solvent upon the rate constants is in fair agreement with the Scatchard–Christiansen theory.

4. Empirically it is shown that for this reaction in methanol–water mixtures of constant dielectric constant the following relation holds

$$\left(\frac{\Delta k_0}{\Delta T}\right)_D = -\left(\frac{\Delta k_0}{\Delta D}\right)_T$$

5. The influence of ionic strength upon the observed critical increments at zero ionic strength is in good agreement with equations previously derived. It is observed that the critical increment decreases with decreasing dielectric constant in media of constant dielectric constant.

BUFFALO, N. Y. RECEIVED OCTOBER 8, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Thermodynamics of Hydrochloric Acid in Dioxane–Water Mixtures from Electromotive Force Measurements. II. Density Data

BY HERBERT S. HARNED AND CALVIN CALMON

As a part of the general investigation of the thermodynamics of hydrochloric acid in dioxane-water mixtures, it is necessary to know the concentration of the electrolyte, c, in moles per liter of solution. Extensive measurements of cells suitable for studying the properties of hydrochloric acid in these solutions have been made in this Laboratory and, for practical reasons, the concentrations of the acid have been expressed in molalities, m. Since c is related to m by the equation

$$c/m = 1000d/(1000 + mM) \qquad (1)$$

where d is the density and M the molecular weight of the solute, density determinations of the solutions are required. This communication contains the result of density determinations of 20, 45, 70 and 82% dioxane in water solutions covering a range in temperature from 0 to 50° and ranges of concentration from 0 to 3 M hydrochloric acid for the first two mixtures, from 0 to 1.5 M for the third, and from 0 to 0.7 M in the case of the fourth mixture, respectively.

Experimental Measurements and Density Data

The materials were purified and the solutions were prepared according to the directions given by Harned and Morrison.[1] For the determinations of the 20, 45 and 70% solutions, both pycnometers and dilatometers were employed. The density of each solution was determined at 25° by pycnometers of about 30-cc. capacity, and the densities of the solutions at other temperatures were computed from volume changes measured by dilatometers. The volumes of the dilatometers were about 110 cc. and the capillaries were 3 mm. in diameter and one meter in length. The volumes of the dilatometers were determined by means of conductivity water. The temperature control was better than ±0.02°. The thermometers used were calibrated against a standard resistance thermometer.

In the case of the 82% dioxane solutions, only the dilatometers were used. The pure solvent was used to standardize the apparatus. The densities of the pure solvent, d_0, necessary for this purpose were obtained from the data of Hovorka, Schaefer, and Dreisbach[2] by plotting the isothermal values against mole fraction of dioxane. From these curves, d_0 was obtained at 10° intervals from 10 to 60°. By means of Newton's extrapolation formula values of d_0 were obtained at 5° intervals from 5 to 45°.

By these means, density measurements were obtained at molalities 0.1, 0.2, 0.3, 0.5, 0.7, 1, 1.5, 2 and 3 M in the cases of the 20 and 45% dioxane mixtures, at 0.1, 0.2, 0.3, 0.5, 0.7, 1 and 1.5 M for the 70% mixtures, and at 0.002, 0.003, 0.005, 0.007, 0.015, 0.02, 0.03, 0.05, 0.07, 0.1, 0.3, 0.5 and 0.7 M in the case of the 82% dioxane mixtures.

Since the results were so voluminous, they have been expressed by equations which give the densities, d, at each temperature as a function of the molality of the acid. It was found that a linear equation was not sufficient to represent the results to within ±0.03% except in one case, nor were quadratic equations adequate. The best simple representation of the results is given by the equation

$$d = d_0 + am - bm^3 + em \log m \qquad (2)$$

where d_0 is the density of solvent, and a, b, e are

---

(1) Harned and Morrison, THIS JOURNAL, **58**, 1908 (1936); *Am. J. Sci.*, **33**, 161 (1937).

(2) Hovorka, Schaefer and Dreisbach, *ibid.*, **58**, 2264 (1936).

TABLE I

DENSITIES OF PURE SOLVENTS AND CONSTANTS OF EQUATIONS (2) AND (3)

I. Mixtures containing 20% by weight dioxane

$d = d_0 + am - bm^3 + em \log m$

t,° C.	d_0	a	b	e	Δ_1	A	Δ_2
0	1.0271	0.0133	0.00032	0.008	0.02	0.02159	0.16
5	1.0245	.0142	.00035	.007	.02	.02116	.12
10	1.0219	.0149	.00025	.004	.02	.02077	.09
15	1.0193	.0154	.00005	.000	.02	.02038	.05
20	1.0167	.0160	.00013	...	.02	.02013	.03
25	1.0141	.0161	.00013	...	.01	.01989	.02
30	1.0115	.0167	.00019	...	.02	.01965	.01
35	1.0090	.0168	.00020	...	.01	.01954	.01
40	1.0063	.0168	.00018	...	.02	.01933	.01
45	1.0038	.0166	.00015	...	.02	.01922	.02
50	1.0014	.0164	.00014	...	.01	.01933	.02

II. Mixtures containing 45% dioxane

$d = d_0 + am - bm^3$

t,° C.	d_0	a	b	Δ_1	A	Δ_2
0	1.0484	....	.....	..	(0.02267)[a]	0.07
5	1.0450	0.0143	0.00005	0.01	.02223	.05
10	1.0419	.0145	.00008	.01	.02209	.05
15	1.0386	.0144	.00002	.01	.02171	.07
20	1.0353	.0147	.00004	.01	.02148	.06
25	1.0319	.0150	.00010	.01	.02138	.04
30	1.0282	.0153	.00011	.01	.02109	.03
35	1.0246	.0156	.00012	.01	.02072	.02
40	1.0210	.0157	.00012	.01	.02052	.01
45	1.0175	.0160	.00013	.01	.02021	.02
50	1.0139	.0163	.00016	.01	.01995	.01

III. Mixtures containing 70% dioxane

$d = d_0 + am + em \log m$

t,° C.		a	e	Δ_1	A	Δ_2
0	1.0619	....	....	..	(0.02559)[a]	..
5	1.0570	0.0123	0.0085	0.03	.02489	0.13
10	1.0522	.0128	.0080	.03	.02420	.12
15	1.0474	.0135	.0060	.02	.02352	.11
20	1.0426	.0142	.0040	.02	.02275	.07
25	1.0378	.0150	.0020	.02	.02200	.05
30	1.0332	.0155	.0015	.01	.02128	.05
35	1.0285	.0159	.0000	.01	.02077	.02
40	1.0239	.0165	....	.01	.01998	.02
45	1.0194	.0167	....	.01	.01968	.02
50	1.0148	.0169	....	.01	.01926	.02

IV. Mixtures containing 82% dioxane

$d = d_0 + am$

t	d_0	a	Δ_1	A	Δ_2
5	1.0540	0.0152	0.01	0.0224	0.01
10	1.0488	.0159	.02	.0220	.02
15	1.0436	.0165	.02	.0212	.02
20	1.0387	.0165	.01	.0210	.01
25	1.0338	.0166	.01	.0210	.01
30	1.0288	.0165	.01	.0206	.01
35	1.0236	.0173	.01	.0198	.01
40	1.0183	.0178	.01	.0198	.02
45	1.0130	.0183	.03	.0178	.05

[a] Extrapolated.

isothermal constants. In some cases, *b* or *e*, or both *b* and *e* equalled zero.

The equation and constants used in each of the dioxane mixtures are given in Table I. Δ_1, the average deviation of the calculated from observed values in per cent. is given at each temperature. A maximum deviation of ±0.05% occurred in a very few cases.

In order to compute *c* from *m*, the simple and approximate equation

$$c/m = d_0 - Am \qquad (3)$$

may be employed. Values of the isothermal constant *A* are given in Table I. In the last column Δ_2, the average deviation in per cent. of the observed values of c/m from the calculated ones, are given. It is clear that in most cases this equation represents the results to within 0.1%.

Summary

The densities of solutions of hydrochloric acid in dioxane-water mixtures containing 20, 45, 70 and 82% dioxane have been determined from 0 to 50° at 5° intervals. The results have been represented by convenient equations. An equation is given with suitable constants which permits the calculation of normal from molal concentrations with comparative ease.

NEW HAVEN, CONN. RECEIVED NOVEMBER 9, 1937