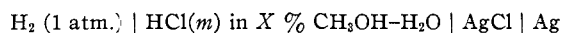


[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Molal Electrode Potential of the Silver-Silver Chloride Electrode in Methyl Alcohol-Water Mixtures

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In order to study the effects of medium changes upon the thermodynamic properties of a strong electrolyte and upon the ionization constants of weak electrolytes as determined by electromotive force measurements, the molal electrode potential of the silver-silver chloride electrode in the solvent in question must be known. To meet this requirement for methyl alcohol-water mixtures, measurements of the cells



over the temperature range from 0 to 40° and at concentrations from 0.005 to 0.1 *M* have been made. Two solvents have been employed containing methyl alcohol of 10 and 20% by weight in water. By employing these solvents, we are reasonably certain that no complications (caused by the association of ions) will arise. The mean distance of approach of the ions of hydrochloric acid *a* has been found by Harned and Ehlers to be about 4.3 Å. in water. According to Bjerrum's theory of ionic association, if *a* > *g*, the electrolyte will be completely dissociated. In water *g* = 3.5 Å. in 20% methanol-water mixtures, *g* ~ 4 Å. Therefore, if "*a*" remains constant with change in solvent, a fact which will be verified later, then no association of ions occurs and we may employ the theory of Debye and Hückel, for the purpose of extrapolation, without ramification.^{2,3} In solutions of 30% methyl alcohol and greater, the effects of ionic association may be expected to appear.

In order to correct the hydrogen electrode to one atmosphere pressure, it was necessary to know the vapor pressures of the mixtures under consideration. These were determined from 0 to 40° at 5° intervals. For purposes of theoretical calculations, it was also necessary to know the concentrations of the acid in moles per liter of solution as well as the molalities. To meet this requirement suitable density determinations were made.

(1) This communication contains material from a dissertation presented by Henry C. Thomas to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1935.

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

(3) Bjerrum, *Kg. Danske Videnskab. Selskab.*, **VII**, 9 (1926).

Materials, Experimental Technique and Results

1. **Materials.**—Hydrochloric acid of the analyzed grade was purified by distillation. Methyl alcohol of the best analyzed grades was purified by distillation through an efficient fractionating column 110 cm. in length. The first portion of the distillate as well as a considerable portion of the residual liquid was discarded. The material finally employed gave no test with Schiff's aldehyde reagent.

2. **Solutions.**—Stock solutions of hydrochloric acid were analyzed gravimetrically. The molality of the acid in all the solutions reported may be relied upon to within ±0.05%. Solvent solution was made in large quantities, usually of about 18 liters, by weighing on a balance sensitive to 1 g. The major portion of the methyl alcohol was weighed in from a flask equipped with a siphon, using a more sensitive balance. The remainder of the alcohol was added in a calculated quantity from a Mohr pipet.

No entirely independent check on the accuracy of these solutions is available. Density determinations at 20° when compared with the data of the "International Critical Tables"^{3a} invariably gave somewhat high values for the composition. Independent determinations of the density of carefully prepared methyl alcohol-water mixtures always yielded results lower than those given in the tables. This discrepancy cannot be explained by the presence of small quantities of water in the methyl alcohol. The compositions of the alcohol solutions are considered to be known to well within the limit of ±0.2%.

Stock solutions of hydrochloric acid in the alcohol solvents were made up by weight from the strong aqueous solutions which had been analyzed previously. Analyses of these solutions yielded values for the hydrochloric acid content which agreed within the error of ±0.05% with those computed from the original stock solution of strong hydrochloric acid. These stock solutions were carefully protected against change in concentration. The cell solutions were prepared by weight dilution of these solutions.

In order to remove the air, all solutions were swept with a rapid stream of hydrogen before introduction into the cells. The hydrogen was first passed through a saturator filled with the solvent. The solutions never changed in weight during this process by more than 0.2 g. in 2000 g., which change was always ascribable to the displacement of air in the flask employed by hydrogen.

3. **Electrodes.**—The electrodes were similar to those employed by Harned and Ehlers,² and need not be described. Suffice it to say that all precautions regarding purity of materials used in making the electrodes were observed.

4. **Cells.**—The cells consisted of U-tubes of approximately 1.9 cm. bore. These were equipped with suitable

(3a) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1928, Vol. III, p. 115.

attachments for introduction of hydrogen, for filling in vacuum and for removing the solutions. Large saturator tubes were provided to ensure that the incoming hydrogen was in vapor equilibrium with the cell solution. A vacuum technique was employed. These cells were found to give excellent results if the solutions contained 0.1 *M* hydrochloric acid or less. In working with solutions more concentrated than those reported in this study a cell designed to prevent diffusion and mechanical mixing of the solution in the two electrode compartments must be used.

Each set of cells was measured over a 20° temperature range at 5° intervals. One series was made from 0 to 20° and another from 20 to 40°. The accuracy of the electromotive force measurements was of the order of that obtained in aqueous solution, or ± 0.05 mv. No evidence appeared to indicate that the accuracy was less than this at any temperature.

Since the observations were so numerous, we shall resort to the expedient of giving the actual measurements at 25° in Table I, and later express the smoothed results at the other temperatures by suitable equations. Each result recorded in Table I is the mean of three measurements. Similar results were obtained at 0, 5, 10, 15, 20, 30, 35 and 40°.

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS H_2 (1 atm.) | $HCl(m), X\% CH_3OH-H_2O$ | $AgCl$ | Ag at 25° (*X* is Methyl Alcohol by Weight)

<i>X</i> = 10		<i>X</i> = 20	
<i>m</i>	<i>E</i>	<i>m</i>	<i>E</i>
0.004192	0.50051	0.004183	0.49441
.005450	.48739	.005560	.48027
.007135	.47414	.006668	.47129
.007998	.46846	.008214	.46117
.008566	.46516	.009056	.45641
.010139	.45684	.010861	.44751
.013615	.44256	.012626	.44013
.017275	.43093	.013858	.43561
.02212	.41886	.017599	.42389
.02501	.41288	.02035	.41695
.02689	.40941	.02412	.40919
.03219	.40071	.02843	.40093
.04073	.38935	.03509	.39073
.05555	.37446	.04010	.38430
.05622	.37393	.05468	.36956
.07591	.35951	.09958	.34127
.08710	.35293		
.11698	.33880		

5. Vapor Pressures of the Alcohol-Water Mixtures from 0 to 40°.—In order to correct the electromotive forces to one atmosphere hydrogen pressure, it was necessary to know the vapor pressures of the alcohol-water mixtures over the temperature range of 0 to 40°. These were measured by a semi-static device consisting of a bulb equipped with a closed tube manometer. Solution was introduced into the bulb over the mercury of the manometer and boiled *in vacuo* in

(4) These measurements were carried out in collaboration with Dr. Norris D. Embree.

order to free the system from air. The apparatus was mounted in a metal framework which was rocked mechanically in a water thermostat. The height of the mercury was measured by means of a Gaertner cathetometer reading to 0.005 cm. In order to establish a correction for the capillary depression of the mercury in the manometer the vapor pressure of pure water was measured. Over the entire range of temperature a constant correction of 0.8 mm. was found. This correction is approximately that calculated for the size of tube used. All pressures were corrected for the height of the liquid in the bulb and calculated to millimeters of mercury at 0°.

Vapor pressures of five solutions were measured. The results were smoothed by plotting $\log p/p_{H_2O}$ against $1/T$. These smooth values were then plotted against the weight per cent. of alcohol when a straight line relation was obtained at all temperatures. The compositions of these mixtures were determined by density measurements. The vapor pressures of the 10 and 20% methyl alcohol-water mixtures are given in Table II. The corrections to the observed electromotive forces were made by the well-known thermodynamic equation always employed for this purpose.

TABLE II

VAPOR PRESSURES OF METHYL ALCOHOL-WATER MIXTURES IN MM. (AT 0°) (*X* = % METHYL ALCOHOL BY WEIGHT)

<i>t</i>	<i>X</i> = 10	<i>X</i> = 20
0	6.57	8.58
5	9.35	12.50
10	13.11	17.30
15	18.18	23.90
20	24.90	32.65
25	33.7	43.8
30	45.1	58.7
35	59.6	77.1
40	78.1	100.6

6. Density Determinations.—The densities of these mixtures at the temperatures in question are given in Table III.

The Molal Electrode Potentials of the Silver-Silver Chloride Electrode in the Mixtures.—The electromotive forces of the cells under consideration are expressed by the equation

$$E = E_0 + (RT/F) \ln \gamma - (2RT/F) \ln \gamma m = E' - \frac{2k}{2k} \log \gamma m \quad (1)$$

where E_0 is the molal electrode potential of the silver chloride electrode in water E'_0 the molal electrode potential in the solvent under considera-

TABLE III

DENSITIES OF METHYL ALCOHOL-WATER MIXTURES ($X =$
% METHYL ALCOHOL BY WEIGHT)

t	$X = 10$	$X = 20$
0	0.9842	0.9721
5	.9839	.9709
10	.9834	.9696
15	.9825	.9681
20	.9813	.9663
25	.9799	.9644
30	.9782	.9622
35	.9763	.9598
40	.9742	.9572

tion, and γ and m are the activity coefficient and molality of the acid, respectively. In pure water $y = 1$; and $E_0 = E'_0$. y is a measure of the medium effect. Thus

$$\log y = \log (\gamma_1/\gamma_2); m = 0 \quad (2)$$

where γ_1 is the activity coefficient of the acid at zero concentration in water which by convention equals unity, and γ_2 is an activity coefficient of the acid at zero concentration in the other solvents measured in reference to the value in water.

E'_0 has been evaluated by the method suggested by Hitchcock which is derived by substituting for $\log \gamma$ in equation (1) the expression $-u \sqrt{c} + Bc$ where u is the Debye-Hückel constant and B an empirical constant. Upon rearranging the result, we obtain

$$E' = E + 2k \log m - 2ku \sqrt{c} = E' - Bc \quad (3)$$

We note that theory requires c , the concentration in moles per liter of solution. E' may be computed from the concentrations and electromotive forces and if this quantity be plotted against c curves which approach linearity as c decreases are obtained. The extrapolation to zero c may be made with ease and the values of $E'_0 = E'$ ($c = 0$) readily obtained. The values of u were computed from the dielectric constant measurements of Åkerlöf⁵ and the values of the universal constants given by the "International Critical Constant Tables."

These plots were made from the original results which were obtained at 5° intervals from 0 to 40°. The electromotive forces at 25° given in Table I are an example of the results used. From these plots, electromotive forces at round concentrations were obtained at the different temperatures. These may be represented by the equation

$$E = a + b(t - 20) + c(t - 20)^2 \quad (4)$$

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

with an accuracy of ± 0.05 mv. The constants a , b and c were determined by the method of least squares.

Table IV contains u , E'_0 at the nine temperatures in question and also the values of the constants a , b and c at the concentrations designated.

TABLE IV

MOLAL ELECTRODE POTENTIALS AND CONSTANTS OF EQUATION (4)

($X =$ % Methyl Alcohol by Weight)

$t, ^\circ\text{C.}$	u	E'_0	u	E'
0	0.5264	0.22762	0.5786	0.22022
5	.5310	.22547	.5844	.21837
10	.5359	.22328	.5907	.21631
15	.5411	.22085	.5973	.21405
20	.5465	.21821	.6043	.21155
25	.5524	.21535	.6114	.20881
30	.5576	.21220	.6190	.20567
35	.5648	.20892	.6271	.20246
40	.5717	.20550	.6354	.19910

CONSTANTS OF EQUATION (4)

m	$X = 10$			$X = 20$		
	a	$(b \times 10^6)$	$(-c \times 10^6)$	a	$(b \times 10^6)$	$(-c \times 10^6)$
0.001	0.56907	648.20	4.092	0.56260	673.90	4.687
.002	.53480	532.67	4.064	.52840	558.87	4.674
.005	.48989	382.53	4.034	.48361	409.13	4.609
.01	.45629	271.17	4.016	.45012	297.73	4.571
.02	.42303	161.63	3.996	.41697	187.93	4.521
.05	.37960	15.03	3.865	.37374	47.13	4.494
.1	.34698	-84.33	3.903	.34150	-51.83	4.144

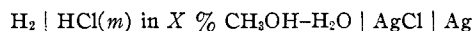
The values of the molal electrode potentials, E'_0 , may be computed with an accuracy of the order ± 0.05 mv. by the numerical equation

$$E'_0 (X=10) = 0.21818 - 555.63 \cdot 10^{-6} (t - 20) - 4.128 \cdot 10^{-6} (t - 20)^2$$

$$E'_0 (X=20) = 0.21151 - 529.10 \cdot 10^{-6} (t - 20) - 4.706 \cdot 10^{-6} (t - 20)^2$$

Summary

1. Electromotive force measurements of the cells



from 0 to 40° at 5° temperature intervals have been made in methanol-water mixtures containing 10 and 20% by weight of methanol.

2. Vapor pressures and densities of methanol-water mixtures of these percentages from 0 to 40° are recorded.

3. From these the molal electrode potentials of the silver-silver chloride electrode have been computed.