current technique. Recent advances in the science and art of electronics have made available two new tools as substitutes for the telephone. Hovorka and Mendenhall[3] have suggested the use of the "electric eye" (a 6E5 Cathode-Ray tube) as a detector for conductance measurements and give a wiring diagram for a combined amplifier and detector.

Lamson[4] has suggested the use of a Cathode-Ray Oscillograph as a detector for alternating current impedance bridges in general but without discussing specifically its use for the measurement of the conductance of the solutions of electrolytes. The Cathode-Ray Oscillograph converts complicated variable electric currents into visual form more successfully than the telephone converts them into audible form. We have found that the Cathode-Ray Oscillograph has important advantages over both the telephone and "electric eye" for conductance measurements and no disadvantages for a person having normal eyesight except greater cost.

The apparatus used in the experiments to be described below consists of the following parts assembled as a unit:

(1) A beat-frequency oscillator (General Radio Company Type 613-B) giving any desired frequency from 10 cycles to 13,500 cycles per sec.

(2) A Jones Conductivity Bridge provided with input and output transformers built by Leeds and Northrup and described by Dike.[5]

(3) A container filled with oil in which the cells are mounted, the temperature of which is automatically controlled by means of a thermoregulator.

(4) A tuned three-tube amplifier, General Radio Company GR-P-430, connected across the midpoint of the bridge through a shielded and grounded transformer. There was also provided an additional tuning device consisting of a variable capacitor of 0.2 μf capacitance and a variable inductor of 1 henry connected in parallel with the output of the amplifier.

(5) A RCA Stock No. 155 Cathode-Ray Oscillograph, whose vertical deflecting plates are connected to the output terminals of the amplifier and whose horizontal deflecting plates are connected to the oscillator. This instrument[6] has a three-inch fluorescent screen and gives an image which is bright enough for easy visual observation without darkening the room.

(6) All electrical connections between the parts are made by shielded wires with the shields grounded except the connections between the cell and the bridge, which are not shielded.

The screen of the oscillograph will show a horizontal straight line when the bridge is perfectly balanced so that there is no voltage coming from the midpoint of the bridge through the amplifier to the vertical plates, while the horizontal plates of the cathode-ray tube are con-

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[1] The earlier papers of this series are: Grinnell Jones and Associates, THIS JOURNAL, **50**, 1049 (1928); **51**, 2407 (1929); **53**, 411, 1207 (1931); **55**, 1780 (1933); **57**, 272, 280 (1935); **59**, 731 (1937).

[2] Mr. K. J. Mysels' address is care of Shell Development Company, San Francisco, California.

[3] F. Hovorka and E. E. Mendenhall, *J. Chem. Education*, **16**, 239 (1939); Shuttleworth, *J. Intern. Soc. Leather Trades Chem.*, **23**, 326 (1939). Circuits involving an electric eye as a detector for inductance or capacitance measurements have also been described by the following: W. M. Breazeale, *Rev. Sci. Instruments*, **7**, 250 (1936); L. C. Waller, *R. C. A. Rev.*, **1**, no. 3, 121 (1937); R. L. Garman, *Rev. Sci. Instruments*, **8**, 327 (1937); J. F. Koehler, *ibid.*, **8**, 450 (1937).

[4] H. W. Lamson, *Rev. Sci. Instruments*, **9**, 272 (1938); General Radio Experimenter, **13**, No. 11 (1939).

[5] P. H. Dike, *Rev. Sci. Instruments*, **2**, 379 (1931).

[6] For a detailed description and wiring diagram of this instrument see a pamphlet entitled "Cathode-Ray Oscillograph, Stock No. 155" available on request from the RCA Manufacturing Company, Camden, New Jersey. Other models differing in size of screen, sensitivity, price and maker are commercially available. The list price of the "RCA No. 155 Cathode-Ray Oscillograph" is $63.95.