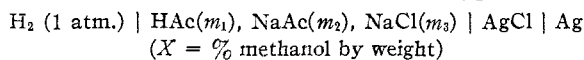


[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

## 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,<sup>1</sup> and Harned and Owen,<sup>2</sup> 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



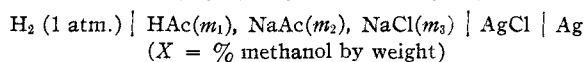
were employed. Buffered acid cells of this type were first used for this purpose by Harned and Ehlers.<sup>3</sup>

### Experimental Results

The solutions were made from air-free stock solutions. Vacuum technique was employed. The concentrations were expressed in molalities ( $m = \text{moles per 1000 g. of solvent}$ ). 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.<sup>4</sup> 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  $\pm 0.05 \text{ mv.}$  in

the case of the 10% methanol series, and  $\pm 0.1 \text{ mv.}$  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:



(1) X = 10							
$m_1$	...	0	$m_1 = m_2 \times 0.9997 = m_3 \times 1.0086$				
			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							
$m_3$	...	0	$m_3 = m_2/0.9996 = m_1/1.0002$				
			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

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

where  $E'_0$  is the molal electrode potential of the silver-silver chloride electrode,  $K$  the ionization constant of acetic acid, and  $\gamma$  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,<sup>4</sup> 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  $\mu$  were straight lines. The values of this quantity at zero  $\mu$  is  $(-\log K)$ , since the term involving the activity

(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

$t$	Wt. % methanol = 10			Wt. % methanol = 20		
	$E'_0$	$K \times 10^5$	$K$ (Eq. 2) $\times 10^5$	$E'_0$	$K \times 10^5$	$K$ (Eq. 2) $\times 10^5$
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:  $\Theta = 22.6$ ,  
 $\log K_m = 5.2456$   
 Wt. % methanol = 10:  $\Theta = 27$ ,  
 $\log K_m = 5.0959$   
 Wt. % methanol = 20:  $\Theta = 31.5$ ,  
 $\log K_m = 6.9207$

In a recent article we<sup>5</sup> have shown that  $\log K$  as a function of  $t$  for all weak electrolytes in aqueous solution may be expressed by the quadratic equation

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

in which  $K_m$  is the maximum value of  $K$  at a temperature  $\Theta$  and  $p$  is a universal constant equal to  $5 \times 10^{-5} \text{ deg.}^{-2}$ . 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  $0^\circ$  is  $[\log K_m - p\theta^2]$ . Since  $p$  is known,  $\log K_m$  and  $\theta$  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  $\theta$  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  $\log K$

$$\begin{aligned} \log K &= 5.0585 + 0.0027 t - 5 \times 10^{-5} t^2; \\ &\quad \text{wt. \% MeOH} = 10 \\ \log K &= 6.881 + 0.00282 t - 5 \times 10^{-5} t^2; \\ &\quad \text{wt. \% MeOH} = 20 \end{aligned} \quad (3)$$

The values of  $K$  computed from this equation are given in the fourth and seventh columns of Table

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

II. The deviation between the observed and calculated values of  $K$  is within  $\pm 0.5\%$  when wt. % methanol = 10, and within  $\pm 0.7\%$  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  $\Theta$  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  $\Theta$  for acetic acid in water from which it is apparent that  $\Theta$  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.<sup>6</sup> 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,  
 $\text{H}_2 | \text{HAc}(m_1), \text{NaAc}(m_2), \text{NaCl}(m_3) | \text{AgCl} | \text{Ag}$   
 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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(6) Values of  $D$  were taken from the data of Åkerlöf, *ibid.*, **54**, 4125 (1932).