density at 20°, also $C = 12936 - 8734n$ when C is the same as above but n is the refractive index for the D line at 20°.

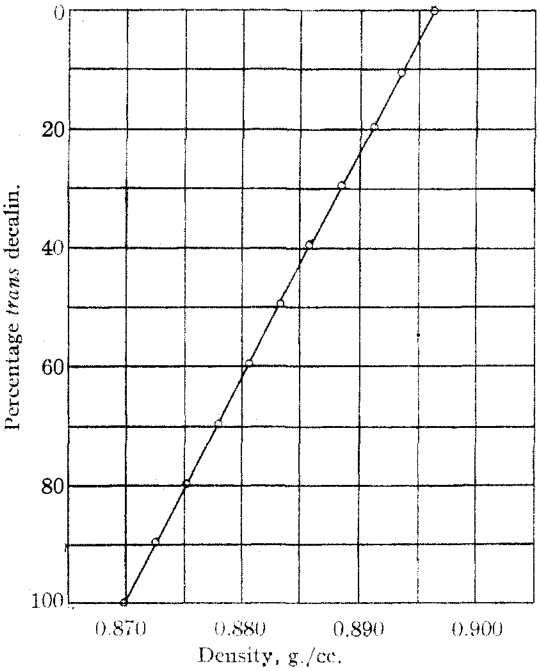

Fig. 6.

Attempts were made to determine the freezing points of the various mixtures by placing them in partially filled bulbs of about 20 cc. capacity. Because of the great amount of supercooling necessary and the low heat conduction of the hydrocarbons the results were only of qualitative significance. They indicated that the eutectic temperature lies between −60 and −70°.

A summary of the physical constants of the *cis* and *trans* forms of decahydronaphthalene is given in the following table.

TABLE III

	d^{20}_4	n^{20}_D	F. p., °C.	B. p. (760 mm.), °C.
cis form	0.8963	1.48113	− 43.26 ± 0.04	194.6
"Int. Crit. Tables"	.898			
Hückel[2]	.8952		− 51	
trans form	.8699	1.46968	− 31.47 ± 0.04	185.5
"Int. Crit. Tables"	.872	1.4701	−125	
Hückel[2]	.8695	1.46958	− 36	

Summary

1. Pure forms of *cis* and *trans* decahydronaphthalene have been prepared and some of their physical properties measured.
2. The freezing points were found to be higher than those so far recorded.
3. The densities and refractive indices of nine mixtures of the two forms were measured and it was shown that both these properties were linear functions of the compositions.

VANCOUVER, B. C. RECEIVED MAY 18, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Thermodynamics of Hydrochloric Acid in Dioxane-Water Mixtures from Electromotive Force Measurements. V. Properties of the 45% Dioxane Mixtures

BY HERBERT S. HARNED AND JOHN G. DONELSON

Measurements of the electromotive forces of the cells

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

in 45% dioxane–water mixtures and at acid concentrations varying from 0.003 to 0.1 M have been reported by Harned and Morrison.[1] These measurements have been extended so as to include concentrations from 0.003 to 3 M. From these results and the standard potential of the cell,[2] the activity coefficient, relative partial molal heat content and specific heat have been computed. Similar results have been obtained by Harned and Ehlers[3] in water and by us[4] in 20% dioxane–water mixtures which in conjunction with present results yield an accurate and very comprehensive study of the thermodynamics of this acid in media of dielectric constants of approximately 80, 60, and 40.

Experimental Results

No further changes in the technique described by Harned and Morrison[5,1] and modified in a few details by us[4] have been made. The present results were obtained with the same care and

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(1) Harned and Morrison, THIS JOURNAL, **58**, 1908 (1936).

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

(3) Harned and Ehlers, *ibid.*, **55**, 2179 (1933).

(4) Harned and Donelson, *ibid.*, **60**, 339 (1938).

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

accuracy as in the earlier investigations. The cell reproducibility at all concentrations was ±0.05 mv.

Six cells were measured at each concentration, all of which were equilibrated and measured at 25°. Three of these were measured at 5° intervals up to 50° and then brought back to 25°. The other three were measured at 5° intervals until 0° was reached and finally brought back to 25°. All results were finally accepted if and only if all the 25° readings at a given concentration checked to within ±0.05 mv.

The results at eleven temperatures were found to conform to the quadratic equation

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

The constants, a and b, obtained by the method of least squares, and the values of the electromotive forces at 25°, are given in Table I. The fifth column contains the maximum deviations in millivolts between the observed values and those calculated by equation (1). The last column contains the average deviation.

TABLE I

CONSTANTS OF EQUATION (1)

X = 45% by weight of dioxane

m	E_{25}	$-a \times 10^4$	$-b \times 10^6$	Δ(max.)	Δ(max.)
0.10943	0.30896	5.185	2.90	0.05	0.02
.19378	.28371	5.882	2.84	.05	.02
.32247	.26014	6.596	2.72	.05	.03
.52079	.23645	7.065	2.50	.06	.03
.6467	.22500	7.477	2.34	.07	.04
1.0305	.19760	7.892	2.24	.11	.04
1.5496	.16917	8.274	2.28	.07	.04
2.0546	.14575	8.567	2.14	.08	.04
3.1105	.10209	8.850	1.80	.10	.04

Combined with the data of Harned and Morrison[1] suitable observations were available at eighteen concentrations between 0.003 and 3 M. These results were smoothed to round concentrations from suitable large scale plots. The values of a and b also were smoothed and the final values of all these quantities which subsequently were used for the computations are contained in Table II.

In the last row of the table are given the constants of the equation

$$E_0' = E_{0(25)}' + a_0(t - 25) + b_0(t - 25)^2 \qquad (2)$$

in which E_0' is the standard potential at a temperature t, $E_{0(25)}'$ the standard potential at 25°, and a_0 and b_0 empirical constants. These values were obtained from the standard potentials computed by Harned[2] by use of the Gronwall, La Mer, and Sandved extension of the Debye and Hückel theory. The values of $E_{0(25)}'$ and b_0 differ slightly from those obtained by Harned.

TABLE II

ELECTROMOTIVE FORCES AT ROUND CONCENTRATIONS. CONSTANTS OF EQUATION (1)

m	E_{25}	$-a \times 10^4$	$-b \times 10^6$
0.003	0.47082	0.78	3.30
.005	.44670	1.38	3.24
.007	.43108	1.80	3.20
.01	.41470	2.23	3.17
.02	.38343	3.10	3.09
.03	.36549	3.61	3.05
.05	.34316	4.23	2.99
.07	.32848	4.65	2.95
.1	.31290	5.08	2.91
.2	.28236	5.90	2.80
.3	.26358	6.40	2.71
.5	.23855	7.03	2.52
.7	.22061	7.46	2.34
1	.19951	7.91	2.12
1.5	.17162	8.44	1.84
2	.14811	8.82	1.62
3	.10711	9.38	1.29
	$E_{0(25)}'$	$-a_0 \times 10^4$	$-b_0 \times 10^6$
0 (a = 1)	0.16352	11.35	3.70

Activity Coefficients

Values of the activity coefficients γ, computed by means of the equation of the cell

$$-\log \gamma = \frac{(E - E_0')\,F}{4.6052\,RT} + \log m \qquad (3)$$

are given in Table III. Values of the dielectric constant of the solvent[6] at the designated temperatures are given in the last row of the table. Judging from the errors involved in the experiments and the extrapolation, it is estimated that these results possess an accuracy of ±0.001.

TABLE III

ACTIVITY COEFFICIENTS

m	0°	10°	20°	25°	30°	40°	50°
0.003	0.849	0.846	0.844	0.842	0.839	0.834	0.828
.005	.824	.817	.811	.808	.803	.795	.786
.007	.802	.793	.786	.782	.777	.767	.757
.01	.776	.766	.758	.753	.747	.737	.725
.02	.720	.707	.697	.692	.686	.673	.660
.03	.683	.671	.661	.654	.649	.635	.622
.05	.637	.624	.613	.607	.600	.586	.573
.07	.605	.593	.583	.577	.570	.557	.545
.1	.579	.566	.553	.547	.540	.525	.512
.2	.529	.514	.503	.496	.488	.474	.459
.3	.511	.496	.484	.476	.466	.453	.438
.5	.503	.487	.473	.465	.456	.440	.423
.7	.513	.495	.480	.471	.461	.443	.424
1.	.547	.526	.508	.497	.485	.463	.442
1.5	.640	.612	.585	.570	.555	.524	.496
2.	.773	.733	.695	.676	.655	.614	.575
3.	1.191	1.112	1.037	1.001	.962	.887	.818
D	44.3	41.9	39.6	38.5	37.4	35.4	33.4

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(6) Åkerlöf and Short, THIS JOURNAL, **58**, 124 (1936).

TABLE IV

PARAMETERS OF EQUATIONS (4) AND (7). $\overline{L}_2$ AND $(\overline{C}_p - \overline{C}_{p0})$ AT 25°

m	$(-\alpha)$	β	$\overline{L}_{2(25)}$	$(\overline{C}_p - \overline{C}_{p0})_{25}$
0.003	640	0.00923	180	5.5
.005	619	.01061	324	6.3
.007	630	.01154	395	6.9
.01	609	.01223	478	7.3
.02	651	.01408	600	8.4
.03	669	.01500	664	8.9
.05	703	.01638	753	9.8
.07	735	.01730	802	10.2
.1	754	.01823	866	10.9
.2	839	.02077	1007	12.4
.3	934	.02284	1096	13.6
.5	1179	.02723	1241	16.2
.7	1430	.03138	1359	18.7
1	1704	.03646	1536	21.7
1.5	1999	.04292	1815	25.6
2	2169	.04799	2095	28.6
3	2285	.05561	2657	33.1

Relative Partial Molal Heat Content and Heat Capacity.—The heat data have been computed by the method described by Harned and Thomas[7] and mentioned by us.[4] The relative partial molal heat content, $\overline{L}_2$, is expressed by

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

α and β are given by

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

$$\beta = 23{,}074(b - b_0) \qquad (6)$$

respectively. $\overline{L}_2$ is in calories. The relative partial molal heat capacity may be computed by the equation

$$(\overline{C}_p - \overline{C}_{p0}) = 2\beta T \qquad (7)$$

Table IV contains the parameters α and β, from which $\overline{L}_2$ may be computed at all temperatures from 0 to 50° with an accuracy of the order of ±30 cal. by equation (4), and $(\overline{C}_p - \overline{C}_{p0})$ with an accuracy of the order of ±1 cal. by equation (7). Values of $\overline{L}_2$ and $(\overline{C}_p - \overline{C}_{p0})$ at 25° are given in the fourth and fifth columns of the table, respectively.

Summary

1. The electromotive forces of the cells

H_2 | HCl (m), Dioxane (45%), H_2O (55%) | AgCl–Ag

have been measured at 5° intervals from 0 to 50°, and from 0.1 to 3 M acid concentrations with an accuracy of ±0.05 mv.

2. From these and the results of Harned and Morrison in the dilute concentration range (0.003 to 0.1 M) the activity coefficient, the relative partial molal heat content and the heat capacity of the acid have been computed throughout these ranges of temperature and pressure.

NEW HAVEN, CONN.

RECEIVED JUNE 21, 1938

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[7] Harned and Thomas, THIS JOURNAL, **58**, 761 (1936).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Thermodynamics of Hydrochloric Acid in Dioxane–Water Mixtures from Electromotive Force Measurements. VI. Extrapolations in the 70% Dioxane Mixtures and Standard Potentials

BY HERBERT S. HARNED AND CALVIN CALMON[1]

In an earlier communication in this series,[2] it was shown that accurate evaluations of the standard potentials of the cell

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

in mixtures containing 20 and 45% dioxane could be made by employing the Gronwall, La Mer and Sandved extension of the Debye and Hückel theory. At the same time, an extrapolation was made with the results obtained in a mixture of 70% dioxane–30% water at 25°. Since experimental results below 0.003 M were not available, a slight uncertainty in the extrapolation was suspected, and further calculations discontinued for the moment. This communication contains an attempt to obtain results at still lower concentrations, and to determine the lower limit of concentration at which reliable results can be obtained with the technique available.

Experimental Results

The preparation of solutions and the cell technique was carried out with all the precautions and in the same manner as that described by

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[1] This communication contains material from a dissertation presented by Calvin Calmon to the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1938.

[2] Harned, THIS JOURNAL, **60**, 336 (1938).