[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Ionization Constant of Acetic Acid in Methyl Alcohol–Water Mixtures from 0 to 40°

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The ionization constants of weak acids, bases, and ampholytes in mixtures of water and non-aqueous solvents, or in non-aqueous solvents are not known with any degree of certainty. The data available for the determination of this quantity in any medium other than water are scarce and in most cases where such data exist the accuracy is insufficient to demand serious consideration. The investigations of Harned and Robinson,[1] and Harned and Owen,[2] have shown that accurate values of the ionization constant of a weak acid can be obtained both in water and in water containing large quantities of the undissociated weak acid molecule from cells without liquid junctions. In particular, Harned and Owen have computed the ionization constant of acetic acid in water and acetic acid–water mixtures from the electromotive forces of suitable cells with an accuracy of 1%. The present communication contains a determination of the ionization constant of acetic acid from 0 to 40° in water–methanol solutions of 10 and 20% methanol by weight. To this end, cells of the type

$$H_2 \text{ (1 atm.)} \mid \text{HAc}(m_1),\ \text{NaAc}(m_2),\ \text{NaCl}(m_3) \mid \text{AgCl} \mid \text{Ag}$$
$$(X = \%\ \text{methanol by weight})$$

were employed. Buffered acid cells of this type were first used for this purpose by Harned and Ehlers.[3]

Experimental Results

The solutions were made from air-free stock solutions. Vacuum technique was employed. The concentrations were expressed in molalities (m = moles per 1000 g. of solvent). Corrections to one atmosphere hydrogen pressure were made by employing values of the total vapor pressures of the solvent mixtures measured recently in this Laboratory.[4] The concentrations m_1, m_2 and m_3 were known with an accuracy of 0.1%. Each recorded electromotive force is the average of those of three cells except at 25° where it is the average of six independent measurements. The electromotive force reproducibility was ±0.05 mv. in the case of the 10% methanol series, and ±0.1 mv. for the 20% series. Table I contains these mean electromotive forces and all other data necessary for the computation of the ionization constant.

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS:

$$H_2 \text{ (1 atm.)} \mid \text{HAc}(m_1),\ \text{NaAc}(m_2),\ \text{NaCl}(m_3) \mid \text{AgCl} \mid \text{Ag}$$
$$(X = \%\ \text{methanol by weight})$$

(1) X = 10

$m_1 = m_2 \times 0.9997 = m_3 \times 1.0086$

m_1	0	10	20	25	30	40
0.01237	0.59946	0.60720	0.61490	0.61868	0.62256	0.62996
.01796	.59079	.59822	.60557	.60920	.61290	.61988
.02399	.58418	.59128	.59837	.60189	.60538	.61216
.03010	.57891	.58578	.59271	.59615	.59949	.60618
.03382	.57631	.58309	.58990	.59325	.59662	.60307
.04487	.56972	.57626	.58274	.58604	.58930	.59560

(2) $X = 20$

$m_3 = m_2/0.9996 = m_1/1.0002$

m_3	t....0	10	20	25	30	40
0.004814	0.62395	0.6329	0.6417	0.6462	0.6505	0.6590
.007198	.6148	.6233	.6319	.6361	.6402	.6484
.010784	.60505	.6133	.6214	.6255	.6295	.6373
.01261	.6018	.60975	.6178	.62175	.6256	.6333
.01647	.59545	.6032	.6111	.6149	.6186	.6261
.02047	.5905	.59805	.6057	.60945	.6130	.6203
.03421	.5784	.5855	.5925	.5961	.5994	.6060
.04306	.5731	.5800	.5868	.5903	.5935	.6000

The Ionization Constant.—The equation for the electromotive force of the cell may be transposed to

$$\frac{F}{2.3026\ RT}(E - E') + \log\frac{(m_1 - m_{\text{H}})m_{\text{Cl}}}{(m_3 + m_{\text{H}})} =$$
$$\log\frac{\gamma_{\text{H}}\gamma_{\text{Cl}}\gamma_{\text{HAc}}}{\gamma_{\text{H}}\gamma_{\text{Ac}}} - \log K = -\log K' \quad (1)$$

where E_0' is the molal electrode potential of the silver–silver chloride electrode, K the ionization constant of acetic acid, and γ and m are the activity coefficients and molalities of the species denoted by subscripts. In order to evaluate K, the left side of the equation, $-\log K'$, was computed from the observed electromotive forces, the values of E_0' determined by Harned and Thomas,[4] and the values of the concentrations. In the present instance $(m_1 - m_{\text{H}})$ and $(m_3 + m_{\text{H}})$ may be replaced by m_1 and m_3 without causing an error greater than the experimental. The plots of these values of $(-\log K')$ *versus* μ were straight lines. The values of this quantity at zero μ is $(-\log K)$, since the term involving the activity

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(1) Harned and Robinson, THIS JOURNAL, **50**, 3157 (1928).

(2) Harned and Owen, *ibid.*, **52**, 5079 (1930).

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

(4) Harned and Thomas, *ibid.*, **57**, 1666 (1935).

coefficients vanishes. In Table II the ionization constants at the temperatures designated are given as well as the values of E_0' used in their computation.

TABLE II

OBSERVED AND CALCULATED IONIZATION CONSTANTS

	Wt. % methanol = 10			Wt. % methanol = 20		
t	E_0'	$K \times 10^5$	K (Eq. 2) $\times 10^5$	E_0'	$K \times 10^6$	K (Eq. 2) $\times 10^6$
0	0.22762	1.138	1.144	0.22022	7.38	7.43
10	.22328	1.200	1.204	.21631	7.94	7.91
20	.21821	1.242	1.238	.21155	8.24	8.20
25	.21535	1.247	1.244	.20881	8.34	8.30
30	.21220	1.237	1.243	.20567	8.30	8.32
40	.20550	1.214	1.220	.19910	8.19	8.26

Constants of (Eq. 2): Wt. % methanol = 0: $\Theta = 22.6$, $\log K_m = \bar{5}.2456$

Wt. % methanol = 10: $\Theta = 27$, $\log K_m = \bar{5}.0959$

Wt. % methanol = 20: $\Theta = 31.5$, $\log K_m = \bar{6}.9207$

In a recent article we[5] have shown that log K as a function of t for all weak electrolytes in aqueous solution may be expressed by the quadratic equation

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

in which K_m is the maximum value of K at a temperature Θ and p is a universal constant equal to 5×10^{-5} deg.$^{-2}$. If $[\log K + pt^2]$ is plotted against t, a straight line should be obtained the slope of which is $2p\Theta$ and the intercept at t equals 0° is $[\log K_m - p\Theta^2]$. Since p is known, log K_m and Θ may be computed readily from such a plot.

The relation represented by equation (2) was derived from data in aqueous solutions and the question now arises as to the extent to which it is valid in non-aqueous solutions. As far as the present results are concerned, equation (2) was found to be valid within narrow limits. The characteristic constants Θ and log K_m were determined and are to be found at the bottom of Table II. Introduction of the numerical constants in equation (2) leads to the following equations for log K

$$\log K = \bar{5}.0585 + 0.0027\,t - 5 \times 10^{-5}\,t^2; \quad \text{wt. \% MeOH} = 10$$

$$\log K = \bar{6}.881 + 0.00282\,t - 5 \times 10^{-5}\,t^2; \quad \text{wt. \% MeOH} = 20 \qquad (3)$$

The values of K computed from this equation are given in the fourth and seventh columns of Table II. The deviation between the observed and calculated values of K is within ±0.5% when wt. % methanol = 10, and within ±0.7% when wt. % methanol = 20, which may be within the limits of the over-all error of experiment.

Our equation requires a maximum in dissociation constant at a temperature Θ for all weak electrolytes. In the present case, this maximum occurs within the range of temperature over which measurements have been made. In the table we have also included the values of log K_m and Θ for acetic acid in water from which it is apparent that Θ increases regularly as we pass from water to the alcoholic solutions.

Insufficient results have been obtained to test thoroughly in an exact manner how the log K varies with the change in composition of the medium. However, since we know this quantity in water, 10 and 20% methanol at various temperatures a preliminary investigation can be made. Plots of log K *versus* $(1/D)$ at constant temperature where D is the dielectric constant of the medium were found to be straight lines within the limit of experimental error.[6] These may be used with some degree of safety in extrapolating to 30% or perhaps 40% methanol mixtures. It would not be safe to employ such graphs for purposes of extrapolation to $D = \infty$.

Summary

1. The electromotive forces of the cells,

$$H_2 \mid HAc(m_1),\ NaAc(m_2),\ NaCl(m_3) \mid AgCl \mid Ag$$

in 10 and 20% by weight methanol–water mixtures have been measured at 0, 10, 20, 25, 30 and 40°.

2. From these and the molal electrode potentials of the silver–silver chloride electrode in these mixtures, the ionization constant of acetic acid has been computed.

3. The values of log K as a function of T may be computed by the equation previously employed by us for similar calculations in aqueous solutions.

4. The present results indicate that as a first approximation log K varies linearly with $(1/D)$. The data are not numerous enough to thoroughly test this relation.

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

[6] Values of D were taken from the data of Åkerlöf, *ibid.*, **54**, 4125 (1932).