TABLE III

VALUES OF THE EXTRAPOLATION FUNCTION, $E' - E_{Ex}$ AT 10, 25, 45°

m	t....10°	25°	45°
0.03203	0.08961	0.06372	0.02720
.01927	.08984	.06400	.02746
.009612	.09003	.06399	.02727
.006950	.08972	.06391	.02704
.005188	.08970	.06389	.02708
.003292	.08965	.06393	.02718
.003164	.08970	.06390	.02699
.002366	.08970	.06400	.02709
.001043	(.0900)	(.0634)	(.0265)
.001001	(.0892)	(.0632)	(.0255)
.000815	(.0899)	(.0632)	(.0274)
E_0' (m = 0)	.08970	.06395	.02705

solutions where D equals approximately 20 and where the actual ionization in dilute solutions is high ($\alpha > 0.9$). In media of dielectric constant of 10 (82% dioxane), the second method seems to be more suitable than the one which employs the extended term theory since values of the ionization constant are known, and since the electrolyte is considerably weaker ($K \sim 0.0002$). Also in these solutions values of "a" computed by Bjerrum's theory are more reliable than in those of high dielectric constant.

In Table IV, the standard potentials at all temperatures are given. These results may be expressed by the equation

$$E_0' = 0.06395 - 17.67 \times 10^{-4}(t - 25) - 3.70 \times 10^{-6}(t - 25)^2 \quad (6)$$

The deviations between the observed values and those computed by this equation are given in parentheses immediately following the result. They are in hundredths millivolt and are positive when the calculated is greater than the observed value.

TABLE IV

STANDARD POTENTIAL OF THE CELL

H_2 | HCl (m), DIOXANE (70%), H_2O | AgCl–Ag

t	E_0'	t	E_0'
0	0.10584 (−3)	30	0.05500 (+3)
5	.09784 (−3)	35	.04587 (+4)
10	.08970 (−8)	40	.03661 (+1)
15	.08123 (+2)	45	.02705 (+8)
20	.07267 (+2)	50	.01746 (+1)
25	.06395 (+0)		

Summary

1. Electromotive forces of the cells

H_2 | HCl (m), dioxane (70%), H_2O | AgCl - Ag

have been obtained at 0.0008, 0.001, 0.002 and 0.003 M from 0 to 50° at 5° intervals.

2. From these and Harned and Morrison's results from 0.003 to 0.02 M, the standard potential of the cell has been evaluated.

NEW HAVEN, CONN. RECEIVED JUNE 21, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Thermodynamics of Hydrochloric Acid in Dioxane–Water Mixtures from Electromotive Force Measurements. VII. Properties of the 70% Dioxane Mixtures

BY HERBERT S. HARNED, JOHN G. DONELSON AND CALVIN CALMON

Two earlier communications[1,2] contain electromotive forces of the cells

H_2 | HCl (m), dioxane (70%), H_2O | AgCl–Ag

at fourteen concentrations between 0.0008 and 0.2 M, and at temperatures from 0 to 50°. From these, the standard potentials of the cells have been computed throughout this temperature range.[2] To complete this study, measurements have been made at seven concentrations between 0.1 and 1.5 M. From the combined data, the activity coefficient, the relative partial molal heat content, and heat capacity of the acid have been computed. This completes the first comprehensive study of these properties of an electrolyte in a medium of dielectric constant of approximately 20.

Experimental Results

The results obtained from 0 to 50° at 5° intervals have been expressed by the equation

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

The values of E_{25}, and the constants a and b are given in Table I. The fifth column of the table gives the maximum deviations in millivolts of the observed results from those calculated, and the last column contains the mean deviations.

These data were combined with those of Harned and Morrison[1] and Harned and Calmon[2] and

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

[2] Harned and Calmon, *ibid.*, **60**, 2130 (1938).

TABLE I

CONSTANTS OF EQUATION (1)

m	E_{25}	$-a \times 10^4$	$-b \times 10^6$	$\Delta_{\text{max.}}$	$\Delta_{\text{av.}}$
0.10707	0.25924	8.754	2.28	0.04	0.01
.20852	.23292	9.466	2.12	.05	.02
.31025	.21593	9.798	1.96	.08	.03
.53772	.18864	10.351	1.82	.09	.04
.72377	.17181	10.561	1.62	.10	.06
1.03675	.14754	10.731	1.42	.10	.04
1.55511	.11308	10.778	1.16	.13	.04

smoothed by means of suitable large scale graphs. Values of E_{25}, a, and b, suitable for all subsequent calculations, are given in Table II. At the bottom of the table are given the values of $E_0'_{(25)}$, a_0 and b_0 of the equation for the standard potential E_0', namely

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

TABLE II

CONSTANTS OF EQUATIONS (1) AND (2) AT ROUND CONCENTRATIONS

m	E_{25}	$-a \times 10^4$	$-b \times 10^6$
0.001	0.43716	4.50	3.14
.0015	.42006	4.95	3.02
.002	.40796	5.25	2.92
.003	.39145	5.78	2.85
.005	.37130	6.20	2.71
.007	.35850	6.50	2.65
.01	.34525	6.80	2.60
.02	.32008	7.33	2.48
.03	.30554	7.71	2.42
.05	.28739	8.11	2.33
.07	.27523	8.38	2.28
.1	.26195	8.67	2.22
.2	.23477	9.20	2.09
.3	.21744	9.53	1.98
.5	.19274	9.95	1.80
.7	.17383	10.22	1.64
1	.15010	10.54	1.45
1.50	.11638	10.90	1.19
	$E_0'(25)$	$-a_0 \times 10^4$	$-b_0 \times 10^6$
$0(a = 1)$	0.06395	17.67	3.70

Activity Coefficients

The activity coefficients, computed by the equation

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

are given in Table III at some of the temperatures. The last row contains the dielectric constants of the solvent at these temperatures.

Relative Partial Molal Heat Content and Heat Capacity.—The relative partial molal heat content, $\overline{L}_2$, and heat capacity are given by the equations

$$\overline{L}_2 = \alpha + \beta T^2 \tag{4}$$

$$(\overline{C}_p - \overline{C}_{p0}) = 2\beta T \tag{5}$$

TABLE III

ACTIVITY COEFFICIENTS

m	t....0°	10°	20°	25°	30°	40°	50°
0.001	0.719	0.713	0.705	0.700	0.696	0.686	0.675
.0015	.672	.665	.656	.651	.647	.636	.624
.002	.641	.633	.623	.618	.613	.601	.589
.003	.589	.582	.573	.568	.563	.552	.540
.005	.530	.521	.510	.505	.499	.487	.473
.007	.488	.479	.468	.462	.457	.444	.431
.01	.446	.436	.425	.418	.413	.401	.388
.02	.369	.359	.348	.342	.336	.324	.312
.03	.328	.318	.308	.303	.297	.286	.275
.05	.283	.274	.264	.258	.253	.243	.232
.07	.259	.249	.239	.234	.229	.219	.208
.1	.236	.226	.217	.212	.207	.197	.188
.2	.204	.194	.185	.180	.175	.165	.156
.3	.193	.182	.173	.168	.163	.154	.144
.5	.191	.179	.169	.163	.158	.147	.137
.7	.200	.187	.175	.168	.162	.150	.139
1.0	.227	.211	.195	.187	.179	.165	.151
1.5	.303	.277	.252	.240	.228	.207	.187
D	20.4	19.25	18.2	17.7	17.2	16.3	15.4

where α and β are defined by equations (6) and (7) of Harned and Donelson's communication.[3] These equations have a range of validity from 0 to 50°, inclusive. The parameters α and β are given in Table IV. Values of $\overline{L}_2$ and $(\overline{C}_p - \overline{C}_{p0})$ at 25° are given in the fourth and fifth columns of this table.

TABLE IV

PARAMETERS OF EQUATIONS (4) AND (5), $\overline{L}_2$ AND $(\overline{C}_p - \overline{C}_{p0})$ AT 25°

m	$(-\alpha)$	$(\beta) \times 10^2$	$\overline{L}_{2(25)}$	$(\overline{C}_p - \overline{C}_{p0})_{25}$
0.001	701	1.29	446	7.7
.0015	862	1.57	533	9.4
.002	994	1.80	606	10.7
.003	1121	1.96	621	11.7
.005	1233	2.28	793	13.6
.007	1266	2.42	884	14.4
.01	1270	2.54	987	15.1
.02	1299	2.82	1207	16.8
.03	1348	2.95	1273	17.6
.05	1389	3.16	1419	18.8
.07	1397	3.28	1518	19.6
.1	1413	3.41	1617	20.3
.2	1417	3.71	1880	22.1
.3	1477	3.97	2051	23.7
.5	1558	4.38	2334	26.1
.7	1635	4.75	2586	28.3
1.0	1697	5.19	2915	30.9
1.5	1700	5.79	3445	34.5

Summary

1. Electromotive forces of the cells

$$\text{H}_2 \mid \text{HCl}\,(m),\ \text{dioxane}\,(70\%),\ \text{H}_2\text{O} \mid \text{AgCl-Ag}$$

have been obtained from 0 to 50° at 5° intervals and at seven concentrations between 0.1 and 1.5 M.

2. These in combination with previous results through a concentration range of 0.0008

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[3] Harned and Donelson, THIS JOURNAL, **60**, 339 (1938).

to 0.1 *M* have been employed to compute the activity coefficient, relative partial molal heat content and heat capacity of the acid in this solvent.

3. The accuracy of the experimental results is of the order of ±0.1 mv., leading to an error of about ±0.001 in the relative activity coefficient and ±30 cal. in the relative heat content. A greater source of error in these values may reside in the uncertainty of the extrapolation. A general discussion of these thermodynamics properties will be reserved until the investigation of the 82% dioxane–water mixtures of dielectric constant of approximately 10 is completed.

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[CONTRIBUTION FROM THE DIVISION OF BIOCHEMISTRY, MAYO FOUNDATION, AND THE DEPARTMENT OF PHYSIOLOGY, UNIVERSITY OF MINNESOTA MEDICAL SCHOOL]

The Distribution Coefficients of Porphyrins between Ether and Hydrochloric Acid and Applications to Problems of Quantitative Separation

BY ANCEL KEYS AND JOACHIM BRUGSCH[1]

Differential solubility in various solvents is the basic means of separating porphyrins in mixtures.[2-6] The most useful solvents are ether, chloroform and hydrochloric acid.[7,8] These three reagents have been used to effect separation of biological porphyrins by a procedure involving repeated crystallizations.[9,10] No proof of the quantitative accuracy of this method has been given; in any case it suffers from three limitations: (1) it is very time-consuming; (2) it serves only to isolate the principal porphyrin in the mixture; (3) it is stated that at least 50 micrograms of porphyrin is needed, but the work reported has generally involved much more; these amounts are not always available in biological work.

The porphyrins known or believed to occur in the normal or pathological human metabolism are: protoporphyrin ($C_{32}H_{32}N_4(COOH)_2$), coproporphyrin ($C_{32}H_{34}N_4(COOH)_4$), mesoporphyrin ($C_{32}H_{36}N_4(COOH)_2$) deuteroporphyrin ($C_{28}H_{28}N_4(COOH)_2$), and uroporphyrin ($C_{32}H_{30}N_4(COOH)_8$). All but the last named (uro-) are soluble in ether acidified by glacial acetic acid. Except in extremely rare cases, uroporphyrin occurs naturally only in the most minute amounts. Traces of other unidentified porphyrins have been reported in biological materials but these questionable substances may be neglected for the present.

Most of the natural porphyrins are soluble in chloroform, but repeated trials convinced us that chloroform extraction is not suitable for quantitative separation of porphyrins from natural mixtures unless extraordinary precautions are taken. Traces of impurities, especially colloids, may enable some of the porphyrins to go into colloidal solution in chloroform, prevent their extraction or cause loss by adsorption on the walls of the vessels used.

Willstätter and Stoll[11] made a qualitative separation of the ether-soluble porphyrins by extraction of the ethereal solution with hydrochloric acid. Willstätter[12] has characterized as the "HCl number" that concentration of hydrochloric acid which will extract two-thirds of the porphyrin from an equal volume of porphyrin solution. The available information on hydrochloric acid solubility of the porphyrins is in terms of Willstätter's "HCl number."

Since the naturally occurring porphyrins are reported to differ widely from one another in their hydrochloric acid numbers, a quantitative separation on this basis should be feasible, provided: (1) the hydrochloric acid solubility is a fixed characteristic, (2) the hydrochloric acid solubility for a given porphyrin is independent of

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