water formed a clear pale yellow solution. Acidification with dilute hydrochloric acid gave 0.4 g. of the *anti* oxime melting at 120–125°; mixed with the *anti* oxime it melted at 128–133° and mixed with the *syn* oxime it melted below 110°. Crystallization from benzene and ligroin gave the pure *anti* oxime.

Pyrolysis of the Acetate (VIII, R = CH_3).—When 0.2 g. of the acetate was vacuum distilled, it charred badly and the yield of distillate, a yellow oil, was poor. Dissolved in alcohol and diluted with water it gave 0.1 g. of a solid melting by 70° and whose melting point was raised by admixture with either the isoxazole (VI, R = CH_3) or the oxazole (V, R = CH_3). Careful crystallization from alcohol gave a small amount of 3-phenyl-5-methylbenzisoxazole (VI, R = CH_3) melting at 91–92° and whose melting point was not lowered by mixing with the pure benzisoxazole, m. p. 92–93°, but which was lowered to 70° by mixing with the oxazole, m. p. 102–103°.

Summary

It has been suggested that the cleavage of acylated α-benzoin oximes by alkali is a consequence of incipient hydrogen bond formation in these compounds. By an examination of acylated *o*-hydroxybenzophenone oximes it has been shown that hydrogen bond formation, sterically conditioned, does take place and that its occurrence is accompanied by behavior comparable to that observed in the acylated α-benzoin oximes. It is pointed out that the existence of stereoisomers, only one of which contains a hydrogen bond, makes possible a study of the chemical effects associated with hydrogen bonding.

WASHINGTON, D. C. RECEIVED JULY 20, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Thermodynamics of Hydrochloric Acid in Dioxane–Water Mixtures from Electromotive Force Measurements. I. Standard Potentials

BY HERBERT S. HARNED AND JOHN OWEN MORRISON[1]

The further development of the physical chemistry of ionized solutes and ionic equilibria requires a knowledge of the variation of the fundamental thermodynamic property, the relative partial molal free energy, as a function of all the intensive variables. Such a comprehensive study of many electrolytes by different methods of measurement is a tremendous task, only to be carried out by many investigators over a long period of time. As a part of this general scheme, we have undertaken in this Laboratory a comprehensive study of the relative partial molal free energy of a single electrolyte as a function of its concentration, the temperature and dielectric constant of the solvent medium over as wide a range of values of these variables as will be found possible.

To achieve this purpose, the cell

$$H_2\ (1\ \text{atm.})\ |\ \text{HCl}\ (m),\ X\%\ \text{Dioxane},\ Y\%\ H_2O\ |\ \text{AgCl–Ag} \qquad (1)$$

is peculiarly adapted. The cell reaction is well known and the electrodes are very reproducible. Dioxane–water mixtures because of their complete miscibility and because of the low dielectric constant of pure dioxane (∼2) afford a wide range of variation of the dielectric constant. These properties have been shown to be of great value by Kraus and Fuoss[2] and Fuoss and Kraus,[3] who measured conductances of some electrolytes in these mixtures.

As part of this program, Åkerlöf and Short[4] have determined the dielectric constant of dioxane–water mixtures from 0 to 80°. The present communication contains electromotive force measurements of the above cells containing 20, 45 and 70% dioxane, respectively. Measurements have been made from 0 to 50° at 5° intervals, and from them the standard potentials of the cell from 0 to 50° inclusive have been calculated.

Experimental Procedure

In order to obtain electromotive forces in these mixtures with an accuracy equal to that obtained by Harned and Ehlers in water[5] and Harned and Thomas[6] in methanol–water mixtures, it was necessary to develop a new type of cell and a specialized technique. It was found that complete air elimination in all-glass apparatus was essential. Any contact of vapor or liquid in the cells with rubber rendered the measurements erratic and uncertain. Upon elimination of these difficulties, very accurate results may be obtained with a potentiometer circuit and a high sen-

---

[1] This communication contains material from a dissertation presented by John Owen Morrison to the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1936.

[2] Kraus and Fuoss, THIS JOURNAL, **55**, 21 (1933).

[3] Fuoss and Kraus, *ibid.*, **55**, 1019 (1933).

[4] Åkerlöf and Short, *ibid.*, **58**, 1241 (1936).

[5] Harned and Ehlers, *ibid.*, **55**, 2179 (1933).

[6] Harned and Thomas, *ibid.*, **57**, 1666 (1935); **58**, 761 (1936).

sitivity galvanometer in solutions of dielectric constant ranging from 80 to 10. With a quadrant electrometer or an amplified galvanometer circuit, we have reason to believe that accurate results may be obtained in media of dielectric constant of the order 5, or even less.

Dioxane was purified by distillation over sodium and subsequent recrystallization. The freezing point of the material used was always within 11.76–11.78°, a value which agrees with the value 11.78° reported by Kraus and Vingee.[7]

The composition of the water–dioxane mixtures prepared from this material was known to within ±0.01%. The hydrochloric acid content of any mixture employed was known to within less than ±0.05%.

The hydrogen electrodes, consisting of platinum foils 0.4 cm. by 2.5 cm., were plated with platinum black. The silver–silver chloride electrodes were those designated by Harned[8] as type 2.

All electromotive forces were measured by an Eppley Feussner type calibrated potentiometer and Leeds and Northrup HS galvanometer. Saturated Weston cells certified by the Eppley Laboratory were used as final standards of electromotive force. The correction of pressure to 1 atm. hydrogen was made by the usual method. The solvent vapor pressures were determined by Mr. Dale Dreisbach of the Morley Chemical Laboratory of Western Reserve University, who employed the method of Hovorka and Dreisbach.[9] These were placed at our disposal by Mr. Dreisbach, for which kindness we are most grateful. The temperature control was ±0.02°.

Cells were run in triplicate. If the values of E deviated from the mean by more than ±0.05 mv., they were discarded. Each set of cells was measured over a temperature range of 25°. One series was begun at 25° and measured at 5° intervals up to 50°, then brought back to 25°. Although six to twelve hours had elapsed between the two readings at 25°, during which the cells were rather severely treated, the difference between the two readings at 25° never exceeded 0.1 mv. and was in most cases less than 0.05 mv. A second series of cells were begun at 25°, reduced to 0°, and finally brought back to 25°. The agreement of the two readings at 25° was excellent. Indeed, in some cases after sufficient experimental skill was acquired, cells were measured at 25°, reduced to 0° by 5° changes in temperature, brought back to 25°, raised to 50° by 5° changes in temperature, and then finally lowered to 25°. The agreement of the three measurements at 25° was very good (∼0.05 mv.) even though the measurements had been extended over periods of twenty-four to thirty-six hours.

Electromotive Forces

Since the cells containing the 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 resorted to the expedient of expressing the results by the quadratic equation

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

E is the cell electromotive force at the centigrade temperature, t; E_{25} the electromotive force at 25°; and a and b are constants. m is the molality of the acid (moles per 1000 g. solvent). The solvent consisted of $X\%$ by weight dioxane and $Y\%$ by weight of water. Table I contains the constants of the equation at the molalities actually employed in 20, 45 and 70% dioxane-water mixtures. These values were determined by the method of least squares. In the fifth column of the table, the maximum deviation, Δ_M, between the observed and calculated results is given.

TABLE I

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

E = Electromotive Force of the Cell

H_2 (1 atm.) | HCl (m), $X\%$ dioxane − $Y\%$ water | AgCl–Ag

m	E_{25}	$a \times 10^6$	$(-b \times 10^6)$	Δ_M	Δ_A
$X = 20\%$					
0.0031249	0.50385	268.727	3.665	0.08	0.03
.0047459	.48340	199.618	3.561	.11	.05
.007088	.46398	133.673	3.629	.05	.02
.009760	.44839	80.436	3.567	.07	.03
.019132	.41618	− 21.891	3.672	.07	.02
.030042	.39473	− 81.927	3.562	.04	.02
.045631	.37505	−150.418	3.397	.05	.02
.06847	.35601	−210.327	3.565	.07	.03
.11469	.33183	−276.982	3.404	.11	.07
.18726	.30863	−343.436	3.215	.06	.03
$X = 45\%$					
0.0031321	0.46879	− 62.127	3.409	0.05	0.02
.005136	.44542	−133.454	3.239	.03	.01
.006804	.43242	−173.636	3.205	.08	.03
.010099	.41426	−224.836	3.155	.05	.02
.020305	.38278	−316.527	3.135	.02	.01
.032601	.36186	−373.727	3.016	.10	.03
.05412	.33964	−438.818	3.040	.03	.01
.07741	.32420	−479.818	2.967	.04	.01
.11172	.30808	−520.945	2.862	.05	.02
.18442	.28593	−580.636	2.812	.03	.01
$X = 70\%$					
0.0031639	0.38934	−577.200	2.852	0.03	0.015
.0051877	.36993	−622.818	2.630	.03	.02
.006950	.35878	−651.327	2.716	.09	.04
.009612	.34669	−673.709	2.606	.05	.015
.019270	.32142	−732.945	2.417	.05	.02
.032031	.30321	−772.473	2.315	.06	.025
.05633	.28315	−815.582	2.250	.03	.01
.07735	.27163	−842.382	2.186	.04	.02
.11362	.25726	−875.109	2.189	.04	.015
.17753	.24002	−916.509	2.090	.05	.015

In the sixth column, Δ_A represents the average deviation, or the sum of the magnitudes of the deviations at the eleven temperatures divided by eleven. Equation (2) is applicable over the temperature range of 0 to 50°.

---

[7] Kraus and Vingee, THIS JOURNAL, **56**, 511 (1934).

[8] Harned, *ibid.*, **51**, 416 (1929).

[9] Hovorka and Dreisbach, *ibid.*, **56**, 1664 (1934).

It is clear that a quadratic equation affords a very close representation of the results. The data in the two solvents richer in dioxane are somewhat more consistent than in the 20% mixtures. Since the 20% mixtures were the first to be studied, we attribute this greater consistency to the skill acquired with longer experience with the technique.

The Evaluation of the Standard Potentials

As expressed by Harned and Thomas,[6] the electromotive force of cell (1) in a mixture of any composition may be expressed by

$$E = E_0 + \frac{RT}{F} \ln y - \frac{2\,RT}{F} \ln \gamma\, m = E' - 2\,k \log \gamma\, m \quad (3)$$

E_0 is the standard potential in water, E_0' the standard potential in the solvent in question and k equals 2.3026 RT/F. γ and m are the activity coefficient and molality of the acid, respectively. In water, $y = 1$, $E_0 = E_0'$. The term containing y is a measure of the medium effect.

Since the law of Debye and Hückel is to be employed in the evaluation of E_0', it is necessary to use the rational activity coefficient, f, which is related to γ according to the equation

$$a = \gamma\, m = f\, N\, s' \quad (4)$$

where a is the relative activity, and N is the mole fraction of the acid, s' a constant factor required to take care of the convention that f becomes unity in a given solvent when N or m equal zero. From this we find that

$$\log \gamma = \log f + \log s' - \log (1 + 0.002\, m\, G_0) + \log 0.001\, G_0 \quad (5)$$

where G_0 "the mean molecular weight" of solvent is given by

$$G_0 = 100 \Big/ \left(\frac{X}{M_1} + \frac{Y}{M_0}\right) \quad (6)$$

M_1 and M_0 are the molecular weights of dioxane and water, respectively. According to equation (5), f equals unity when m equals zero only when $\log s' = -\log 0.001\, G_0$, or $s' = 1/0.001\, G_0$. Imposing this condition, equation (5) becomes

$$\log \gamma = \log f - \log (1 + 0.002\, m\, G_0) \quad (7)$$

It also follows that

$$E = E' - 2\,k \log \gamma\, m = E' - 2\,k \log s' - 2\,k \log N f = E_0'' - 2\,k \log N f \quad (8)$$

where E_0'' is the standard potential on the mole fraction scale. We note that the standard potential, E_0'', on the f scale differs from that on the γ scale by the term 2 k log 0.001 G_0. We shall employ the Debye and Hückel limiting equation with a linear term, namely

$$\log f = -\frac{1.843 \times 10^6}{(DT)^{3/2}} \sqrt{c} + B\, c = -u \sqrt{c} + B\, c - \ldots \quad (9)$$

Combining equations (3), (7) and (9) and rearranging, we obtain

$$E + 2\,k \log m - 2\,k\,u \sqrt{c} - 2\,k \log (1 + 0.002\, G_0\, m) = E' = E_0' - Bc \quad (10)$$

a convenient form for purposes of extrapolation. If the left of equation (10) which we represent by E' be plotted against c, its value at zero c is the desired standard potential, E_0'.

For c we have substituted md_0 where d_0 is the density of the pure solvent. This will cause no error in extrapolation since at the limit ($m = 0$), it is strictly true. The values of the densities of the dioxane–water mixtures, at the desired compositions and temperatures, were obtained from suitable graphs of the density data of Mr. Dale Dreisbach of Western Reserve University. We thank Mr. Dreisbach for placing these results at our disposal before publication.

The values of the dielectric constants of the mixtures required for the computation of the limiting slopes, u, were taken from the data recently obtained in this Laboratory by Åkerlöf and Short.[4]

Table II contains the values of the densities, the dielectric constants and the limiting slopes, which combined with the electromotive force data in Table I made possible the computation of the left side of equation (10). Values of all fundamental constants employed in these computations were those adopted by the "International Critical Tables."

The actual plots of E' *versus* c uniformly exhibited a slight curvature which nearly vanished in the neighborhood of the intercept. The uncertainty in reading the values at the intercept was estimated to be of the order of ±0.05 mv. All experimental results were plotted without any sort of experimental smoothing. In the case of the 20% series, the plotted points differed from the plot used for extrapolation only at the lowest acid concentration ($m \sim 0.005$). In the cases of the 45 and 70% series, the extrapolations were made directly through the large majority of points. Of the points not lying directly on the plots, less than 10% were farther distant than 0.2 mv., and for not a single point was the deviation greater than 0.3 mv.

TABLE II

DENSITIES, DIELECTRIC CONSTANTS AND LIMITING SLOPES FOR 20, 45 AND 70% DIOXANE–WATER MIXTURES

	$X = 20\%$			$X = 45\%$			$X = 70\%$		
t, °C.	d_0	D	u	d_0	D	u	d_0	D	u
0	1.0271	69.16	0.6989	1.0505	44.28	1.364	1.0619	20.37	4.373
5	1.0245	67.39	.7072	1.0467	43.05	1.385	1.0570	19.81	4.437
10	1.0219	65.68	.7156	1.0431	41.86	1.406	1.0522	19.25	4.510
15	1.0193	64.01	.7245	1.0393	40.70	1.429	1.0474	18.72	4.581
20	1.0167	62.38	.7339	1.0356	39.57	1.453	1.0426	18.20	4.657
25	1.0141	60.79	.7437	1.0319	38.48	1.477	1.0378	17.69	4.738
30	1.0115	59.94	.7540	1.0282	37.41	1.503	1.0332	17.20	4.820
35	1.0090	57.73	.7648	1.0246	36.37	1.530	1.0285	16.72	4.907
40	1.0063	56.26	.7760	1.0210	35.37	1.557	1.0239	16.26	4.995
45	1.0038	54.83	.7877	1.0173	34.39	1.586	1.0194	15.80	5.092
50	1.0014	53.43	.7999	1.0139	33.43	1.616	1.0149	15.37	5.185

The values obtained for the electrode potential of the cell E_0' are given in Table III. These results were then expressed by the quadratic equation

TABLE III

STANDARD POTENTIALS

	$X = 20$	$X = 45$	$X = 70$
t, °C.	E_0'	E_0'	E_0'
0	0.21983 (−4)	0.18940 (−5)	0.10783 (−4)
5	.21689 (−7)	.18445 (6)	.09982 (−3)
10	.21369 (−2)	.17947 (3)	.09152 (11)
15	.21033 (−3)	.17434 (−1)	.08337 (−6)
20	.20682 (−2)	.16910 (−10)	.07475 (8)
25	.20315 (−4)	.16344 (7)	.06620 (−2)
30	.19920 (+4)	.15780 (6)	.05720 (17)
35	.19510 (+8)	.15205 (−1)	.04855 (−15)
40	.19092 (+4)	.14612 (−5)	.03930 (−3)
45	.18650 (+4)	.14000 (−7)	.03005 (−8)
50	.18196 (−1)	.13355 (8)	.02040 (11)

	$E_{0(25)}'$	$a_0 \times 10^6$	$b_0 \times 10^6$
$X = 20$	0.20311	− 757.0	−3.58
$X = 45$	.16351	−1114.5	−3.24
$X = 70$	.06618	−1745.6	−3.25

$$E_0 = E_{0(25)}' + a_0\,(t - 25) + b_0\,(t - 25)^2 \quad (11)$$

The constants were evaluated by the method of least squares. The deviations between the observed values and those computed by equation (11) are indicated by the numbers in parentheses immediately following the result. These deviations are given in hundredths millivolt and are positive when the calculated is greater than the observed value. The constants of equation (11) are given at the bottom of the table.

Our experience indicates that there is little doubt as to the reproducibility and reliability of the experimental results. An uncertainty arises in the extrapolation in the more concentrated dioxane solutions which is due to the fact that we have employed the Debye and Hückel function when perhaps a more extended function containing a factor to account for ionic association would be better. We shall reserve such considerations for future discussion when more results in media of low dielectric constant are available. The discussion of different extrapolations in pure methyl alcohol solutions ($D = 31.5$) given by Harned and Thomas[6] is a partial answer to this difficulty. Their computations indicate that our standard potentials are very near the true values.

Summary

1. Measurements of the cells

H_2 (1 atm.) | HCl (m), $X\%$ dioxane, $Y\%$ H_2O | AgCl–Ag

have been made at 5° intervals from 0 to 50° in solutions containing 20, 45 and 70% dioxane and hydrochloric acid at various concentrations between 0.003 and 0.2 M.

2. From these the standard electrode potentials have been evaluated.

NEW HAVEN, CONN.

RECEIVED JULY 6, 1936