

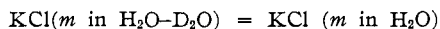
these authors do not align well with those determined in this Laboratory<sup>17</sup> by conductance and by the use of thermodynamically exact cells. It seems certain that the data obtained with cell (18) will require some revision.

### Summary

1. Measurements of the cell with transference Ag-AgCl/KCl(*m* in H<sub>2</sub>O-D<sub>2</sub>O)/KCl(*m* in H<sub>2</sub>O)/AgCl-Ag have been made at 0.1 *m* over a wide range of deu-

(17) La Mer and Chittum, *THIS JOURNAL*, **58**, 1642 (1936); ref. 5a; Yates, unpublished conductance measurements.

terium content and at 5, 25 and 45°. The partial molal free energy, entropy and heat content changes have been evaluated for the process



which corresponds to the process occurring in the cell when the differential transport of the waters is neglected.

2. The absolute activity coefficients of potassium chloride in isotopic mixtures have been calculated referred to potassium chloride at infinite dilution in H<sub>2</sub>O as unity.

NEW YORK, N. Y.

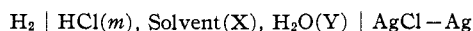
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

## The Properties of Electrolytes in Mixtures of Water and Organic Solvents. I. Hydrochloric Acid in Ethanol- and Isopropanol-Water Mixtures of High Dielectric Constant

BY HERBERT S. HARNED AND CALVIN CALMON

In order to investigate further the effects of different solvent mixtures on the thermodynamic properties of a strong electrolyte, we have measured the electromotive forces of the cells



in mixtures containing 10 and 20% ethyl alcohol and 10% isopropyl alcohol at 25°. In these media of high dielectric constant, hydrochloric acid is completely ionized so that considerations regarding the results will not be complicated by the effects of ionic association to be found in media of lower dielectric constant ( $D < 50$ ). These results along with similar data in dioxane-, methanol- and glycerol-water mixtures will serve as an introduction to this complicated subject.

### Electromotive Force and Density Data

The electromotive forces were obtained in the usual manner with silver-silver chloride electrodes made by heating silver oxide, and subsequently electrolyzing in hydrochloric acid solutions. The density determinations were made with pycnometers of about 30-cc. capacity. The alcohols were purified by fractional crystallization. Density determinations of the alcohol-water mixtures agreed to within less than 0.005% with those in the "International Critical Tables." Table I contains the electromotive force, density data, and the vapor pressures employed for correcting cell

electromotive forces to one atmosphere hydrogen pressure.

The densities have been expressed by the equation

$$d = d^0 + a'm - b'm^2 + e'm^3 \dots \quad (1)$$

the constants of which are contained in Table II. The ratio of concentration in moles per liter solution, *c*, to molality, *m*, may be expressed to within  $\pm 0.05\%$  by the useful equation

$$c/m = d^0 - A'm \quad (2)$$

The constant *A'* is also included in the table.

### Standard Potentials

The standard potentials of the cells were obtained by the use of the function *E'*, defined by the equation

$$E' = E + 0.1183 \log m - \frac{0.1183 u \sqrt{c}}{1 + A \sqrt{2c}} - 0.1183 \log (1 + 0.002 m M_{xy}) = E_m^0 + f(m) \quad (3)$$

where *E* is observed electromotive force, *u* the Debye and Hückel constant, *A* the parameter which involves the mean distance of approach of the ions, *a*, and *M<sub>xy</sub>* the mean molecular weight of solvent. ( $A = Ka$  and  $M_{xy} = 100/(X/M_1 + Y/M_2)$  where *a* is in Ångströms and *M<sub>1</sub>* and *M<sub>2</sub>* are the molecular weights of organic solvent and water, respectively.) These quantities are given in Table II. The value of "a" employed was 4.3 Å. as found by Harned and Ehlers<sup>1</sup> for aqueous solu-

(1) Harned and Ehlers, *THIS JOURNAL*, **55**, 2179 (1933).

TABLE I  
 ELECTROMOTIVE FORCES OF THE CELLS AND DENSITIES OF SOLUTIONS AT 25°

H <sub>2</sub>   HCl( <i>m</i> ), ROH( <i>X</i> ), H <sub>2</sub> O( <i>Y</i> )   AgCl-Ag								
X = % by weight of ROH; cell reproducibility = ±0.05 mv.								
(1) Ethanol-Water (X = 10)			(2) Ethanol-Water (X = 20)			(3) Isopropanol-Water (X = 10)		
V. p. = 29.6 mm.			V. p. = 35.6 mm.			V. p. = 27.0 mm.		
<i>m</i>	<i>E<sub>25</sub></i>	<i>d</i>	<i>m</i>	<i>E<sub>25</sub></i>	<i>d</i>	<i>m</i>	<i>E<sub>25</sub></i>	<i>d</i>
0.0	.....	0.98038	0.0	.....	0.96640	0.0	.....	0.98122
.006309	0.47933	.98050	.004703	0.48729	.96649	.001862	0.53930	.98129
.007579	.47030	.98056	.007872	.46200	.96655	.004019	.50096	.98130
.010875	.45261	.98064	.010154	.44955	.96661	.006356	.47830	.98132
.01987	.42326	.98078	.01983	.41715	.96677	.008616	.46335	.98137
.04210	.38711	.98114	.04150	.38183	.96716	.008921	.46164	.98138
.05100	.37794	.98133	.05166	.37145	.96733	.02089	.42025	.98158
.07085	.36222	.98170	.07123	.35623	.96762	.03556	.39459	.98183
.08000	.35640	.98189	.08161	.34976	.96778	.04856	.37971	.98208
.08846	.35158	.98199	.09237	.35378	.96795	.06685	.36444	.98242
.10911	.34152	.98240	.10421	.33823	.96812	.07947	.33618	.98265
.19903	.31254	.98393	.3078	.28698	.97133	.11188	.33983	.98320
.2999	.29240	.98562	.4751	.26410	.97392	.19215	.31387	.98457
.5050	.26568	.98908	.7309	.24115	.97776	.2990	.29213	.98638
.7014	.24793	.99238	1.0216	.22168	.98208	.4451	.27189	.98875
.9946	.22776	.99726	1.5492	.19516	.98996	.6993	.24767	.99313
1.4987	.20163	1.00501	2.079	.17351	.99784	.8863	.23417	.99600
1.9938	.18140	1.01180	.....	.....	.....	1.0000 <sup>a</sup>	.22704	.99825 <sup>a</sup>

<sup>a</sup> Extrapolated.

 TABLE II  
 CONSTANTS OF EQUATIONS (1) AND (2)  
 Parameters of equation (12):  $a = 4.3 \text{ \AA.}$ ;  $A = Ka$ 

	<i>d</i> <sup>0</sup>	<i>a</i> '	<i>b</i> '	<i>c</i> '	<i>A</i> '
Ethanol-water (X = 10)	0.98038	0.0178	0.00094	-0.00004	0.0180( <i>m</i> < 1) .0185( <i>m</i> > 1)
Ethanol-water (X = 20)	.96640	.0170	.00248	.00080( <i>m</i> < 1) .00064( <i>m</i> > 1)	.0191( <i>m</i> < 1) .0188( <i>m</i> > 1)
Isopropanol-water (X = 10)	.98122	.0173	.0005	.001	.0184
	<i>D</i>	<i>u</i>	<i>A</i> √2	<i>K</i>	<i>M<sub>xy</sub></i>
Ethanol-water (X = 10)	72.8	0.5675	1.467	0.2413	19.19
Ethanol-water (X = 20)	67.0	.6428	1.529	.2515	20.52
Isopropanol-water (X = 10)	71.4	.5842	1.482	.2437	19.48

tions, and Harned and Thomas<sup>2</sup> for methanol-water mixtures. The plots of *E'* versus *m* are straight from the lowest concentrations measured to 0.1 *M* acid. From them the standard potentials  $E_m^0$  could be evaluated with a certainty of ±0.05 mv.

The standard potential of the cell in these mixtures, obtained by equation (3) involving the molality and denoted  $E_m^0$ , differs from the standard potentials,  $E_c^0$  and  $E_N^0$ , derived using moles per liter of solution and mole fractions, respectively. These latter quantities can be obtained from  $E_m^0$  by the relations

$$E_c^0 = E_m^0 - 0.1183 \log d^0 \quad (4)$$

$$E_N^0 = E_m^0 + 0.1183 \log 1000/M_{xy} \quad (5)$$

where  $d^0$  is the solvent density. The reference

(2) Harned and Thomas, *THIS JOURNAL*, **58**, 761 (1936).

state for  $E_m^0$  is a solution of unit molality with the activity coefficient,  $\gamma$ , of unity in a given solvent; that for  $E_N^0$  is a solution of unit mole fraction of electrolyte, *N*, and unit rational activity coefficient, *f*, or *a/N*; and that for  $E_c^0$  is unit concentration of moles per liter, and a unit activity coefficient, *y*, or *a/c*. For purposes of thoroughness in examining the standard potential as a function of the dielectric constant, we have computed  $E_m^0$ ,  $E_c^0$  and  $E_N^0$  for the solvent-water mixtures. The results are given in Table III along with similar values for cells containing glycerol-water, methanol-water and dioxane-water mixtures previously determined by Lucasse,<sup>3</sup> Harned and Thomas,<sup>4</sup> and Harned and Morrison,<sup>5</sup> respectively.

(3) Lucasse, *Z. physik. Chem.*, **121**, 254 (1926).

(4) Harned and Thomas, *THIS JOURNAL*, **57**, 1666 (1935).

(5) Harned and Morrison, *ibid.*, **58**, 1908 (1936); Harned, *ibid.*, **60**, 336 (1938).

TABLE III  
STANDARD POTENTIALS OF THE CELLS  
 $\text{H}_2 \mid \text{HCl}(m), \text{Solvent}(N_2), \text{H}_2\text{O}(N_1) \mid \text{AgCl}-\text{Ag}$   
 $N_1, N_2 = \text{mole fractions}$

	$N_2$	$D$	$E_m^0$	$E_c^0$	$E_N^0$
	0	78.54	0.22239	0.22327	0.42876
Methanol-water	0.0588	74.0	.21535	.21639	.41946
	.1233	69.2	.20881	.21070	.41052
Ethanol-water	.0417	72.8	.21442	.21544	.41761
	.0891	67.0	.20736	.20911	.40709
Glycerol-water	.01	77	.2196	.2191	.4239
	.05	72	.2082	.2058	.4057
Isopropanol-water	.0323	71.4	.21363	.21460	.41631
Dioxane-water	.0487	60.8	.20303	.20231	.40052

The dielectric constants of the mixtures were taken from the data of Åkerlöf,<sup>6</sup> and Åkerlöf and Short.<sup>7</sup>

As typical of the characteristics of these standard potentials as function of the reciprocal of the dielectric constant, the values of  $E_m^0$  are plotted against  $1/D$  in the lower part of Fig. 1. The origin of the plots at the left of the figure represents  $E_m^0$  for pure water. None of these plots are straight lines. Further, they exhibit pronounced individual characteristics. The two straight lines (dashed) represent plots of Born's equation

$$E_m^0 = E_{m(w)}^0 - 1.21 \times 10^2 \frac{D_1 - D_2}{D_1 D_2} \sum \frac{1}{r_i} \quad (6)$$

where  $D_1$  is the dielectric constant of water,  $D_2$  that of the solvent-water mixture,  $E_{m(w)}^0$  the standard potential in pure water,  $E_m^0$ , that in the solvent, and  $\sum \frac{1}{r_i}$  is the sum of the reciprocals of the ionic radii in Ångström units. In this case, we have used 1.2 (lower plot) and 0.9 (upper plot) for  $\sum \frac{1}{r_i}$ . 1.2 corresponds roughly to the values of ionic radii derived from crystallographic data,<sup>8,9</sup> while 0.9 is the value of  $\sum \frac{1}{r_i}$  corresponding to an average ionic diameter of 4.3 Å. which we employed for the extrapolation. Although agreement with the over-simplified theory expressed by Born's equation is not good, we note that the magnitude of the theoretical prediction is sufficient to account for the results with the exception of the glycerol-water mixtures. Plots of  $E_c^0$  and  $E_N^0$  versus  $1/D$  have similar characteristics and require no further discussion.

The electromotive force of these cells may be represented by two equations

(6) Åkerlöf, THIS JOURNAL., 54, 4125 (1932).

(7) Åkerlöf and Short, *ibid.*, 58, 1241 (1936).

(8) Pauling, *ibid.*, 49, 765 (1927).

(9) Bragg, *Phil. Mag.*, [6] 40, 169 (1920).

$$E = E_{m(w)}^0 - 0.05915 \log m_{\text{HCl}} - 0.05915 \log \gamma_{\text{H}} \gamma_{\text{Cl}} \quad (7)$$

$$E = E_m^0 - 0.05915 \log m_{\text{HCl}} - 0.05915 \log \gamma_{\text{H}}^* \gamma_{\text{Cl}}^* \quad (8)$$

In these,  $E_{m(w)}^0$  is the standard potential in water,  $\gamma_{\text{H}} \gamma_{\text{Cl}}$  is the activity coefficient in any solution relative to unity at infinite dilution in water,  $E_m^0$  is the standard potential in any mixture relative to unit activity coefficient,  $\gamma_{\text{H}}^* \gamma_{\text{Cl}}^*$ , at infinite dilution in that solvent. Combining these equations, we obtain

$$E_{m(w)}^0 - E_m^0 = 0.05915 \log \frac{\gamma_{\text{H}} \gamma_{\text{Cl}}}{\gamma_{\text{H}}^* \gamma_{\text{Cl}}^*} \quad (9)$$

Further by utilizing the thermodynamic relationships of the reaction:  $\text{H}^+ + \text{Cl}^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Cl}^-$ , which prevails in the solutions of high water content, equations (7) and (8) may be converted to

$$E_{m(w)}^0 - (E_m^0 - 0.05915 \log a_{\text{H}_2\text{O}}) = 0.05915 \log \frac{\gamma_{\text{H}_3\text{O}} \gamma_{\text{Cl}}}{\gamma_{\text{H}_3\text{O}}^* \gamma_{\text{Cl}}^*} \quad (10)$$

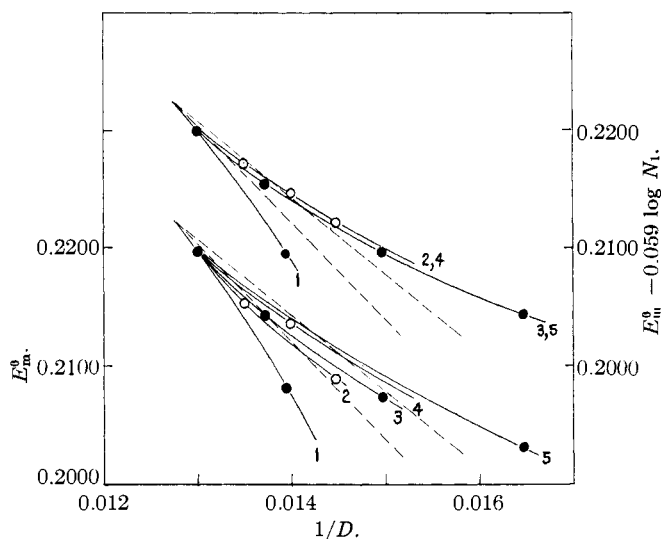


Fig. 1.— $E_m^0$  and  $E_m^0 - 0.05915 \log N_1$  versus  $1/D$  in media of high dielectric constant: Curve (1) glycerol-water; Curve (2) methanol-water; Curve (3) ethanol-water; Curve (4) isopropanol-water; Curve (5) dioxane-water.

where  $a_{\text{H}_2\text{O}}$  is the activity of the water in any mixture. The activity of pure water has been taken to be unity. This latter equation suggests that a plot of  $(E_m^0 - 0.05915 \log a_{\text{H}_2\text{O}})$  versus  $1/D$  should be investigated. The partial vapor pressure data indicated that  $N_1$ , the mole fraction of water, could be substituted for  $a_{\text{H}_2\text{O}}$  without great sacrifice in accuracy. Consequently, the plots of the function  $(E_m^0 - 0.059 \log N_1)$  are given in the upper part of Fig. 1. With the exception of

the graph of the glycerol-water mixtures, this procedure does bring the results closer together. We doubt that this has much significance since similar graphs of the standard potentials,  $E_c^0$ , and  $E_N^0$ , do not exhibit as great a concordance. We note, however, that in the mixtures of high water content, the Born equation (dashed line) agrees closely with all the results except those obtained with the glycerol-water mixtures.

The characteristics of the variation of  $E_m^0$  over wider variations of dielectric constants are shown in Fig. 2. Curve (2) represents  $E_m^0$  versus  $1/D$

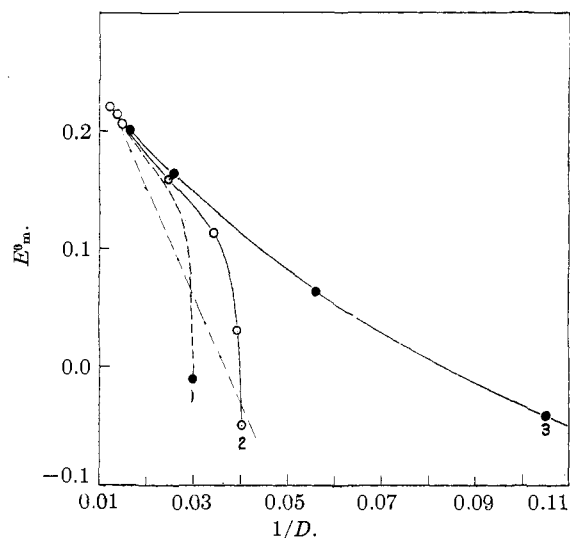


Fig. 2.— $E_m^0$  versus  $1/D$  over wide variation of dielectric constant: Curve (1) methanol-water; Curve (2) ethanol-water; Curve (3) dioxane-water.

for ethanol-water mixtures from pure water to pure alcohol.  $E_m^0$  for the pure alcohol was obtained from the data of Woolcock and Hartley,<sup>10</sup> and some intermediate values from the data of Harned and Fleysler.<sup>11</sup> Curve (1) for methanol-water mixtures was drawn tentatively to the value in pure alcohol obtained from the data of Nonhebel and Hartley.<sup>12</sup> Curve (3) represents the results obtained in dioxane-water mixtures. The final result is in 82% dioxane solutions of dielectric constant 9.6. This is still quite far from pure dioxane solutions which have a dielectric constant of 2.1. The dashed line represents the results computed by the Born equation.

The transfer of the acid from the water to the non-aqueous medium is accompanied by a large increase in activity relative to water. The curves

show that the Born formula ( $\sum \frac{1}{r_i} = 1.2$ ) is more than sufficient to account for a change of this magnitude in media containing 2 to 100% water. This, of course, is also true for the transfer of ( $H_3O^+ + Cl^-$ ) since the plots of  $E_m^0 - 0.05915 \log a_{H_2O}$  lie above those given in the figure. The very rapid decrease in  $E_m^0$  with  $1/D$  as the water content of the mixture becomes small takes place under conditions where the oxonium ion,  $H_3O^+$ , is being replaced by  $SH^+$  according to the reaction:  $H_3O^+ + S \rightleftharpoons H_2O + SH^+$ . The concentration of dioxane in the dioxane-water mixtures is not sufficient to show this effect.

### Activity Coefficients

Values of the activity coefficients in the ethanol- and isopropanol-water mixtures may be computed readily from the electromotive forces in Table I and the standard potentials in Table III by means of the equation

$$-\log \gamma = \frac{E - E_m^0}{0.1183} + \log m \quad (11)$$

The Debye and Hückel equation with a linear term

$$\log \gamma = -\frac{u \sqrt{c}}{1 + A \sqrt{2c}} + bm - \log(1 + 0.002 M_{xy}m) \quad (12)$$

yields a very close representation of  $\gamma$  from 0 to 1.5  $M$  if the parameters given in Table II are employed. The values found for the linear parameter,  $b$ , are 0.1345, 0.1376 and 0.1373 for the 10 and 20% ethanol mixtures, and the 10% isopropanol mixtures, respectively. The values of  $b$  suitable for a similar computation in the cases of the 10 and 20% methanol-water mixtures were found by Harned and Thomas to be 0.1315 and 0.1293, respectively.

### Summary

1. Electromotive forces at 25° of the cells  $H_2 | HCl(m), ROH(X), H_2O(Y) | AgCl-Ag$  have been obtained for ethanol-water mixtures of 10 and 20%, and for 10% isopropanol-water mixtures. The range of hydrochloric acid concentration was from 0.005 to 2  $M$ .
2. Densities of the solutions were obtained.
3. The standard potentials of the cells in these mixtures were evaluated with an estimated accuracy of  $\pm 0.05$  mv.
4. The variation of the standard potential of the cell as a function of the reciprocal of the dielectric constant in these and in methanol-, glycerol- and dioxane-water mixtures is discussed.

NEW HAVEN, CONN.

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(10) Woolcock and Hartley, *Phil. Mag.*, [7] **5**, 1133 (1928).

(11) Harned and Fleysler, *THIS JOURNAL*, **47**, 82 (1925).

(12) Nonhebel and Hartley, *Phil. Mag.*, [6] **50**, 729 (1925).