[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Thermodynamics of Hydrochloric Acid in Dioxane–Water Mixtures from Electromotive Force Measurements. III. Extrapolations According to the Gronwall–La Mer Extension of the Debye and Hückel Theory

BY HERBERT S. HARNED

In the introductory contributions to the study of the thermodynamics of hydrochloric acid in dioxane–water mixtures, Harned and Morrison[1,2] have shown that the electromotive force measurements of the cells

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

may be obtained with an accuracy comparable to that obtained in water, and described a technique by which this result could be accomplished. They obtained measurements of these cells in 20, 45, and 70% dioxane–water mixtures of which the dielectric constants were approximately 60, 40, and 20, respectively. The acid concentrations were from 0.003 to 0.1 *M*, and the measurements were made from 0 to 50° at 5° intervals. A first approximation of the standard potentials of the cells was made by means of the Debye and Hückel limiting law without the refinement of the extended theory of Gronwall, La Mer and Sandved.[3] In the present communication the results have been reëxamined from the point of view of the extended term theory and a slight revision of the standard potentials has been made. In the media of higher dielectric constant ($D > 30$), the results afford an excellent illustration of the effect of the extended terms.

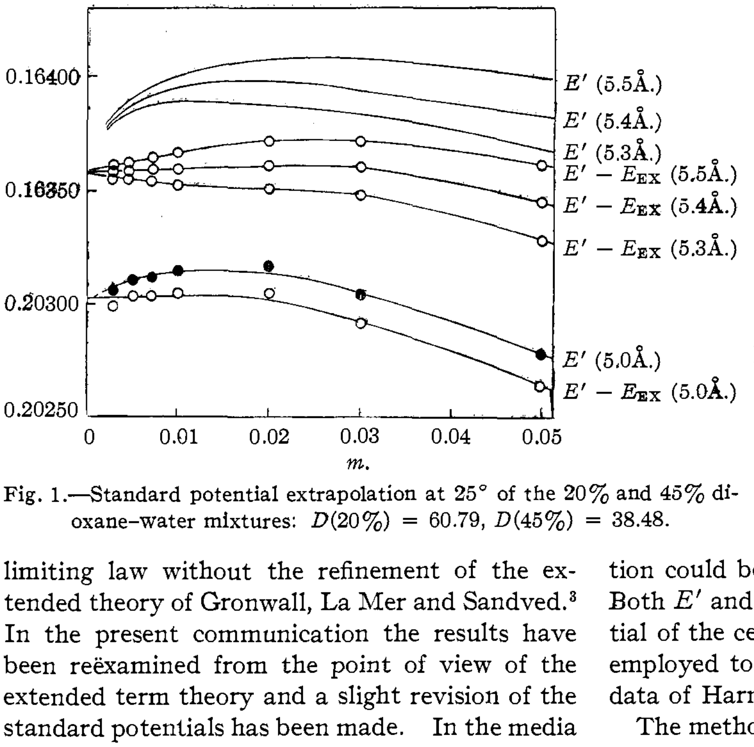

Fig. 1.—Standard potential extrapolation at 25° of the 20% and 45% dioxane–water mixtures: $D(20\%) = 60.79$, $D(45\%) = 38.48$.

Extrapolations at 25°.—The extrapolations were carried out by employing the function E', defined by

$$E' = E + 2k \log m - \frac{2ku\sqrt{c}}{1 + A\sqrt{2c}} - 2k \log (1 + 0.002\ G_0 m) = E'_0 + f(m) \qquad (1)$$

E is the observed electromotive force of the cell, k equals $2.3026\ RT/F$, u is the universal constant of the Debye and Hückel theory, A is the parameter which involves the apparent ionic diameter, a, G_0 is the mean molecular weight of solvent (ref. 1, Eq. 6), and E'_0 is the standard potential of the cell. E' was first calculated using a preliminary value for the apparent ionic diameter, a. Then the value of the Gronwall, La Mer, and Sandved correction, corresponding to this value of "a," was computed from their functions and their Table 5. This quantity multiplied by 2 k shall be designated E_{EX}, since it is the contribution to the electromotive force corresponding to the extended terms of the theory. The functions E' and $E' - E_{EX}$ were plotted, and if $E' - E_{EX}$ was not constant at the lower concentrations ($m > 0.02\ M$), another value of "a" was employed. This process was repeated until such constancy was obtained. With a little experience this method of arithmetical approximation could be accomplished in two to three trials. Both E' and $E' - E_{EX}$ equal the standard potential of the cell, E'_0, when m equals 0. Values of c employed to compute E' were obtained from the data of Harned and Calmon.[4]

The method of extrapolation is clearly shown in Fig. 1. The group of six curves at the top of the figure represent the values of E' and $E' - E_{EX}$ of the 45% dioxane–water cells at 25°. The three

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

[2] Harned and Morrison, *Am. J. Sci.*, **33**, 162 (1937).

[3] Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928); La Mer and Parks, THIS JOURNAL, **53**, 2040 (1931); Cowperthwaite and La Mer, *ibid.*, **53**, 4333 (1931).

[4] Harned and Calmon, *ibid.*, **60**, 334 (1938).

top curves are plots of E' *versus* m, and the three lower curves are similar plots of $E' - E_{\mathrm{EX}}$ for values of "a" equal to 5.5, 5.4, and 5.3 Å., respectively. We note that when "a" equals 5.4 Å., $E' - E_{\mathrm{EX}}$ becomes constant at the lower concentrations.

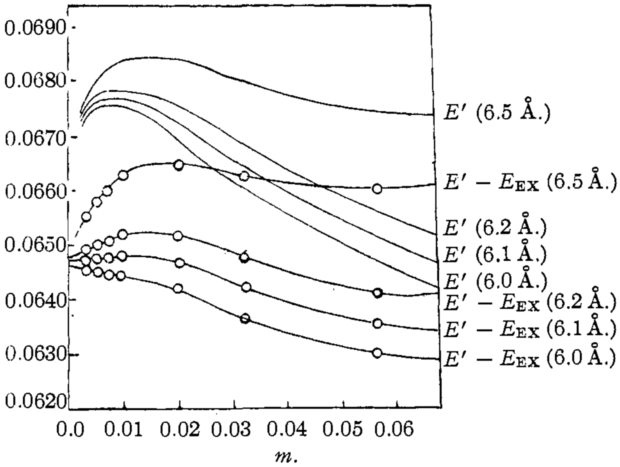

Fig. 2.—Standard potential extrapolation at 25° of the 70% dioxane-water mixtures: $D = 17.69$.

The curves when "a" equals 5.5 and 5.3 Å. have slopes of opposite sign. The result at 5.4 Å. was employed for extrapolation. This method was employed for all the results of the 20 and 45% mixtures.

The two lower curves in Fig. 1 illustrate the behavior of the 20% dioxane-water mixtures at 25°. In this case the dielectric constant of the mixture is 60.79 and consequently the extended term effect is considerably smaller than in the case of the 45% mixtures of dielectric constant 38.48. The results as illustrated in Fig. 1 are a good confirmation of the extended term theory.

The results in media of dielectric constant greater than 30 are not complicated by effects of incomplete ionization. Conductance measurements carried out in this Laboratory indicate practically complete ionization ($K > 1$). On the other hand, the ionization constant of hydrochloric acid from conductance measurements in 70% dioxane-water mixtures of dielectric constant 17.69 is found to be approximately 0.006, and consequently some doubt is present of the validity of the usual method of applying the extended term corrections. Nevertheless, a single illustration of an extended theory extrapolation in 70% dioxane-water mixtures is shown in Fig. 2. The four upper curves are plots of the function E', and the lower curves similar plots of $E' - E_{\mathrm{EX}}$ *versus* m at the designated values of "a." We note that the values of $E' - E_{\mathrm{EX}}$ at 6.1 Å. are constant at concentrations from 0.01 to 0.003 M. The extended correction is about 3 mv. at its maximum. Upon examination of these curves, it becomes evident that results must be obtained at concentrations below 0.003 M before the extrapolation can be accomplished with certainty. For this reason, we have discontinued these computations until we have ascertained whether results of sufficient accuracy in very dilute solutions may be obtained.

The temperature effect of the extended theory is illustrated in a striking manner by Fig. 3 in which the three top curves represent plots of the deviation of the Debye-Hückel function at 0, 25 and 50°, respectively. These plots of $E' - E_0'$ against m show the maxima characteristic of the extended term deviations and the increasing magnitude of the effect with increasing temperature. The three lower curves, the plots of $E' - E_0' - E_{\mathrm{EX}}$ *versus* m, show how the extended term theory takes care of these deviations.

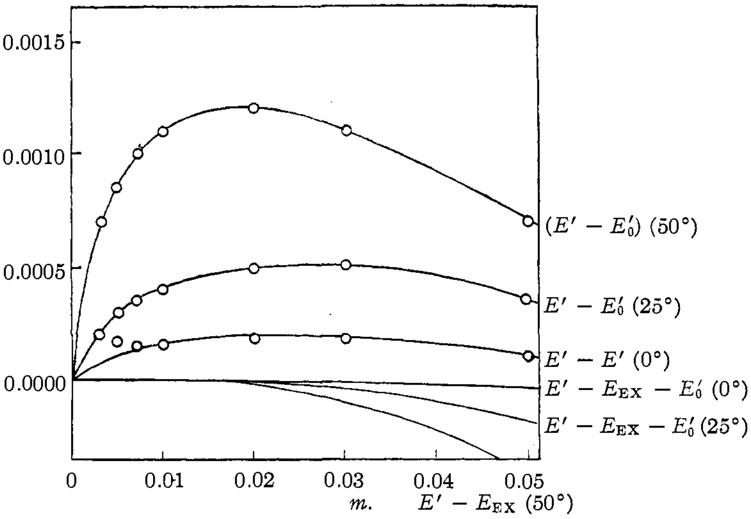

Fig. 3.—Temperature effects on the extrapolation functions, $E' - E_0'$ and $E' - E_0' - E_{\mathrm{EX}}$: $X = 45$; $D_0 = 44.28$; $D_{25} = 38.48$; $D_{50} = 33.43$.

We note that in order to apply this method, values of "a" which decrease with increasing temperature are necessary. 5.7, 5.4 and 4.7 Å. were employed at 0, 25 and 50°, respectively. There is some doubt about such a trend in "a"

TABLE I

VALUES OF EXTRAPOLATION FUNCTION, $E' - E_{EX}$

	$X = 20$[1]	$X = 45$[a]			$X = 70$[b]	
m	25°	0°	25°	50°	m	25°
0.000	(0.20303)	(0.18946)	(0.16358)	(0.13282)	0.00000	(0.06472)
.003	.20298	....	.16357	....	.00316	.06471
.005	.20304	.18957	.16358	.13288	.00519	.06473
.007	.20303	.18948	.16359	.13283	.00645	.06474
.01	.20305	.18937	.16361	.13282	.00961	.06477
.02	.20305	.18932	.16360	.13286	.01927	.06465
.03	.20291	.18932	.16345	.13274	.03203	.06415
.05	.20265	.18934	.16325	.13244	.05633	.06342
D	60.79	44.28	38.48	33.43		17.69

[a] From results smoothed to round concentrations. [b] From original electromotive forces. (Values of dielectric constants and limiting slopes are given in Table II, Harned and Morrison.[1])

since the extrapolation has been made without consideration of other parameters such as the one which corresponds to the change in dielectric constant of the medium caused by electrolyte addition.

The accuracy of estimating E_0' by this method is shown by the results in Table I. $E' - E_{EX}$ is given at some concentrations for the cases illustrated in the figures. The values at m equals 0 are the standard potentials as estimated.

In most cases, the numerical uncertainty in this estimation is very small and of the order of a few hundredths millivolt. The worst result of all is the one at 0° in column three where the results at the lowest concentration show a trend which indicates an error. However, the uncertainty is not greater than ±0.07 mv. The last row in the table contains values of the dielectric constant, D.

The Standard Potentials

Table II contains the standard potentials derived by this method of extrapolation. The second and fourth columns give the values "a" necessary to render the extrapolation function, $E' - E_{EX}$, constant at the lower concentrations ($m < 0.02$ M). Since no other effects beyond the extended Debye and Hückel theory were considered, we doubt whether this trend in the parameter is significant. The value for "a" in the neighborhood of 5 Å. agrees with the value of 5.6 Å., recently reported by Shedlovsky and MacInnes from their measurements in aqueous solution.

TABLE II

STANDARD POTENTIALS

	$X = 20$		$X = 45$	
t, °C.	a	E'_0	a	E'
0	5.4	0.21975 (−2)	5.7	0.18938 (2)
5	5.3	.21677 (−1)	5.6	.18468 (−3)
10	5.2	.21362 (+1)	5.6	.17972 (−2)
15	5.1	.21025 (+1)	5.5	.17454 (0)
20	5.1	.20674 (0)	5.5	.16916 (1)
25	5.0	.20303 (0)	5.4	.16358 (2)
30	5.0	.19914 (0)	5.2	.15778 (4)
35	5.0	.19505 (0)	5.1	.15182 (2)
40	4.9	.19080 (−1)	4.9	.14560 (5)
45	4.9	.18634 (1)	4.8	.13925 (0)
50	4.8	.18171 (1)	4.7	.13282 (−16)

The results can be expressed accurately by the quadratic equations

$$X = 20;\ E_0' = 0.20303 - 0.0007605\,(t - 25) - 0.0000037\,(t - 25)^2 \qquad (2)$$

$$X = 45;\ E_0' = 0.16360 - 0.001135\,(t - 25) - 0.00000412\,(t - 25)^2 \qquad (3)$$

The numbers in the table in parentheses immediately following the values of E_0' represent the deviations in hundredths of a millivolt between the observed results and those computed by equations (2) and (3). These are positive when the calculated is greater than the observed value.

The extended theory extrapolations yield values of E_0' which in the 20% dioxane–water mixtures differ little from those obtained by the simple Debye and Hückel extrapolations made in our preliminary estimate.[1] Thus, at 0, 25 and 50°, the refined extrapolations lead to values 0.08, 0.12 and 0.25 mv. lower, respectively, than those previously obtained. Larger differences are obtained in the case of the 45% dioxane–water mixtures. At 0° the difference is 0.02 mv., at 25° the refined extrapolation is 0.14 mv. higher than the preliminary, and at 50° it is 0.72 mv. lower. In the 70% dioxane–water mixtures, the recently estimated value at 25° is 1.5 mv. lower than that obtained by the simpler theory. The probability of the necessity of this correction was mentioned in the earlier communication.

Summary

1. The standard potentials of the cells

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

have been evaluated in solutions containing 20 and 45% dioxane by employing the Debye and Hückel theory as extended by Gronwall, La Mer and Sandved.

2. The results afford excellent confirmation of the general theory.

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The Thermodynamics of Hydrochloric Acid in Dioxane–Water Mixtures from Electromotive Force Measurements. IV. Properties of the 20% Dioxane Mixtures

BY HERBERT S. HARNED AND JOHN G. DONELSON

Harned and Morrison[1] have reported electromotive forces of the cells

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

in 20% dioxane–water mixtures and at acid concentrations varying from 0.003 to 0.1 M through a temperature range from 0 to 50°. From these results, the standard potentials of the cells have been evaluated by employing the Gronwall, La Mer and Sandved extension of the Debye and Hückel theory.[2] These measurements have now been extended to cover the concentration range from 0.003 to 3 M. From these results, the activity coefficient, relative partial molal heat content, and heat capacity of the acid have been computed and tabulated in convenient form.

Experimental Results

The experimental procedure was similar to that described in detail by Harned and Morrison.[3] The dioxane was purified by refluxing over sodium, distillation and successive freezing. The criterion of purity was the freezing point which was always within 11.77–11.78°. Assuming that the dioxane tested in this manner was pure, the composition of the dioxane–water mixtures was known to within ±0.015%. The stock solution of hydrochloric acid was standardized gravimetrically and its strength was known to within ±0.02%. The hydrochloric acid solutions used in the cells were prepared from this stock solution and their strengths were known to within the same limits.

One modification of Harned and Morrison's cell was made when working with hydrochloric acid at higher concentrations ($m > 0.2$). A piece of 2-mm. bore capillary tubing of 12–15 cm. length was sealed between the two cell compartments. This served to prevent any deposition of silver on the hydrogen electrode.

Six cells containing a given concentration of acid were measured. These were allowed to equilibrate at 25° overnight. Three of these were lowered to 0° at 5° intervals, and then finally brought back to 25°. The other three were measured at 5° intervals up to 50° and then brought back to 25°. The reproducibility of the measurements at 25° before and after these temperature changes was taken as a criterion of the accuracy of the results. Reasonable reproducibility was obtained at all acid concentrations since the readings checked to within ±0.05 mv.

The cell electromotive force was corrected to 1 atm. hydrogen pressure by the usual method making allowance for the vapor pressure of the solvent and a further correction for the lowering of the vapor pressure of the solvent by the hydrochloric acid. The latter was made by assuming Raoult's law and complete ionization of the acid. Since the largest correction due to this lowering was 0.3 mv. at 3 M acid concentration and 50°, any error caused by these assumptions is less than the experimental error in electromotive force.

The results have been expressed by the equation

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

the constants of which are given in Table I. The fifth column contains the maximum deviations in millivolts of the observed values from those

TABLE I

CONSTANTS OF EQUATION (1)

X = 20% by weight of dioxane

m	E_{25}	$-a \times 10^4$	$-b \times 10^6$	Δ(max.)	Δ(av.)
0.11139	0.33332	2.774	3.48	0.05	0.02
.20314	.30548	3.585	3.30	.05	.02
.25252	.29437	3.926	3.32	.05	.01
.40348	.27110	4.618	3.16	.04	.02
.7067	.24118	5.394	3.08	.06	.03
1.0341	.21897	5.920	2.80	.08	.04
1.5440	.19249	6.426	2.52	.06	.03
2.0691	.17015	6.811	2.22	.07	.03
3.0977	.13328	7.319	1.98	.06	.03

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

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

[3] Harned and Morrison, *Am. J. Sci.*, **33**, 162 (1937).