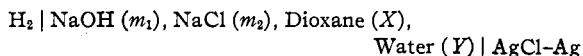


[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Properties of Electrolytes in Mixtures of Water and Organic Solvents. II. Ionization Constant of Water in 20, 45 and 70% Dioxane-Water Mixtures

BY HERBERT S. HARNED AND LESLIE D. FALLON¹

Very little is known concerning the ionization constant of water in solvents other than water. In order to determine this quantity in media of lower dielectric constant, the electromotive forces of the cells



have been measured. The results cover the temperature range from 0 to 50° throughout which results of high accuracy may be obtained. The measurements were made in media containing 20, 45 and 70% dioxane by weight.

Experimental Data

The solutions were prepared with an accuracy greater than that caused by the errors in the measurements of the electromotive forces. In the 20% dioxane mixtures the reproducibility was 0.05 mv. and in the 45 and 70% dioxane solutions it was 0.1 mv. The technique with slight modifications was that employed previously for measurements of this kind.²

Unfortunately, an unforeseen circumstance made an accurate determination of the ionization constant impractical in the mixtures containing over 70% dioxane. With the 20% dioxane solutions, one to one ratios of sodium chloride to hydroxide yielded very satisfactory results. In the case of the cells containing 45% dioxane and a one to one ratio of salt to hydroxide, the cell electromotive forces were very erratic. However, when the ratio of salt to hydroxide was three to one or greater, a reproducibility of 0.1 mv. was obtained. With the 70% dioxane-water mixtures, erratic results were obtained until a fifteen to one ratio of chloride to hydroxide or greater was employed. With this latter condition the cell reproducibility was again 0.1 mv.

This behavior is attributed to the change in relative solubility of silver chloride and hydroxide in passing from pure aqueous solutions to those containing the higher percentages of dioxane. Since in the media containing much dioxane,

(1) This communication contains material from a dissertation presented by Leslie D. Fallon to the Graduate School of Yale University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, June, 1939.

(2) Harned and Morrison, *Am. J. Sci.*, **33**, 161 (1937).

suitable points on the graph used for extrapolation could not be obtained near the zero axis, the determination of ionization constant is somewhat uncertain. Since both silver bromide and iodide are less soluble than the chloride in water, cells containing these electrodes would have been more suitable for the present purpose. Unfortunately, the standard potentials of these electrodes in dioxane-water mixtures have not yet been determined.

In Table I, the observed electromotive forces of the cells have been recorded.

Ionization Constant and Derived Thermodynamic Quantities.—The electromotive force, E , of the cell is given by the equation

$$E - E_0 + \frac{RT}{NF} \ln \frac{m_{\text{Cl}}}{m_{\text{OH}}} = \frac{RT}{NF} \ln \frac{\gamma_{\text{H}}\gamma_{\text{OH}}}{\gamma_{\text{H}}\gamma_{\text{Cl}}a_{\text{H}_2\text{O}}} - \frac{RT}{NF} \ln K^{3,4} \quad (1)$$

where E_0 is the standard potential, m_{Cl} and m_{OH} are the stoichiometrical molalities of the chloride and hydroxide, γ_{H} , γ_{OH} and γ_{Cl} , the activity coefficients of the species denoted by subscripts, $a_{\text{H}_2\text{O}}$ the activity of water, and K the ionization constant. In these computations, $a_{\text{H}_2\text{O}}$ as well as $\gamma_{\text{H}}\gamma_{\text{OH}}$ and $\gamma_{\text{H}}\gamma_{\text{Cl}}$ have been assigned the value unity at zero electrolyte concentration in each solvent. Since

$$K = \frac{\gamma_{\text{H}}\gamma_{\text{OH}}}{a_{\text{H}_2\text{O}}} m_{\text{H}}m_{\text{OH}} \quad (2)$$

it is equal to $m_{\text{H}}m_{\text{OH}}$ at zero ionic strength in all solvents.

That the extrapolation in the case of the 20% dioxane mixtures can be carried out with high accuracy is shown in Fig. 1. Here the radii of the circles equal 0.01 mv. and the estimation of $\log K$ from the graphs is within ± 0.02 mv. The standard potentials employed were those computed by Harned⁵ from the data of Harned and Morrison.⁶ It is probable that the largest source of error in the absolute magnitude of $\log K$ is caused by the error in determining E_0 . An error of 0.1 mv. in E_0 causes an error of 0.002 in $\log K$ or 0.5% in K .

(3) Roberts, *THIS JOURNAL*, **52**, 3877 (1930).

(4) Harned and Hamer, *ibid.*, **55**, 2194 (1933).

(5) Harned, *ibid.*, **60**, 336 (1938).

(6) Harned and Morrison, *ibid.*, **58**, 1908 (1936).

TABLE I
ELECTROMOTIVE FORCES OF THE CELLS:
 $H_2|NaOH (m_1), NaCl (m_2), Dioxane (X), Water (Y)|AgCl-|Ag$
(1) $X = 20\%$ by weight

t	$m_1 = m_2 = \text{moles per 1000 g. solvent; } \mu = m_1 + m_2$					
	$m_1 = m_2 \dots \dots$	0.02426	0.03433	0.04344	0.05301	0.07621
0		1.06352	1.06358	1.06363	1.06371	1.06377
5		1.06438	1.06443	1.06447	1.06454	1.06460
10		1.06524	1.06528	1.06531	1.06537	1.06543
15		1.06610	1.06613	1.06615	1.06620	1.06626
20		1.06696	1.06698	1.06699	1.06703	1.06709
25		1.06782	1.06783	1.06783	1.06786	1.06792
30		1.06868	1.06868	1.06867	1.06869	1.06875
35		1.06954	1.06953	1.06951	1.06952	1.06958
40		1.07040	1.07038	1.07035	1.07035	1.07041
45		1.07126	1.07123	1.07119	1.07118	1.07124
50		1.07212	1.07208	1.07203	1.07201	1.07206

t	(2) $X = 45\%$. $m_1 = 0.01$							
	$m_2 \dots \dots$	0.03	0.04	0.05	0.06	0.07	0.08	0.09
0		1.06601	1.05877	1.05334	1.04876	1.04477	1.04130	1.03851
5		1.06588	1.05855	1.05303	1.04835	1.04430	1.04086	1.03796
10		1.06575	1.05833	1.05272	1.04794	1.04382	1.04032	1.03741
15		1.06562	1.05811	1.05241	1.04753	1.04335	1.03978	1.03686
20		1.06549	1.05789	1.05210	1.04712	1.04287	1.03924	1.03631
25		1.06536	1.05767	1.05179	1.04671	1.04240	1.03870	1.03576
30		1.06523	1.05745	1.05148	1.04630	1.04192	1.03816	1.03521
35		1.06510	1.05723	1.05117	1.04589	1.04145	1.03762	1.03466
40		1.06497	1.05701	1.05086	1.04548	1.04097	1.03708	1.03411
45		1.06484	1.05679	1.05056	1.04507	1.04050	1.03654	1.03356
50		1.06471	1.05657	1.05024	1.04466	1.04002	1.03600	1.03301

t	(3) $X = 70\%$. $m_1 = 0.01$					
	$m_2 \dots \dots$	0.15	0.2	0.25	0.3	
0			1.05204	1.04346	1.03599	1.02993
5			1.05046	1.04177	1.03412	1.02795
10			1.04888	1.04008	1.03225	1.02597
15			1.04730	1.03839	1.03038	1.02399
20			1.04572	1.03670	1.02851	1.02201
25			1.04414	1.03501	1.02664	1.02003
30			1.04256	1.03332	1.02477	1.01805
35			1.04098	1.03163	1.02290	1.01607
40			1.03940	1.02994	1.02103	1.01409
45			1.03782	1.02825	1.01916	1.01201
50			1.03624	1.02656	1.01729	1.01013

Figure 2 shows the extrapolations in the cases of 45 and 70% mixtures. Although straight lines could be drawn through the points corresponding to the left side of the equation, the extrapolation becomes less certain as the percentage of dioxane increases because the values of μ are so far from the zero axis. As previously explained, it is impossible to remedy this difficulty as long as silver-silver chloride electrodes are employed. The derived values of K in the 45% mixtures are clearly more certain than those for the 70% dioxane mixtures and the absolute values are probably known to within ± 0.2 mv. This error in extrapolation is greater than the estimated error

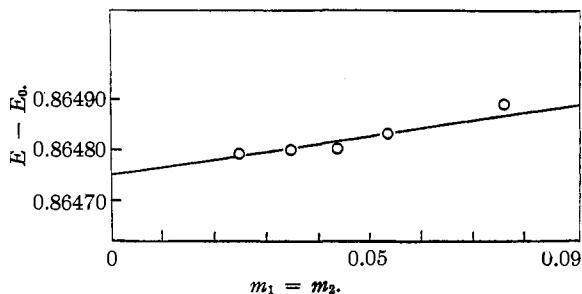


Fig. 1.—Extrapolation of 20% dioxane-water mixtures at 25°. (Diameter of circles equals 0.02 mv.)

of ± 0.1 mv. in the evaluation of E_0 . However, since extrapolations at all temperatures were made

TABLE II
IONIZATION CONSTANT OF WATER IN 20, 45 AND 70% DIOXANE-WATER MIXTURES

t	$K \times 10^{14}$ $X = 0$	ΔH_i^a	$K \times 10^{14}$ $X = 20$	ΔH_i	$K \times 10^{17}$ $X = 45$	ΔH_i	$K \times 10^{19}$ $X = 70$	ΔH_i
0	0.1133	14,600	2.702	14,730	2.114	14,530	1.789	13,870
5	.1846	14,390	4.375	14,480	3.409	14,260	2.819	13,630
10	.2920	14,160	6.761	14,240	5.349	13,990	4.348	13,380
15	.4503	13,940	10.67	13,990	8.188	13,720	6.511	13,140
20	.6909	13,720	16.22	13,740	12.34	13,450	9.654	12,900
25	1.008	13,480	23.99	13,500	18.09	13,190	13.95	12,660
30	1.468	13,230	34.77	13,250	25.94	12,920	19.74	12,410
35	2.089	13,000	49.42	13,000	36.55	12,650	27.43	12,170
40	2.917	12,760	69.47	12,760	50.77	12,380	37.79	11,930
45	4.018	12,540	95.31	12,510	69.14	12,110	50.64	11,690
50	5.474	12,300	128.7	12,260	92.77	11,840	67.19	11,430

^a Evaluated from the combined data of Harned and Hamer,⁴ Harned and Donelson,⁹ and of Harned and Geary.¹⁰

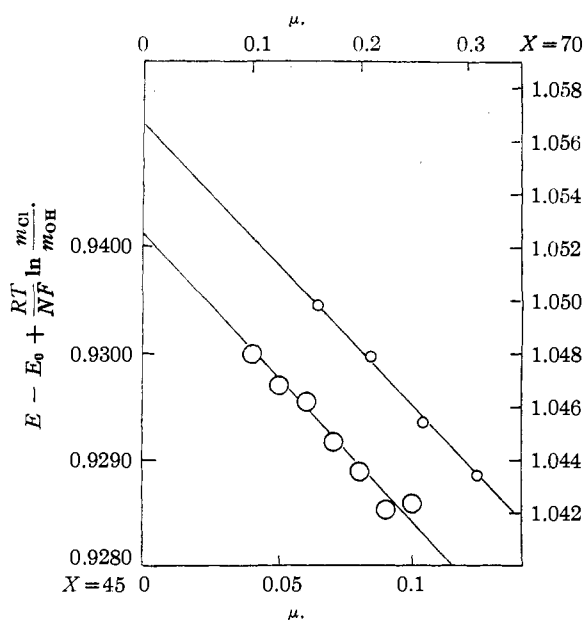


Fig. 2.—Extrapolation of 45 and 70% dioxane-water mixtures at 25°: lower plot ($X = 45$) (diameter of circles equals 0.2 mv.); upper plot ($X = 70$) (diameter of circles equals 0.4 mv.).

in the same manner, the temperature variation of K should be known quite accurately. This is also true of the values of K of the 70% dioxane mixtures in which case the absolute accuracy may not be greater than 0.5 to 1 mv. The values of the standard potentials employed in the case of the 45% dioxane mixtures were those given by Harned and Donelson⁷ and for the 70% dioxane mixtures, those obtained by Harned and Calmon.⁸ The values of K are given in Table II. For the sake of completeness, values in pure water deter-

(7) Harned and Donelson, *THIS JOURNAL*, **60**, 2128 (1938).

(8) Harned and Calmon, *ibid.*, **60**, 2130 (1938).

(9) Harned and Donelson, *ibid.*, **59**, 1280 (1937).

(10) Harned and Geary, *ibid.*, **59**, 2032 (1937).

mined by the same method have been included.¹¹

In order to compute the change in heat content and heat capacity of the ionization reaction, we have employed the equation

$$\frac{d \log K}{dT} = \frac{\Delta H_i}{RT^2} \quad (3)$$

and the assumption that ΔH_i varies linearly with temperature. This leads to the equations

$$\log K = (A/T) + B \log T + C \quad (4)$$

$$\Delta H_i = -2.303 RA + BRT = A' - B'T \quad (5)$$

$$\Delta C_p = BR \quad (6)$$

for K , ΔH_i and ΔC_p , respectively. The constants of these equations derived by the method of least squares are contained in Table III. The

TABLE III
CONSTANTS OF EQUATIONS (4), (5) AND (6)

	$X = 20$	$X = 45$	$X = 70$
A	-6161.329	-6377.395	-5926.389
B	-24.814	-27.006	-24.415
C	67.447	72.472	62.437
A'	28.19	29.18	27.12
B'	49.31	55.66	48.51
ΔC_p	-49.3	-53.7	-48.5

values of the change in heat content, ΔH_i , are given in Table II. Equation (4) with these numerical constants reproduces the observed values of $\log K$ with an average accuracy better than ± 0.001 . It is difficult to estimate the accuracy of this determination of ΔH_i . As previously mentioned, the temperature variation of $\log K$ is probably determined fairly accurately even in the case of the 70% dioxane mixtures even though the absolute values of K are somewhat in error. As a tentative estimate, we regard the accuracy of determination of ΔH_i to be of the order of ± 50 cal.

ΔC_p according to the method of calculation is

(11) Harned, *J. Franklin Inst.*, **225**, 623 (1938).

taken to be constant over the temperature range. The accuracy of its determination is of the order of ± 5 cal.

Summary

1. From measurements of the cells, $\text{H}_2 | \text{NaOH} (m_1), \text{NaCl} (m_2), \text{Dioxane} (X), \text{H}_2\text{O} (Y) | \text{AgCl}-\text{Ag}$, the ionization constant of water has been determined in 20, 45 and 70% dioxane mixtures, and at 5° intervals from 0 to 50° inclusive.

2. The heat content and heat capacity changes of the ionization reaction have been evaluated.

3. The uncertainty in the determination of the ionization constant increases with the dioxane content of the solvent. This is caused by the change in relative solubility of silver chloride and hydroxide and cannot be remedied as long as silver-silver chloride electrodes are employed. Cells containing silver-silver bromide or iodide electrodes would probably be more suitable, but, unfortunately, their standard potentials are not known in these media.

NEW HAVEN, CONN.

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The Properties of Electrolytes in Mixtures of Water and Organic Solvents. III. Ionization Constant of Acetic Acid in an 82% Dioxane-Water Mixture

BY HERBERT S. HARNED AND LESLIE D. FALLON

From the measurements of the electromotive forces of the cells

$\text{H}_2 | \text{HAC} (m_1), \text{NaCl} (m_2), \text{NaCl} (m_3), \text{Dioxane} (X), \text{H}_2\text{O} (Y) | \text{AgCl}-\text{Ag}$

Harned and Kazanjian¹ determined the ionization constant of acetic acid in 20, 45 and 70% dioxane-water mixtures. The first computations depended on standard potentials derived by the Debye-Hückel theory without the use of the extended terms, and have been revised somewhat by Harned.² These results have now been extended to 82% dioxane mixtures.

Experimental Results

It was more difficult to obtain high accuracy with these cells than with those containing mixtures of higher dielectric constant. This is caused by the long period of time for equilibrium to be reached, particularly in the cases of cells containing ions at low ionic strengths. However, the average reproducibility of the cells was of the order of ± 0.3 mv. The concentrations of acetic acid, sodium acetate and sodium chloride were made equal. These concentrations were known with an accuracy of 0.1% and, consequently, any error from this source was less than that caused by error in the electromotive force measurements. Cells were run in triplicate and the mean values of the electromotive forces taken. These results are compiled in Table I.

(1) Harned and Kazanjian, *THIS JOURNAL*, **58**, 1912 (1936).

(2) Harned, *J. Phys. Chem.*, **43**, 275 (1939).

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS: $\text{H}_2 | \text{HAC} (m_1), \text{NaAc} (m_2), \text{NaCl} (m_3), \text{DIOXANE} (X), \text{H}_2\text{O} (Y) | \text{AgCl}-\text{Ag}$
 $X = 82\%$ BY WEIGHT IN SOLVENT, $m_1 = m_2 = m_3 = \text{MOLES PER 1000 G. SOLVENT}$; $\mu = m_2 + m_3$

t	0.01	0.02	0.03	0.05	0.068	0.08	$K \times 10^{11}$
5	0.6903	0.6715	0.6637	0.6501	0.6404	0.6362	7.4
10	.6911	.6739	.6644	.6508	.6413	.6372	7.6
15	.6929	.6750	.6656	.6519	.6423	.6379	7.6
20	.6945	.6766	.6663	.6532	.6432	.6384	7.6
25	.6962	.6782	.6671	.6540	.6440	.6391	7.2
30	.6978	.6795	.6688	.6549	.6448	.6399	6.9
35	.6994	.6808	.6698	.6559	.6458	.6406	6.6
40	.7011	.6821	.6714	.6568	.6465	.6413	6.0
45	.7028	.6834	.6730	.6577	.6472	.6420	5.4

Ionization Constant

The equation for the cell may be written in the form³

$$\frac{F(E - E_0)}{2.303 RT} + \log \frac{m_1 m_3}{m_2} = - \log \frac{\gamma_{\text{H}^+} \gamma_{\text{Cl}^-} \gamma_{\text{HAc}}}{\gamma_{\text{H}^+} \gamma_{\text{Ac}^-}}$$

$$\log K = - \log K' \quad (1)$$

If the left side or $-\log K'$ is plotted against μ , the intercept at zero μ equals $-\log K$. In Fig. 1, plots of $\log K'$ versus μ are shown and it is clear that the values of $-\log K$ can be determined to within ± 0.005 , or about ± 0.2 mv. This uncertainty is very much less than that in the values of the standard potentials, E_0 . The difficulty of obtaining E_0 in media of as low a dielectric constant as the present one ($D_{25} = 9.53$) has been discussed carefully by Harned, Walker and Calmon.⁴

This situation suggests that the present cell

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

(4) Harned, Walker and Calmon, *ibid.*, **61**, 44 (1939).