4. This agrees with the observation of Noyes that Milner's virial is $^2/_3$ that of Debye and Hückel.

5. The osmotic pressure can be calculated from ΔA and hence from ΔF, without a knowledge of the temperature coefficient of the dielectric constant of water.

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THE ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN GLYCEROL-WATER MIXTURES

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Comparatively few measurements of the electromotive force of concentration cells in other than aqueous solutions have been made. In the main these have been limited to cells with lithium chloride in a number of different alcohols and to hydrochloric acid in ethyl alcohol and alcohol-water mixtures.[1] In the present paper are given the results of measurements of the electromotive forces at 25° ± 0.01° of cells of the type, $H_2 \mid HCl\ (M) \mid AgCl \mid Ag$, in which the solvents used were 1 and 5 mole-per cent. of glycerol.

Apparatus, Materials and Procedure

The cell was of the usual H-shaped type into one arm of which the silver chloride electrode was inserted while the other bore the platinum electrode together with an outlet tube for the hydrogen. At the base of this latter arm was a pointed inlet tube through which the hydrogen passed in small bubbles over the platinized platinum electrode.

The silver-silver chloride electrodes were made in the manner described by Noyes and Ellis,[2] the silver being formed from silver oxide as was done by Lewis.[3] The silver chloride was formed on the electrode by making it the anode in a 0.75 *M* hydrochloric acid solution for five hours with a current of 0.004 ampere. A number of different sets of electrodes were made throughout the course of the investigation. The hydrogen electrodes consisted of platinized platinum foil and were remade after every third or fourth determination.

The hydrochloric acid was prepared by diluting by about one-half a high grade acid and redistilling. The middle fraction was diluted with distilled water and the concentration determined by gravimetric analysis. The glycerol used was a high grade product and no attempt was made to further purify it. Its water content was determined by measurements of its density. The solutions were made up in each case by adding to a weighed amount of the redistilled hydrochloric acid sufficient distilled water

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[1] Pearce and Mortimer, THIS JOURNAL, **40**, 509 (1918). Pearce and Hart, *ibid.*, **44**, 2411 (1922). Danner, *ibid.*, **44**, 2832 (1922). Harned and Fleysher, *ibid.*, **47**, 82 (1925). Nonhebel and Hartley, *Phil. Mag.*, [6] **50**, No. 298, 729 (1925).

[2] Noyes and Ellis, THIS JOURNAL, **39**, 2532 (1917).

[3] Lewis, *ibid.*, **28**, 166 (1906).

and glycerol to make the desired molality, account being taken of the water present in the acid and in the glycerol. In all cases the solutions were made up on the same day that they were used.

After the cell had been placed in the thermostat and the hydrogen started through, about five hours were allowed to elapse in order that the cell might come to equilibrium. From four to six readings were then taken over a period of about two and a half hours, the mean constituting the measurement of the cell. The variation in the reading was extremely small, seldom more than a few hundredths of a millivolt.

Results

From the data obtained in each series an attempt was made to extrapolate to zero concentration in the manner described by Lewis and Randall.[4] The variation in the electromotive force between duplicate determinations below 0.01 M and the reliability of the electrodes at low concentrations prevented this being done with any degree of certainty. These variations at the lower concentrations were due in part no doubt to the high internal resistance of the cells containing small amounts of acid. At higher concentrations the points lay very well on the curve.

The activity coefficients were, therefore, calculated by the method described by Hückel[5] which permits extrapolation to zero concentration from the data obtained in the less dilute solutions where greater accuracy is obtainable. For a single univalent electrolyte Hückel's equation giving the activity coefficient takes the form

$$\log \gamma = -\frac{A\sqrt{2c}}{1+\alpha\sqrt{2c}} + B\,2c - \log\,(1 + 0.002\,m\,M_0) \qquad (1)$$

Here γ is the activity coefficient of the electrolyte, c its concentration in moles per liter; thus $2c$ the concentration of the ions in moles per liter. The constant A was obtained from its defining equation, and the constants α and B were obtained as described by Hückel[6] from the measurements at 0.01, 0.2 and 1 M. In the above equation m represents the concentration of the electrolyte in moles per 1000 g. of solvent and M_0 the mean molecular weight of the solvent. The concentration (c) in terms of formula weights per liter of solution was obtained by use of the approximate equation, $c = m/([1/d_0] + km)$, in which m is the molality, d_0 the density of the pure solvent, and k a number which varies slightly with the concentration but which was here considered a constant and given the value of 0.02. The value of d_0 was taken from a plot of the data of Henkel and Roth and of Drucker.[7]

The choice of a value for D_0, used in determining the constants, leaves considerable question in the present case. The only data available for

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[4] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., **1923,** p. 334.

[5] Hückel, *Physik. Z.*, ***26,*** 93 (1925).

[6] Ref. 5, p. 123.

[7] Landolt-Börnstein, "Physikalisch-Chemische Tabellen," Springer, Berlin, **1912.**

mixtures of glycerol and water are those of Thwing.[8] The values here recorded for the two pure components, however, vary largely from the more commonly accepted ones. The curve showing the change in dielectric constant with the composition manifests a characteristic point at about 56 weight-per cent. of glycerol, indicating the formation of a hydrate at this composition and showing thus that the change in the dielectric constant is not a straight-line function of that of the two components. The deviation from a straight line between the two pure liquids is, however, very small up to 10% and only about 2 units at 25% of glycerol. The matter is further complicated by the fact that the dielectric constant of pure glycerol changes considerably with the wave length.[7] Since the value selected by Hückel for pure water was that determined by Drude at $\lambda = 75$ it was decided to use the value found for glycerol by this same worker at the same wave length. From the value found at 15° was subtracted the change found by Jezewski[9] over this temperature interval to bring the value to 25°. Using the values 78.77 for water and 22.9 for glycerol the dielectric constants for the mixtures were found by assuming the dielectric constant to be a linear function of the weight composition. For the reasons expressed above this method can be considered as giving only approximate values of the constants.

TABLE I

CONSTANTS FOR HYDROCHLORIC ACID

Solvent	D_0	A	α	B	$a \times 10^8$	2δ
Water............	78.8	0.357	0.940	0.0713	4.05	26.26
1 mole-% glyc.....	76.0	.374	1.083	.0673	4.59	28.30
5 mole-% glyc.....	66.9	.452	1.429	.0655	5.68	29.90
50 mole-% alc.....	37.1	1.105	1.374	.129	4.06	13.16
Alcohol...........	25.2	1.973	1.830	.023	4.46	1.73

In Table I, together with the values for D_0, are given the values of the constants used in calculating the activity coefficient from the equation above. The values given under $a \times 10^8$ were calculated by means of Hückel's equation (95*c*) and represent the mean diameter of the ions. The values of 2δ were calculated at 1 *M* acid concentration from Equation 95*b* and give the change in dielectric constant on the addition of one mole of acid to one liter of solution. There are included also in the table, for comparison, the values calculated by Scatchard[10] from his data on hydrochloric acid in water and those of Harned and Fleysher[11] on hydrochloric acid in alcohol and alcohol-water mixtures.

In Table II are given the results obtained from the cells containing various amounts of acid in one mole-per cent. of glycerol. In the first

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[8] Thwing, *Z. physik. Chem.*, **14**, 286 (1894).

[9] Jezewski, *J. phys. radium*, **3**, 293 (1922).

[10] Scatchard, THIS JOURNAL, **47**, 2098 (1925).

[11] Harned and Fleysher, *ibid.*, **47**, 82 (1925).

TABLE II

THE ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN ONE MOLE-PER CENT. OF GLYCEROL

m	E, volt	Av. dev., mv.	γ, calcd.	γ, obs.	E_0, volt
0.001	0.57768 (3)	0.71	0.964	0.940*	0.22090
.002	.54147 (2)	.94	.951	.951	.21960
.005	.49590 (2)	.32	.926	.924	.21974
.01	.46149	..	(.902)	(.902)	.21959
.02	.42758	..	.872	.873	.21955
.05	.38335	..	.827	.826	.21968
.1	.34951 (2)	.25	.792	.798	.21923
.2	.31610	..	(.764)	(.764)	.21958
.28	.29933	..	.756	.756	.21956
.38	.28391	..	.754	.753	.21969
.5	.26966	..	.758	.755	.21981
.7	.25124	..	.774	.772	.21975
1.0	.23039 (2)	.06	(.810)	(.810)	.21956
1.5	.20412 (2)	.03	.890	.901	.21896
2	.18298	..	.987	1.019	.21792
2.5	.16486	..	1.099	1.161	.21680
3	.14793	..	1.226	1.345	.21484
4	.11840	..	1.526	1.792	.21134

column is given the concentration (m) of the acid in terms of formula weights per 1000 g. of solvent (1 mole of glycerol + 99 moles of water), and in the second the electromotive force of the cell corrected by the usual thermodynamic equation to one atmosphere of dry hydrogen. The correction was approximated by assuming that Raoult's law held for the mixed solvent and disregarding the effect of the acid on the vapor pressure. All measurements made are included in the table. When more than one determination was made at the same concentration the mean of these is given followed by the number of determinations and, in the next column, the average deviation from the mean expressed in millivolts. These duplicate measurements consisted in completely rebuilding the cell using freshly made solutions and usually different electrodes.

The values of the activity coefficient calculated from Equation 1 are given in the fourth column. The values in the fifth column were obtained from the equation $\Delta E = 0.1183 \log (\gamma_1 m_1/\gamma_2 m_2)$. In the present case γ_2 was assigned the value calculated from Hückel's equation at 0.01 M and thus ΔE was the difference between the electromotive force at m_1 and at 0.01 M.

In the last column are given the values of E_0 calculated from the equation, $E_0 = E + 0.1183 \log \gamma\, m$, in which E is the measured electromotive force at the concentration m, and γ the calculated activity coefficient. If Equation 1 were strictly obeyed these values would be constant within experimental error. The constancy from 0.01 to 1 M is obviously very good. The mean value of E_0 in this range is 0.21960 volt and the mean deviation, positive and negative, from this value is 0.106 mv.

TABLE III

THE ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN FIVE MOLE-PER CENT. GLYCEROL

m	E, volt	Av. dev., mv.	γ, calcd.	γ, obs.	E_0, volt
0.001	0.56812 (3)	0.12	0.957	0.908*	0.21096
.002	.53232 (2)	.25	.941	.912*	.20991
.005	.48600 (2)	.06	.913	.898	.20911
.01	.45115	..	(.885)	(.885)	.20827
.02	.41715	..	.853	.858	.20800
.05	.37299	..	.805	.810	.20794
.1	.33970	..	.771	.775	.20803
.2	.30614	..	(.744)	(.744)	.20826
.28	.28929 (2)	.02	.738	.738	.20827
.38	.27360 (3)	.22	.737	.738	.20822
.5	.25955	..	.744	.737	.20874
.7	.24073 (2)	.07	.762	.760	.20844
1.0	.21969	..	(.801)	(.801)	.20829
1.5	.19281	..	.884	.901	.20731
2	.17112	..	.984	1.030	.20590
2.5	.15224	..	1.098	1.190	.20412
3	.13510	..	1.227	1.385	.20205
4	.10369	..	1.530	1.914	.19676

In Table III are given the results obtained from cells containing various amounts of acid in five mole-per cent. glycerol. The significance of the column headings is the same as in Table II and the values were obtained in the same manner. The mean value of E_0 from 0.01 to 1 M is 0.20825 and the average deviation, positive and negative, in this range is 0.158 millivolt.

By the nature of the calculation the observed and calculated values of the activity coefficient placed in brackets in Tables II and III must be identical at the same concentration in each series. The agreement between the observed and calculated results is as good as could be expected betweeen 0.01 and 1 M and is well within the experimental error. The agreement seems to be slightly better in the 1 mole-per cent. solutions than in the 5 mole-per cent. solutions and to extend over a slightly greater range. The observed values designated with an asterisk are obviously in error. Since the average deviations from the mean values are not large with these points, especially in the 5 mole-per cent. solution, the results indicate that this type of electrode does not function properly at high dilutions in glycerol-water solutions. Results below 0.002 M in 1 mole-per cent. of glycerol and below 0.005 M in 5 mole-per cent. glycerol are obviously not dependable and thus no extrapolation to zero concentration could be made from experimental data in this region.

Above 1 mole-per cent. of acid the observed results rise above the calculated, those in the 5 mole-per cent. solution being higher than those in the 1 mole-per cent. It is interesting to note that this same reversal takes place in the calculated results but to a less extent. The curves of the observed results cross at about 1.5 *M* acid concentration and the calculated curves at about 2.5 *M*. The departure of the observed and calculated results at higher acid concentrations can scarcely be attributed to reaction between the acid and the solvent because of the self-consistency of the results. Further, since the production of glycerol chlorohydrin takes place by the action of concd. hydrochloric acid or dry hydrogen chloride on glycerol at moderately high temperatures, it seems unlikely that this reaction would take place in the relatively dilute solutions at 25° in the time required for a determination. We may rather believe the disagreement between the calculated and observed results above 1 *M* acid to be due to the approximations in determining the concentrations in moles per liter, the uncertainty of the values of the dielectric constant, or causes which are not taken into consideration in this calculation.

In order to attempt to fit the observed and calculated results along the entire curve more closely, constants were calculated for the one mole-per cent. solution using the results at 0.01, 0.2 and 4 *M*. By the nature of the calculation the observed and calculated values agree up to these points. However, it was found that up to 2 *M* the agreement between the two was better, using the constants given above. Since the greatest experimental accuracy is doubtless obtainable between 0.01 and 1 *M* and the validity of the equation greatest in this region it was thought preferable to use the constants given above although the differences between the observed and calculated values of the activity coefficients rise to about 5, 9 and 15% at 2.5, 3 and 4 *M*, respectively.

Summary

Results are given of the electromotive force at 25° of cells of the type $H_2 \mid HCl \mid AgCl \mid Ag$, in which the solvents were 1 and 5 mole-per cent. of glycerol. The acid concentration was varied from 0.001 *M* to 4 *M*.

From these results the values of the activity coefficient have been calculated by the method of Hückel.

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