[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Ionization Constant of Acetic Acid in Dioxane-Water Mixtures

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Accurate determinations of the ionization constants of weak electrolytes in media other than water are scarce. Harned and Embree[2] have obtained the ionization constant of acetic acid in 10 and 20% by weight methanol-water mixtures from suitable electromotive force measurements. The 20% methanol mixtures possess a dielectric constant of approximately 70 which is not far from that of water. In order to determine this ionization constant over a much wider range of variation of the dielectric constant, we have measured the cells

$$H_2\ (1\ \text{atm.})\ |\ \text{HAc}(m_1),\ \text{NaAc}(m_2),\ \text{NaCl}(m_3),\ X\%\ \text{dioxane}-Y\%\ H_2O\ |\ \text{AgCl-Ag} \quad (1)$$

containing 20, 45 and 70% by weight of dioxane at 5° intervals from 0 to 50°. The dielectric constants of these solvents at 25° are 60.79, 38.48 and 17.69, respectively. From these results, the ionization constant of the acid has been evaluated by the method of Harned and Ehlers.[3]

Experimental Results

The measurements of these cells were made in the manner described by Harned and Morrison.[4] The only detail different from their procedure consisted in the preparation of the buffered acetic acid solution, and the subsequent preparation of the cell solutions.

An approximately 1 *M* hydrochloric acid was standardized by gravimetric analysis. Its strength was estimated to have been known to ±0.02%. A 1.5 *M* sodium hydroxide solution free from carbon dioxide was standardized by weight titration by means of the hydrochloric acid solution. All weighings were reduced to vacuum. These titrations checked to within ±0.02%.

Glacial acetic acid was distilled three times in an all-glass still, the first two times from a 2% solution of chromic anhydride. The middle fraction of the third distillate was diluted with conductivity water to form an approximately 3 *M* solution. The strength of this solution was determined by weight titration against the standard sodium hydroxide solution. Deviations from the mean of several titrations were not more than ±0.03%.

Carefully purified sodium chloride dried in a muffle furnace at 500° was employed.

From these standard solutions a stock buffer solution was prepared. Six kilograms of the standard acetic acid solution was weighed in a bottle on a balance sensitive to less than one gram. To this was added an approximately equal weight of the standard sodium hydroxide solution to produce a buffer containing acetic acid and sodium acetate at nearly equal molalities. Then sufficient sodium chloride was weighed and introduced so as to make its molality equal to that of the sodium acetate. To prevent any change in concentration, the bottle containing the solution was equipped with a bulb containing the solution. It was estimated that the acetic and sodium acetate concentrations were known to within ±0.05%. The error in salt concentration was considerably less than this.

The cell solutions were prepared from this stock buffer solution, conductivity water and dioxane purified as described by Harned and Morrison. About 1800 cc. of solution was prepared in 2-liter solution flasks. Allowing for the water to be added in the buffer solution, about 20 g. less than the desired amount of water was weighed into the solution flask on a balance sensitive to about 0.02 g. Next was added the buffer solution from a weight buret. Finally, the dioxane was introduced and weighed. Vacuum corrections were applied to all weights and the amount of water required to adjust the solvent composition to the desired water-dioxane ratio was added. Errors in the weighings were less than 1 part in 500. The solvent composition was known to within 0.02%. The electrolyte concentration was known to within ±0.05%. All concentrations of electrolytes are expressed in moles per 1000 g. of solvent.

These solutions were rendered air free by the passage of hydrogen.[4] The cell technique and electrode preparation was also carried out according to their directions.

Measurements of electromotive forces were made with an Eppley-Feussner type calibrated potentiometer and with Weston cells frequently calibrated against standard Eppley saturated Weston cells. A Leeds and Northrup Type H. S. galvanometer was employed.

The first readings of the electromotive forces were taken from 6 to 8 hours after the cell had been started. Readings were then taken at one-half hour intervals until constancy was obtained, then the temperature was changed. Two series of measurements were made for each concentration, one from 0 to 25° at 5° intervals, and the other from 25 to 50°. The cells were measured in triplicate. In the 20% dioxane solutions the reproducibility was of the order of ±0.05 mv. In the 45% dioxane solution, the agreement was within ±0.1 mv. Sometimes difficulties were encountered at temperatures from 40 to 50°. In general, the results at the lower temperatures were somewhat more reliable. In the 70% series, the electromotive forces were reproducible to ±0.05 mv. in most cases. In the more dilute solutions, the electromotive forces were more difficult to measure because of the higher internal resistance of the cells. It was possible in all cases,

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[1] This communication contains material from a Dissertation presented to the Graduate Faculty of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1936.

[2] Harned and Embree, THIS JOURNAL, **57**, 1669 (1935).

[3] Harned and Ehlers, *ibid.*, **54**, 1350 (1932).

[4] Harned and Morrison, *ibid.*, **58**, 1908 (1936).

however, to estimate the electromotive forces with a certainty of 0.05 mv.

We have expressed the results by the equation

$$E = E_{25} + a(t - 25) + b(t - 25)^2 \qquad (2)$$

In many cases, the first order differences of E showed no tendency to vary with the temperature so that the constant b was zero. In the other cases b was of a small magnitude. In Table I, E_{25} and the constants a and b are given. In the fifth column of the table, the maximum deviation, Δ_M, between the observed results and those computed by equation (2) are given. In the last column, the average magnitude of the deviations, Δ_A, is given. It is apparent that Δ_A is for all cases 0.06 mv. or less. The range of applicability of equation (2) is from 0 to 50°.

TABLE I

CONSTANTS OF EQUATION (2)

X = % by weight of dioxane

m_1, m_2. m_3 = moles per 1000 g. solvent

$m_2 = m_3 = 1.034\ m_1$

m_1	E_{25}	$a \times 10^6$	$b \times 10^6$	Δ_M(mv.)	Δ_A(mv.)
		$X = 20$			
0.010918	0.63156	683	−0.64	0.09	0.05
.019677	.61683	641	− .64	.11	.03
.04744	.59450	555	− .64	.14	.06
.07627	.58236	513	− .64	.07	.04
.10582	.57400	480	− .64	.11	.05
		$X = 45$			
0.011026	0.65217	568	0	0.15	0.04
.019983	.63706	515	0	.12	.03
.05173	.61258	423	−0.36	.16	.05
.10910	.59304	337	− .60	.11	.03
		$X = 70$			
0.005809	0.68806	420	0	0.10	0.05
.010909	.67144	356	0	.09	.05
.020968	.65404	300	0	.05	.02
.05164	.62937	216	0	.06	.015
.07862	.61774	172	0	.14	.03
.09986	.61081	144	0	.14	.04

The Ionization Constant

The equation for the electromotive force of the cell may be transposed to

$$\frac{F}{2.303\ RT}(E - E_0') + \log \frac{(m_1 - m_H)m_3}{(m_2 + m_H)} = \log \frac{\gamma_H \gamma_{Cl} \gamma_{HAc}}{\gamma_H \gamma_{Ac}} - \log K = -\log K'^{(2)(3)} \qquad (3)$$

where E_0' is the molal electrode potential of the cell, K the ionization constant of acetic acid, and γ and m are the activity coefficients and molalities of the species indicated by subscripts.[2,3] In order to evaluate K, the left side of this equation, $-\log K'$, was computed from the observed molalities, the observed electromotive forces, and the values of E_0' determined by Harned and Morrison.[4] Since K is of the order of 10^{-6} or less, $(m_1 - m_H)$ and $(m_2 + m_H)$ may be replaced by m_1 and m_2, respectively, without causing an error greater than the experimental. $(-\log K')$ was then plotted against the ionic strength, μ, and $(-\log K)$ was read off the intercept at zero μ.

The characteristics of the extrapolation are shown by Fig. 1 where the extrapolation plots of the 20, 45 and 70% series at 25° are shown. In the case of the 20% series, the plot through the points at the four highest concentrations is a straight line which has been continued to the intercept. The point at the lowest concentration lies somewhat below this plot. We feel justified in giving less weight to this result since the function plotted should yield a straight line at low concentrations. In the cases of the 45 and 70% series, the plots have been drawn through the points. There is a slight curvature at the higher concentrations which seems to disappear as the ionic strength decreases. The slope of the 20% curve is slightly positive, that of the 45% curve is slightly negative, while that of the 70% plot is negative. The extrapolation plots at all other temperatures were similar to these.

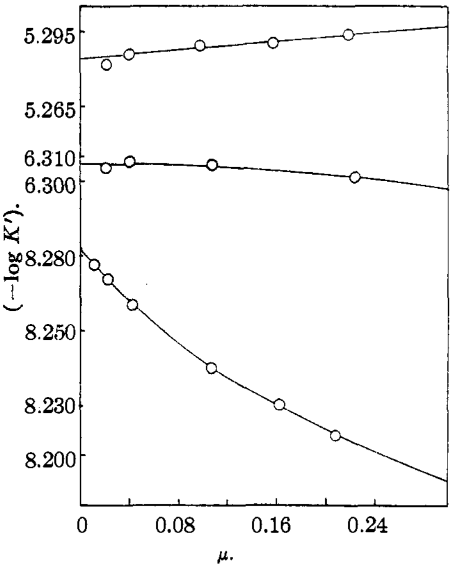

Fig. 1.—Extrapolation plots: diameters of circles correspond to 0.2 millivolt.

It is difficult to estimate the accuracy of this determination of the absolute value of $(-\log K)$. At 25°, an error corresponding to 0.1 mv. corresponds to an error of 0.002 to 0.003 in $(-\log K)$, or an uncertainty of 0.5 to 0.7% in the value of

K. The determination of K is estimated to be better than ±0.7% but not better than ±0.3%. The results in the more concentrated dioxane solutions appear to be the more consistent.

In Table II, the values of K are given at all temperatures at which measurements were made. We observe that K is in molality units. To convert to moles per liter of solution, it is only necessary to multiply by the solvent density. Thus, $K_c = Kd_0$. Examination of the values of K shows that in all solvents this quantity increases, passes through a maximum, and then decreases with increasing temperature. This fact is in accord with the behavior of weak electrolytes in aqueous solution.

TABLE II

IONIZATION CONSTANTS, OBSERVED AND CALCULATED BY EQUATION (5)

	$X = 20$		$X = 45$		$X = 70$	
	$D_{25} = 60.8$		$D_{25} = 38.5$		$D_{25} = 17.7$	
	$K \times 10^6$, obsd.	$K \times 10^6$, calcd.	$K \times 10^7$, obsd.	$K \times 10^7$, calcd.	$K \times 10^9$, obsd.	$K \times 10^9$ calcd.
0	4.77	4.77	4.74	4.75	5.17	5.18
5	4.88	4.89	4.83	4.84	5.25	5.25
10	4.99	4.99	4.91	4.90	5.27	5.29
15	5.07	5.05	4.93	4.94	5.31	5.29
20	5.10	5.10	4.96	4.94	5.25	5.27
25	5.13	5.11	4.93	4.92	5.22	5.21
30	5.09	5.10	4.87	4.87	5.11	5.13
35	5.04	5.05	4.80	4.79	5.04	5.02
40	4.97	4.98	4.69	4.69	4.88	4.88
45	4.89	4.87	4.54	4.56	4.70	4.72
50	4.78	4.75	4.39	4.41	4.50	4.54

Constants of Equation (4)

$X = 20;\ \Theta = 24.6, \log K_m = \bar{6}.7088, K_m = 5.12 \times 10^{-6}$

$X = 45;\ \Theta = 18.5, \log K_m = \bar{7}.6942, K_m = 4.95 \times 10^{-7}$

$X = 70;\ \Theta = 13.4, \log K_m = \bar{9}.7237, K_m = 5.29 \times 10^{-9}$

Harned and Embree[5] have shown that the equation

$$\log K - \log K_m = -p(t - \Theta)^2 \qquad (4)$$

expresses quite well the temperature variation of ionization constants of weak acids, bases and ampholytes in aqueous solution. K_m is the value of K at its maximum, Θ the characteristic temperature at which K is a maximum, and t is the centigrade temperature. p is a constant for all the electrolytes and has a value of 5.0×10^{-5}. Harned and Embree[2] also showed that the ionization constant of acetic acid in some methyl alcohol–water mixtures could be computed by this equation. They thus extended the range of applicability to a medium of dielectric constant of 70. The present results which extend to media of dielectric constant of the order of 18 are excellent for testing the further extension of the equation of Harned and Embree.

Equation (4) may be transposed to

$$\log K = [\log K_m - p\Theta^2] + 2p\Theta t - pt^2 \qquad (5)$$

$(\log K + pt^2)$ was plotted against t using the values of K given in Table II. Straight lines were obtained for the results in all the dioxane–water mixtures which proved the validity of the equation. From these graphs K_m and Θ were evaluated. Values of these quantities are given at the bottom of the table, and values of K computed by means of equation (5) are also given for purposes of comparison. The numerical equations for K in the three mixtures, obtained from equation (5) are

$$X = 20;\ \log K = \bar{6}.6785 + 0.00246\, t - 5 \times 10^{-5} t^2 \qquad (6)$$

$$X = 45;\ \log K = \bar{7}.6771 + 0.00185\, t - 5 \times 10^{-5} t^2 \qquad (7)$$

$$X = 70;\ \log K = \bar{9}.7147 + 0.00134\, t - 5 \times 10^{-5} t^2 \qquad (8)$$

respectively. The agreement between observed and calculated values is excellent. The maximum deviation is 0.6% for the 20% series and 0.5% for the 45% series. In the case of the 70% series, the maximum deviation is 0.4% except for the value at 50° where a 0.9% deviation is observed.

We have not tabulated the heat of ionization, ΔH. According to equation (4), this quantity is given by

$$\Delta H = 4.575 \times 10^{-4}\, T^2 (t - \Theta) \qquad (9)$$

The accuracy of the evaluation of ΔH depends on the accuracy with which Θ can be determined. An error in Θ of 1° will cause an error of 32 cal. at 0° and 48 cal. at 50°.

Summary

1. Measurements of the cells

H_2 (1 atm.) | HAc(m_1), NaAc(m_2), NaCl(m_3), X% dioxane, Y% H_2O | AgCl–Ag

have been made at 5° intervals from 0 to 50° in dioxane–water mixtures containing 20, 45 and 70% by weight of dioxane. The dielectric constants of these solvents at 25° are 60.8, 38.5 and 17.9, respectively.

2. From these data, the ionization constant of acetic acid, in each of the three solvents, has been computed at 5° intervals from 0 to 50° by the method of Harned and Ehlers.[3]

3. These values have been employed to test the empirical equation found by Harned and Embree[5] to express the variation of the dissociation constants of all weak electrolytes with the temperature.

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

The results of this investigation indicate that this general equation without any modification may be valid in non-aqueous solutions. It may at least be said that the Harned and Embree equation is able to reproduce the experimental results in solutions covering a wide range of dielectric constant, extending from 80 in aqueous solutions to 15.4 in a solvent containing 70% dioxane by weight at 50°.

NEW HAVEN, CONN. RECEIVED JULY 25, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

A Redetermination of the Protium-Deuterium Ratio in Water[1]

BY NORRIS F. HALL AND THOMAS O. JONES

Since Bleakney and Gould[2] gave 5000 as the H/D ratio in rain water, several attempts[3] have been made to check this value by preparing water free from deuterium and comparing its density with that of ordinary water. Most of these fall roughly into two groups, resulting in values either near 5500 or near 9000.

Lewis in 1933[4] calculated the value 6500 on the basis of his first electrolytic fractionations. Recently Applebey and Ogden[5] have suggested an upper limit of 7000 on the basis of electrolyses and the assumption of "reasonable" values of the electrolytic separation factor. The opinion has been expressed[6] that Applebey's results definitely discredit values of the H/D ratio in the neighborhood of 9000. By most workers[7] Johnston's recent value ($-18.3\ \gamma$ in density, equivalent to a ratio of 5800) appears to be accepted as the most probable. We have now redetermined this ratio by a method which involves no extrapolation, and in which the final value is approached from both the light and heavy side.

Plan of Work

We prepared nearly deuterium-free water electrolytically by two methods. The first involved the recombination of the electrolytic gases according to the method used by Taylor, Eyring and Frost.[8] We shall refer to this method as "mixed recovery."

In one experiment 55 liters of Lake Mendota water was electrolyzed in potassium hydroxide solution with iron cathodes to about 70% of the original volume, and the 16 liters of water collected was reëlectrolyzed. This procedure was repeated five times until the volume of the last condensate was 150 ml. The amount collected at each stage was about 30% of the preceding volume. In a later experiment this process was independently repeated through four stages of electrolysis.

In the second method, called "separation recovery," we collected the hydrogen separately and burned it in ordinary air. Calculations of the equilibrium constant at high temperatures indicated that exchange effects in the flame could not introduce density differences in the burned water as great as 1 γ, and at the time this work was undertaken the results of Dole, Titani and Greene[9] were not available to us, so that we assumed that air oxygen and surface water oxygen had the same isotopic composition.

By this method two runs were made. In one run (III) through four stages using bell type cells, 30 liters of water was reduced to 150 ml. In the second (run IV), V-type cells (Fig. 1) with a loose plug of glass wool as a diaphragm were used. The initial and final volumes were 24 liters and 400 ml., respectively, and the electrolysis was carried again through four stages.

Because the results of the two types of electrolysis described did not agree, and because we expected on the basis of Johnston's work[3] a displacement of the oxygen isotope ratio during mixed recovery electrolysis, we decided to normalize the oxygen isotope content of some of our samples by equilibration against the standard

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(1) Presented at the Kansas City meeting of the American Chemical Society, April 15, 1936.

(2) Bleakney and Gould, *Phys. Rev.*, **44**, 265 (1933) (5000).

(3) Urey and Teal, *Rev. Modern Phys.*, **7**, 40 (1935) (5000); H. L. Johnston, THIS JOURNAL, **57**, 484, 2737 (1935) (5800); Ingold, Ingold, Whitaker and Whitlaw-Gray, *Nature*, **134**, 661 (1934) (9000); Tronstad, Nordhagen and Brun, *ibid.*, **136**, 515 (1935) (5500); Morita and Titani, *Bull. Chem. Soc. Japan*, **10**, 257 (1935) (5500); Christiansen, Crabtree and Laby, *Nature*, **135**, 870 (1935) (8400).

(4) Lewis and Macdonald, *J. Chem. Phys.*, **1**, 823 (1933).

(5) M. P. Applebey and G. Ogden, *J. Chem. Soc.*, 163 (1936).

(6) S. Glasstone, *Ann. Rep. Chem. Soc.*, **32**, 42 (1935).

(7) *Cf.* E. H. Riesenfeld and T. L. Chang, *Ber.*, **69A**, 1305, 1307, 1308 (1936).

(8) Taylor, Eyring and Frost, *J. Chem. Phys.*, **1**, 823 (1933).

(9) M. Dole, THIS JOURNAL, **57**, 2731 (1935), *J. Chem. Phys.*, **4**, 268 (1936); Morita and Titani, *Bull. Chem. Soc. Japan*, **II**, 36 (1936); C. H. Greene and R. J. Voskuyl, THIS JOURNAL, **58**, 693 (1936).