sion is rendered questionable because of thermal decomposition. Mixtures between the lines DEFH and ABC are emulsions. These mixtures upon cooling become isotropic liquids as they cross the line CB. The slope of the line CB shows that the solubility of the amine salt in water decreases with increased temperature. The emulsion solidifies to a gel as it crosses the line DE. If the emulsion crosses the line EF, the gel assumes a somewhat crystalline appearance. All compositions below the line DEF may differ only in the amount of liquid present. On cooling the isotropic liquid above the line FG, it solidifies to a crystalline mass. All mixtures below the line LMN are crystalline and are probably composed of a mixture of crystals of octadecylamine acetate and ice. The line JK represents a metastable transformation from an emulsion to a gel and transitions along this line occur only if the sample is cooled rapidly and without agitation.

TABLE I

VAPOR PRESSURES OF OCTADECYLAMINE ACETATE–WATER MIXTURES

% C_{18} acetate in water	Temp. of sample, °C.	Dew-point, °C.	Vapor pressure lowering, mm.
50.0	30.0	29.6	0.7
	40.0	39.8	.6
	50.0	49.9	.5
	60.0	59.9	.7
75.0	20.0	19.4	.6
	30.0	29.6	.7
	40.0	39.8	.6
	50.0	49.9	.5
	60.0	59.9	.7
95.0	20.0	19.1	.9
	25.0	24.3	1.0
	30.0	29.4	0.9
	35.0	34.6	.9
	40.0	39.7	.7
	50.0	49.7	1.4
	60.0	59.8	1.4
99.0	30.0	29.2	1.4
	40.0	39.3	2.0
	50.0	49.5	2.3
	60.0	59.8	1.4

Table I shows the lowering of the vapor pressure of water at various temperatures for octadecylamine acetate–water mixtures. These values were determined by the dew-point method previously described. The values obtained indicate a colloidal system.

Summary

1. The systems dodecylamine acetate–water and octadecylamine acetate–water have been investigated.

2. These amine salts show crystalloidal properties in dilute aqueous solutions and colloidal properties in concentrated solutions.

CHICAGO, ILL.

RECEIVED MAY 19, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Ionization Constant of Formic Acid in Dioxane–Water Mixtures

BY HERBERT S. HARNED AND ROBERT S. DONE[1]

The ionization constants of acetic acid and water from 0 to 50° in dioxane–water mixtures have been determined from cells without liquid junction by Harned and Kazanjian,[2] and Harned and Fallon.[3,4] By means of the cells

$$H_2 \mid HF(m),\ NaF(m),\ NaCl(m),\ Dioxane(X),\ Water(Y) \mid AgCl\text{-}Ag$$

we have extended these investigations to include formic acid represented by HF. From the ionization constant and its temperature coefficient, the free energy, heat content, heat capacity and entropy of ionization have been calculated.

Experimental

The solutions were made by diluting an aqueous stock solution containing formic acid, sodium formate and sodium chloride at the same molality with the proper quantities of dioxane and water. Two kilograms of Eastman Kodak Co. formic acid were redistilled twice from an all-glass column still. The first middle fraction was collected over a temperature range of 0.6° and the second and final middle fraction (800 g.) over a temperature range of 0.2°. About 400 g. of the purified acid was added to two liters of water. This solution was analyzed by weight titration against standard carbon dioxide-free sodium hydroxide solution. The standard buffered solution was made by adding enough sodium hydroxide solution to

---

[1] This communication contains material from a dissertation presented by Robert S. Done to the Graduate School of Yale University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, June, 1941.

[2] Harned and Kazanjian, THIS JOURNAL, **58**, 1912 (1936). Also Harned, *J. Phys. Chem.*, **43**, 275 (1939).

[3] Harned and Fallon, THIS JOURNAL, **61**, 2377 (1939). Acetic acid in 82% by weight dioxane–water solution.

[4] Harned and Fallon, *ibid.*, **61**, 2374 (1939).

neutralize exactly one-half of the acid. A sufficient quantity of dried sodium chloride was added to this solution to make the molalities of the formic acid, formate and chloride identical. It was estimated that the concentrations of the formate and acid were known to within 0.04%. The chloride concentration was known to within 0.01%. The molality of each solute in this solution was 0.9150. The cell solutions were made by weighing appropriate amounts of this stock buffer solutions, dioxane and water.

The preparation of the electrodes and cell technique were essentially the same as that described by Harned and Morrison.[5] Measurements of three cells at each buffer concentration were made. If their electromotive forces agreed to within 0.1 mv., the mean value was accepted. The measurements were first carried out at 25°, then changed to other temperatures (*e. g.* 0°) and brought back to 25° after readings were taken at five-degree intervals. If the second readings at 25° agreed to within 0.1 mv. with the initial observations, the measurements were continued at other temperatures (*e. g.* 25–50°), and finally rechecked at 25°. Only those results were accepted when the initial, second and final readings at 25° agreed within 0.1 mv.

The time required for the cells to attain equilibrium varied somewhat for different solvent mixtures and electrolyte concentrations. As an illustration, roughly typical of most of the observations, we cite the cell in 45% dioxane–water at $m = 0.012070$. After equilibrium was established overnight at 0°, it took two hours to attain equilibrium at 5°, one hour at 20°, thirty minutes at 30° and ten minutes at 50°.

The electromotive forces were corrected to one atmosphere hydrogen pressure by employing vapor pressures of the dioxane–water mixtures interpolated from the data of Hovorka, Schaefer and Dreisbach.[6]

Results

Since the cells containing a solution of a given composition were measured at eleven temperatures, a table of all the original data is too voluminous for presentation. In its place, we have expressed the results by the quadratic equation

$$E = E_{25} + a(t - 25) + b(t - 25)^2 \qquad (1)$$

Table I contains the constants of this equation derived by the method of least squares. In the fifth column the maximum deviations in millivolts, Δ_M, between the observed results and those calculated by equation (1) are given. In the sixth column, Δ_A represents the average deviations. In the last column the temperature ranges over which results were obtained are given.

TABLE I

CONSTANTS OF EQUATION (1)

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

$m = m_1 = m_2 = m_3$; X = % dioxane by weight

m	E_{25}	$a \times 10^4$	$-b \times 10^7$	Δ_M	Δ_A	Range, °C.
			$X = 20$			
0.005054	0.58697	5.785	5.4	0.06	0.03	0–50
.007231	.57751	5.436	5.8	.04	.01	0–50
.010220	.56848	5.166	5.9	.03	.02	0–50
.01174	.56489	5.048	6.4	.10	.05	0–50
.02945	.54098	4.224	5.8	.05	.02	0–50
.06343	.52114	3.520	5.4	.07	.03	0–50
.09406	.51098	3.140	5.9	.04	.02	0–50
			$X = 45$			
.008662	.58675	4.330	2.9	.15	.08	0–50
.01207	.57812	4.100	2.9	.05	.03	0–50
.01618	.57053	3.852	4.1	.05	.03	25–40
.01661	.56986	3.780	4.4	.05	.03	0–50
.02532	.55893	3.420	4.0	.07	.03	0–50
.02804	.55630	3.340	5.3	.10	.07	25–50
.04678	.54317	2.800	5.1	.06	.03	0–50
.05846	.53730	2.586	5.0	.07	.04	25–50
.06293	.53509	2.580	4.8	.11	.06	0–50
.07209	.53161	2.480	5.3	.06	.04	0–50
.08482	.52742	2.320	7.8	.05	.03	0–50
			$X = 70$			
.01402	.58800	2.06	3.5	.20	.09	25–50
.02051	.57795	1.74	4.9	.16	.08	25–50
.02211	.57597	1.64	4.3	.09	.04	0–50
.03616	.56273	1.21	5.4	.13	.12	25–50
.04837	.55477	0.94	6.1	.06	.06	0–50
.05510	.55116	.82	6.1	.10	.08	0–50
.06013	.54881	.74	6.2	.04	.04	25–50
			$X = 82$			
.01080	.59455	1.34	7.1	.25	.15	0–50
.01704	.58222	0.94	7.8	.20	.08	0–50
.03001	.56652	.54	11.0	.10	.05	0–50
.04068	.55782	.22	16.0	.15	.06	0–25

Ionization Constants.—The equation for the electromotive force, E, of the cell may be written

$$\frac{F}{2.303\,RT}(E - E_0') + \log \frac{m_{\mathrm{HF}} m_{\mathrm{Cl}}}{m_{\mathrm{F}}} = -\log K - \log \frac{\gamma_{\mathrm{Cl}} \gamma_{\mathrm{HF}}}{\gamma_{\mathrm{F}}} = -\log K' \qquad (2)^7$$

where E_0' is its standard potential in a given solvent, K, the ionization constant of formic acid, and γ and m are the activity coefficients and molalities of the species designated by the subscripts. In order to evaluate K, the left side of the equation, $-\log K'$, was computed from the observed molalities, the observed electromotive forces, and the values of E_0', and then plotted against the ionic strength, μ. Its value at $\mu = 0$ is $-\log K$. Since K is of the order of 10^{-4} to 10^{-5} in the 20 and 45% dioxane–water mixtures, it is necessary to evaluate $m_{\mathrm{HF}} = m - m_{\mathrm{H}}$ and $m_{\mathrm{F}} = m + m_{\mathrm{H}}$ by arithmetical approximation. A preliminary extrapolation was made by assuming m_{H} to be negligibly small. From the value of K thus obtained, m_{H} was computed from the thermodynamic equation for the equilibrium

---

[5] Harned and Morrison, *Am. J. Sci.*, **33**, 162 (1937); THIS JOURNAL, **58**, 1908 (1936).

[6] Hovorka, Schaefer and Dreisbach, *ibid.*, **58**, 2264 (1936).

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

$$K = \frac{\gamma_H\gamma_F}{\gamma_{HF}} \cdot \frac{m_H m_F}{m_{HF}} \qquad (3)$$

The term $\gamma_H\gamma_F/\gamma_{HF}$ was assumed to equal $\gamma_H\gamma_{Cl} = \gamma^2$ for hydrochloric acid in the same solvent and at the same ionic strength. The ratio m_{HF}/m_F was then corrected by employing these values of m_H and a second extrapolation made. This process was repeated until all equations were satisfied. The values of E_0' employed in these calculations were derived from the equations of Harned, Morrison, Walker, Donelson and Calmon.[8]

A typical extrapolation of the results in 20% dioxane at 25° is shown in Fig. 1. Here, all the observed results are plotted on a large scale. We note that the maximum spread of the points corresponds to only 0.2 mv. Very nearly the same value of $-\log K$ may be obtained from the mean electromotive forces given in Table I. The dashed line is the average plot obtained when m_{HF} and m_F are not corrected for the hydrogen ion molality but assumed to equal the stoichiometrical concentration, m. The importance of this correction is obvious for this case where $K = 10^{-4}$. In the 70 and 82% mixtures in which $K = 10^{-7}$ to 10^{-9}, the correction may be neglected. In general, the results are less accurate in the media of increasing dioxane content.

The values of the ionization constants are given in Table II. For completeness we have included the results obtained in water by Harned and Embree.[9]

TABLE II

OBSERVED IONIZATION CONSTANTS

t, °C.	$X = 0^9$ $K \times 10^4$	$X = 20$ $K \times 10^5$	$X = 45$ $K \times 10^6$	$X = 70$ $K \times 10^8$	$X = 82$ $K \times 10^9$
0	1.638	6.402	8.702	11.077	...
5	1.691	6.548	8.702	10.876	1.883
10	1.728	6.625	8.614	10.641	1.836
15	1.749	6.656	8.488	10.347	1.774
20	1.765	6.651	8.318	10.005	1.690
25	1.772	6.605	8.099	9.634	1.588
30	1.768	6.519	7.834	9.213	1.472
35	1.747	6.394	7.537	8.778	1.339
40	1.716	6.243	7.212	8.310	1.208
45	1.685	6.077	6.867	7.842	1.079
50	1.650	5.876	6.510	7.359	...

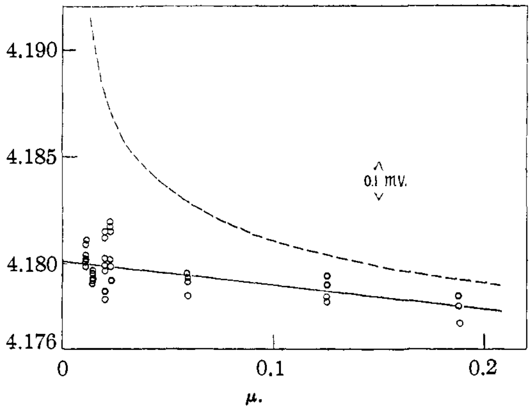

Fig. 1.—Extrapolation in 20% dioxane–water mixtures. Diameter of circles equals 0.015 mv. Dashed line represents $-\log K'$ when correction for m_H is neglected.

Calculation of Ionization Constants and Derived Thermodynamic Functions.—For the computation of the thermodynamic functions, we have employed the equation

$$\log K = -\frac{A^*}{T} + B^* - C^*T \qquad (4)$$

suggested by Harned and Robinson,[10] consistent with the quadratic variation of the electromotive force, to express the variation of the ionization constant with temperature. From this equation, it follows that the free energy, ΔF^0, heat content, ΔH^0, heat capacity, ΔC_p^0, and entropy, ΔS^0, of ionization are given by

$$\Delta F^0 = A' - D'T + C'T^2 \qquad (5)$$

$$\Delta H^0 = A' - C'T^2 \qquad (6)$$

$$\Delta C_p^0 = -2C'T \qquad (7)$$

$$\Delta S^0 = D' - 2C'T \qquad (8)$$

where

$$\left.\begin{aligned} A' &= 2.303RA^* \\ D' &= 2.303RD^* \\ C' &= 2.303RC^* \end{aligned}\right\} \qquad (9)$$

The maximum value of the ionization constant and the temperature at which the ionization constant is a maximum are given by

$$\begin{aligned} \log K_\Theta &= D^* - 2\sqrt{C^*A^*} \\ T_\Theta &= \sqrt{A^*/C^*} \end{aligned} \qquad (10)$$

Values of the empirical constants of these equations, derived by the method of least squares from the values of K in Table II, are given in Table III. T_Θ and $-\log K_\Theta$ are also given in the final columns of this table.

For the 20, 45 and 70% solutions, equation (4) represents the experimental results with an average accuracy of 0.0004 in $\log K$ and with a maximum deviation of 0.0007. For the 82% mixtures these deviations are about 0.001 and 0.002, respectively.

Critique of Accuracy.—In all media, the reproducibility of the cells was of the order of 0.1 mv. or better. Agreement was best in the middle temperature range and worst at low temperatures.

---

[8] Harned, Morrison, Walker, Donelson and Calmon, THIS JOURNAL, **61**, 49(1939).

[9] Harned and Embree, *ibid.*, **56**, 1042 (1934).

[10] Harned and Robinson, *Trans. Faraday Soc.*, **36**, 973 (1940).

TABLE III

CONSTANTS OF EQUATIONS (4) TO (10)

X	A^*	D^*	C^*	A'	D'	C'	T_Θ	$-\log K_\Theta$
0	1342.85	5.2743	0.015168	6143.59	24.1301	0.069395	297.5	3.7519
20	1339.04	5.0628	.015983	6126.17	23.1626	.072917	289.8	4.1766
45	1333.79	4.6393	.017634	6102.16	21.2248	.080676	275.0	5.0602
70	1181.65	1.9920	.016922	5406.09	9.1135	.077419	264.2	6.9513
82	3006.85	13.2110	.040005	13755.07	60.4408	.18302	274.1	8.7232

In extrapolations, greater weight was given to the results which agreed and which recovered their 25° values most closely.

The fact that none of the plots used for extrapolation showed any curvature is an excellent confirmation of the reliability of the method employed for extrapolation.

The most important source of error in determining the absolute values of the ionization constant lies in the uncertainty of the standard potentials, E_0', particularly in the solutions containing 70 and 82% dioxane. The maximum error in the composition of the stock buffer solution, estimated to be 0.05%, corresponds to 0.01 mv. and need not be considered. Errors caused by diluting this buffer are even less. Errors in extrapolation due to the scattering of points differ for each solvent medium and will now be discussed separately.

(1) In the 20% dioxane solutions the best results were obtained. At 25°, the average distance of the mean values of the electromotive force from the line drawn was 0.0002 in log K which is slightly more than 0.01 mv. This average for all eleven temperatures is 0.0005 in log K corresponding to 0.03 mv. Uncertainty in E_0' is about 0.05 mv., or 0.0008 in log K. The sum of these errors is of the order of 0.0015 in log K or 0.35% in the absolute value of K.

(2) In the 45% dioxane solutions, the average deviation from the extrapolation plots was 0.0008 in log K or about 0.05 mv. Uncertainty in E_0' is 0.1 mv. or about 0.0017 log K unit. The gross error in the determination of log K is 0.0025, or about 0.6% in K.

(3) In the 70% solution, the average deviation from the extrapolation line is 0.0008 log K unit. Assuming the error in E_0' to be 0.25 mv., the gross error in the absolute value of K will be 1.3%.

(4) In the 82% mixtures, the average value of the deviations is 0.0013 in log K. In this case E_0' may be in error by a few millivolts[11] and the error in K may be of the order of 10%. At present, a more accurate estimate of the accuracy is not possible.

Since the values of E_0' in the 82% dioxane mixtures are so uncertain, we shall make no estimate of the accuracy with which the thermodynamic functions may be derived. The uncertainty in ΔF^0 in the 20, 45 and 70% dioxane solutions, is found to be 2, 3.5 and 8 cal., respectively. Owing to the difficulty of determining a quantity by differentiation, the values of ΔH^0 are subject to large errors. Assuming that these errors are not greater than 100 cal., ΔS^0 is known to within 0.3 cal. The error in ΔC_p^0 is estimated to be 3 cal.

Summary

1. From the electromotive forces of suitable cells, the ionization constant of formic acid in 20, 45, 70 and 82% dioxane–water mixtures has been determined from 0 to 50°.

2. The variation of the ionization constant with temperature has been expressed by the equation

$$\log K = -\frac{A^*}{T} + B^* - C^*T$$

where A^*, B^*, and C^* are empirical constants. This equation fits the observed values to within the experimental error.

3. Equations for the calculation of the free energy, heat content, entropy and heat capacity of the ionization process are given.

4. The sources of errors in the results and method have been critically examined, and estimates made of the accuracy of the determinations of the ionization constant and the other thermodynamic functions.

NEW HAVEN, CONNECTICUT RECEIVED JULY 17, 1941

---

[11] Harned and Calmon, THIS JOURNAL, **61**, 44 (1939).