[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Thermodynamics of Hydrochloric Acid in Dioxane–Water Mixtures from Electromotive Force Measurements. IX. Properties of the 82% Dioxane Mixtures

BY HERBERT S. HARNED AND FLETCHER WALKER[1]

Harned, Walker and Calmon[2] have reported the electromotive forces of the cells

$$H_2 \mid HCl(m), \text{dioxane}(X), H_2O(Y) \mid AgCl\text{–}Ag$$

in 82% by weight dioxane mixtures at acid concentrations from 0.001–0.01 *M*, inclusive, and at 5° intervals from 5 to 45°. From these, the standard electrode potentials were evaluated. These measurements have been extended to cover the acid concentration range of 0.001 to 0.5 *M*. From the results, the activity coefficient, relative partial molal heat content, and heat capacity have been computed. It is of interest to note that the dielectric constant of this composition of dioxane–water is approximately 10, and that the present measurements represent the only study of this kind in a medium of as low a dielectric constant.

Experimental Results

The results have been expressed by means of the quadratic equation

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

TABLE I

ELECTROMOTIVE FORCE DATA. CONSTANTS OF EQUATIONS (1) AND (2)

m	E_{25}	$-a \times 10^4$	$-b \times 10^6$	$\Delta_{max.}$	$\Delta_{av.}$
0.001	0.36094	8.03	5.54	0.06	0.05
.0015	.34682	8.34	5.23	.13	.05
.002	.33731	8.60	4.80	.09	.04
.003	.32472	9.02	4.19	.14	.08
.005	.30913	9.43	3.45	.08	.05
.007	.29896	9.63	2.90	.14	.06
.01	.28844	9.85	2.80	.13	.04
.015	.27650	10.07	2.40	.10	.05
.02	.26802	10.18	2.35	.04	.02
.03	.25608	10.40	2.31	.12	.05
.05	.24060	10.73	2.29	.24	.08
.07	.23099	11.00	1.96	.10	.06
.1	.21870	11.14	1.85	.09	.04
.15	.20430	11.40	1.80	.19	.11
.2	.19307	11.55	1.65	.18	.07
.3	.17535	11.70	1.30	.09	.03
.5	.14792	11.71	0.65	.12	.09
	$E'_{0(25)}$	$-a_0 \times 10^4$	$-b_0 \times 10^6$		
0 (a_2 = 1)	−0.0413	23.70	8.80	0.3	0.14

(1) This communication contains material from a dissertation presented by Fletcher Walker to the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1936.

(2) Harned, Walker and Calmon, THIS JOURNAL, **60**, 44 (1938).

the constants of which are given in Table I. The last two columns contain the maximum deviations and average deviations in millivolts between the observed results and those computed by equation (1). In the last row of the table are given the constants of the equation for the standard potentials of the cells, namely

$$E'_0 = E'_{0(25)} + a_0(t - 25) + b_0(t - 25)^2 \qquad (2)$$

as derived by Harned, Calmon and Walker.[2] These equations are valid over the temperature range of 5 to 45°.

Activity Coefficient

The values of the activity coefficient, γ, given in Table II, were computed by the equation of the cell

$$-\log \gamma = \frac{E - E'_0}{2k} + \log m \qquad (3)$$

where k equals 2.3026 RT/NF.

TABLE II

ACTIVITY COEFFICIENTS[a]

m	t...5°	15°	25°	35°	45°
0.001	0.4242	0.4129	0.3979	0.3795	0.3592
.0015	.3725	.3627	.3488	.3318	.3129
.002	.3369	.3277	.3147	.2990	.2810
.003	.2862	.2781	.2682	.2553	.2378
.005	.2319	.2267	.2181	.2062	.1916
.007	.2019	.1977	.1900	.1791	.1654
.01	.1744	.1707	.1629	.1529	.1412
.015	.1472	.1440	.1371	.1282	.1176
.02	.1311	.1274	.1213	.1131	.1035
.03	.1112	.1076	.1020	.0946	.0869
.05	.0912	.0876	.0826	.0766	.0698
.07	.0780	.0756	.0713	.0659	.0596
.1	.0701	.0675	.0634	.0582	.0525
.15	.0627	.0597	.0560	.0513	.0460
.2	.0589	.0560	.0521	.0476	.0425
.3	.0563	.0532	.0490	.0443	.0392
.5	.0595	.0554	.0504	.0445	.0386

[a] Calculated from observed electromotive forces, not those calculated by Eq. 1.

It is important to note that these values were computed from standard potentials which may be in error to the extent of a millivolt or more. On the other hand, the actual electromotive forces are known to within ±0.2 mv., and consequently values of γ relative to any of the concentrations at which measurements were made possess a high accuracy (~ 0.2%).

Relative Partial Molal Heat Content and Heat Capacity.—Values of the relative partial molal heat content, $\overline{L}_2$, computed from the data in Table I, have been expressed by the equation

$$\overline{L}_2 = \alpha + \beta T^2 \quad (4)$$

α and β are related to the constants in Table I by the expressions

$$\alpha = -23{,}074[(E_{25} - E'_{0(25)}) - 298.1(a - a_0) + 88{,}864(b - b_0)] \quad (5)$$

$$\beta = 23{,}074[b - b_0] \quad (6)$$

respectively.[3] $\overline{L}_2$ is in calories. α and β were smoothed by a graphical method. The fourth and fifth columns of the table contain the values obtained for $\overline{L}_2$ and $(\overline{C}_p - \overline{C}_p)$ at 25°.

TABLE III

PARAMETERS OF EQUATIONS (4) AND (7)

$\overline{L}_2$ and $(\overline{C}_p - \overline{C}_{p_0})$ at 25°

m	$-\alpha$	β	$\overline{L}_{2(25)}$	$(\overline{C}_p - \overline{C}_{p_0})_{25}$
0.001	5190	0.0752	1493	44.8
.0015	5710	.0824	1612	49.1
.002	6550	.0930	1714	55.4
.003	7800	.1082	1815	64.5
.005	9240	.1258	1939	75.0
.007	10100	.1364	2021	81.3
.01	10500	.1418	2101	84.5
.015	10860	.1468	2185	87.5
.02	11000	.1488	2223	88.7
.03	11120	.1510	2298	90.0
.05	11240	.1538	2427	91.7
.07	11360	.1560	2503	93.0
0.1	11480	0.1589	2640	94.7
.15	11630	.1624	2802	96.8
.2	11860	.1666	2945	99.3
.3	12200	.1742	3280	103.9
.5	12830	.1880	3876	112 1

(3) Harned and Thomas, THIS JOURNAL, **58**, 761 (1936); Harned and Donelson, *ibid.*, **60**, 339 (1938).

Summary

1. Measurements of the electromotive forces of the cells

H_2 | HCl(m), dioxane(X), H_2O(Y) | AgCl–Ag

have been reported in 82% dioxane mixtures which possess a dielectric constant of approximately 10. The measurements cover an acid concentration range 0.001 to 0.5 M, and were obtained at 5° intervals from 5 to 45°. Their accuracy is of the order of ±0.2 mv.

2. From these results and the standard potentials previously evaluated,[2] the activity coefficient, relative partial molal heat content and heat capacity have been evaluated. These results have an accuracy relative to a concentration where the electromotive force was measured comparable to that obtained with mixtures of higher dielectric constant. The greatest uncertainty lies in the estimation of the standard potentials. The extent of the error involved in the required extrapolation cannot be estimated accurately from our present knowledge A general summary and critique of the thermodynamics of all these mixtures will be given in another communication.

NEW HAVEN, CONN. RECEIVED SEPTEMBER 13, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Thermodynamics of Hydrochloric Acid in Dioxane-Water Mixtures from Electromotive Force Measurements. X. General Summary and Critique

BY HERBERT S. HARNED, JOHN OWEN MORRISON, FLETCHER WALKER, JOHN G. DONELSON AND CALVIN CALMON

Our earlier contributions[1–12] to this series contain the measurements of the electromotive forces of the cells

H_2 | HCl(m), dioxane(X), H_2O(Y) | AgCl–Ag

containing solvent mixtures of 20, 45, 70 and 82% dioxane, which correspond roughly to values of the solvent dielectric constant of 60, 40, 20 and 10, respectively. The measurements were carried out over as wide ranges of concentration of acid as was found practical and at 5° temperature intervals from 0 to 50°. All these results possess an accuracy comparable to that obtainable in aqueous solutions. In the previous communications, detailed descriptions of the technique,[1,2] methods of extrapolation,[2,4,7,9] and methods of computing the thermodynamic properties[5,6,8,10] have been reported. In addition, the dielectric constant of

(1) *Am. J. Sci.*, **33**, 161 (1937).
(2) THIS JOURNAL, **58**, 1908 (1936).
(3) **60**, 334 (1938).
(4) **60**, 336 (1938).
(5) **60**, 339 (1938).
(6) **60**, 2128 (1938).
(7) **60**, 2130 (1938).
(8) **60**, 2133 (1938).
(9) **61**, 44 (1939).
(10) **61**, 48 (1939).
(11) Åkerlöf and Short, *ibid.*, **58**, 1241 (1936).
(12) Owen and Waters, *ibid.*, **60**, 2371 (1938).