483. *The Standard Electrode Potential of the Silver–Silver Chloride Electrode in Water–Glucose Mixtures.*

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The standard electrode potential of the silver–silver chloride electrode in various water–glucose mixtures has been determined, cells without liquid junction being used. The mean activity coefficients of hydrochloric acid in such solutions have been measured, and values for the distance of closest approach of ions in such solutions suggested.

The silver–silver chloride electrode is being used as the reference electrode in an investigation into the change of certain electrode potentials in mixed solvents. Values of the standard electrode potential of this electrode in aqueous mixtures of alcohol, glycerol, or dioxan, etc., have been measured by various experimenters, but values of the potential in aqueous glucose mixtures are not on record.

Experimental.

Standard solutions of hydrochloric acid were made from redistilled hydrochloric acid and conductivity water. They were analysed by titration with borax, and the chloride content determined gravimetrically by precipitation with silver chloride.

To the hydrochloric acid solutions was added glucose of " AnalaR " grade, the mixture being made by weight. Immediately dissolution had been attained the solutions were placed in the cell and immersed in a thermostat controlled at 25°. Measurements were then made of the E.M.F. of cells of general type H_2|HCl, water, glucose, AgCl|Ag, a Cambridge potentiometer and a standard Weston cell made by the Cambridge Instrument Company being used.

Preliminary experiments had shown that precipitated silver chloride *in acid solution* is not reduced by glucose even after several days in the absence of light. It would appear therefore that silver–silver chloride electrodes should function satisfactorily in an aqueous hydrochloric acid–glucose solution. Notwithstanding this, and the fact that if such cells were set up steady values of E.M.F. were obtained some few minutes after introduction of the electrodes, if such cells were left for 8—30 hours large fluctuations in the measurements were found and these were not precisely reproducible. It is considered, however, that the non-reproducibility of results in aged cells is not due to deterioration of the silver–silver chloride electrodes but to bacterial action in the glucose solution, because (*a*) such errors remain if a " fresh " silver–silver chloride electrode is immersed in an aged solution, and (*b*) if the cell contains only a trace of hydrochloric acid in the presence of sufficient potassium chloride to maintain the conductance of the solution, the variation of E.M.F. as the solution ages during 1—2 days indicates an increase in hydrogen-ion concentration suggesting bacterial oxidation of the aqueous glucose to an acid product.

The values of E.M.F. were, however, found to be reproducible as long as they were measured 1—2 hours after dissolution of the glucose, and in no cases were the reported readings taken after that time.

Hydrogen electrodes were prepared according to Popoff, Kunz, and Snow (*J. Physical Chem.*, 1928, **32**, 1056), and hydrogen was purified by passage through soda–lime tubes and was saturated with water vapour, before entering the cell, by passage through water–glucose–hydrochloric acid solutions of the same composition as those in the electrolytic cell. Silver–silver chloride electrodes were prepared following Brown (*J. Amer. Chem. Soc.*, 1934, **56**, 646), and the electrodes obtained were all tested in pairs in the same aqueous hydrochloric acid solutions in cells of type Ag|AgCl (I) HCl AgCl|Ag (II) and all pairs which did not give zero E.M.F. were discarded.

All measurements of the glucose cells were made by use of two hydrogen electrodes and two silver–silver chloride electrodes, and each cell was made up twice. The recorded results represent therefore the mean values of at least four readings. The solutions were stirred except when the actual readings were taken. The densities of the various solutions were measured by means of a specific gravity bottle.

Results and Discussion.—Readings were obtained for various concentrations of hydrochloric acid in water–glucose mixtures containing 15, 25, 32, 40, or 50 g. of glucose per 100 g. of mixture. The barometric pressure was read at the time that each E.M.F. reading was made, and after allowance had been made for the water vapour pressure of such solutions at 25°, the observed E.M.F. readings were corrected to a partial pressure of hydrogen of exactly 1 atm. These corrected values are recorded as the " observed " readings. In the following tables m represent the molality of hydrogen chloride, and ρ the density of the water–glucose mixtures; E and $E + (2\boldsymbol{RT}/\boldsymbol{F}) \ln m$ are recorded in volts.

15% Glucose solutions, $\rho = 1{\cdot}0608$.

E	0·3218	0·3468	0·3619	0·3831	0·3959	0·4103	0·4235	0·4501	0·4782	0·5181
m	0·1439	0·0858	0·0625	0·0400	0·0306	0·0225	0·01717	0·01000	0·00562	0·00250
$E + (2\boldsymbol{RT}/\boldsymbol{F}) \ln m$	0·2222	0·2206	0·2195	0·2177	0·2168	0·2158	0·2147	0·2135	0·2118	0·2103

25% Glucose solutions, $\rho = 1{\cdot}1042$.

E	0·3061	0·3382	0·3626	0·3819	0·3994	0·4156	0·4264	0·4599	0·4944
m	0·1646	0·0820	0·0491	0·03274	0·02285	0·01634	0·01305	0·00654	0·00326
$E + (2\boldsymbol{RT}/\boldsymbol{F}) \ln m$	0·2134	0·2097	0·2078	0·2062	0·2052	0·2042	0·2035	0·2015	0·2002

32% Glucose solutions, $\rho = 1{\cdot}1339$.

E	0·3271	0·3439	0·3540	0·3652	0·3780	0·3924	0·4161	0·3414	0·4606	0·5004
m	0·0900	0·0625	0·0506	0·0400	0·0306	0·02250	0·01374	0·01000	0·00562	0·00250
$E + (2\boldsymbol{RT}/\boldsymbol{F}) \ln m$	0·2034	0·2015	0·2007	0·1998	0·1988	0·1975	0·1958	0·1948	0·1930	0·1917

40% Glucose solutions, $\rho = 1{\cdot}1721$.

E	0·2997	0·3176	0·3362	0·3564	0·3760	0·3926	0·4088	0·4198	0·4536
m	0·1317	0·0900	0·06075	0·03929	0·02592	0·01828	0·01314	0·01044	0·00523
$E + (2\boldsymbol{RT}/\boldsymbol{F}) \ln m$	0·1955	0·1939	0·1923	0·1901	0·1883	0·1870	0·1862	0·1854	0·1837

50% Glucose solutions, $\rho = 1{\cdot}2254$.

E	0·2931	0·3049	0·3261	0·3505	0·3699	0·3868	0·4029	0·4139	0·4476
m	0·10975	0·02527	0·05465	0·03274	0·02175	0·01524	0·01095	0·00870	0·00435
$E + (2\boldsymbol{RT}/\boldsymbol{F}) \ln m$	0·1796	0·1784	0·1768	0·1748	0·1732	0·1718	0·1710	0·1702	0·1682

The E.M.F. of the cells measured may be expressed by the equation

$$E = E_0 - (2\boldsymbol{RT}/\boldsymbol{F}) \ln a_{\pm} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $a_{\pm}$ represents the mean activity of the electrolyte and E_0 the standard E.M.F. of the cell. Since by convention the standard electrode potential of hydrogen is taken as zero, E_0 represents the standard electrode potential of the silver–silver chloride electrode in the solvent considered.

There are various methods by which E_0 can be obtained from equation (1). The simplest follows Lewis and Randall (*J. Amer. Chem. Soc.*, 1921, **43**, 1112), who rearranged the equation to the form

$$E + (2\boldsymbol{RT}/\boldsymbol{F}) \ln m = E_0 - (2\boldsymbol{RT}/\boldsymbol{F}) \ln \gamma_{\pm} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $\gamma_{\pm}$ represents the mean activity coefficients of the electrolyte at molality m. A plot of the left-hand side of equation (2) against $m^{\frac{1}{2}}$ gives a line showing little curvature which on extrapolation to zero concentration gives E_0, since at zero concentration the mean activity coefficient equals unity. Owing to the facts that the values of the E.M.F. at very low concentrations are difficult to determine exactly, and that the graph shows a slight curvature, the extrapolation is not absolutely certain.

A more precise extrapolation, originally suggested by Brown and MacInnes (*ibid.*, 1935, **57**, 1356), is obtained for dilute solutions of uni-univalent electrolytes by means of the Debye–Hückel equation expressing the mean activity coefficient as follows :

$$-\log \gamma_{\pm} = \frac{Am^{\frac{1}{2}}}{1 + \beta a_i m^{\frac{1}{2}}} + \log\left(1 + \frac{2mM}{1000}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In this equation $A = 1{\cdot}8123 \times 10^6 \rho^{\frac{1}{2}}/(DT)^{3/2}$ and $\beta = 50{\cdot}288 \times 10^8 \rho^{\frac{1}{2}}/(DT)^{\frac{1}{2}}$, where a_i is the distance of closest approach (in cm.) of the ions, ρ is the density of the solvent, D is the dielectric constant of the medium, and M is the mean molecular weight of the solvent $= 100/(X/M_x + YM_y)$, X and Y being the percentages of water and glucose, respectively, and M_x and M_y their molecular weights.

Substituting equation (3) in equation (2) and representing

$$\frac{4{\cdot}6052\boldsymbol{RT}}{\boldsymbol{F}} \log\left(1 + \frac{2mM}{1000}\right) \text{ by } E_{\rho}$$

we obtain

$$E + \frac{2\boldsymbol{RT}}{\boldsymbol{F}} \ln m = E_0 + \frac{0{\cdot}1183Am^{\frac{1}{2}}}{1 + \beta a_i m^{\frac{1}{2}}} + E_{\rho} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

which on rearrangement gives

$$E - E_\rho + \frac{2\boldsymbol{RT}}{\boldsymbol{F}} \ln m - 0{\cdot}1183Am^{\frac{1}{2}} = E_0 - (E - E_\rho + \frac{2\boldsymbol{RT}}{\boldsymbol{F}} \ln m - E_0)\beta a_i m^{\frac{1}{2}} \quad . \qquad (5)$$

A plot of the left-hand side against $[E - E_\rho + (2\boldsymbol{RT}/\boldsymbol{F}) \ln m - E_0]m^{\frac{1}{2}}$ is made, an approximate value of E_0 being assumed from the plots made according to the method of Lewis and Randall, and the approximation is continued until a straight line is obtained and until the value of E_0 given by the intercept at zero concentration equals the value of E_0 assumed. From the slope of the graph, which equals $-\ \beta a_i$, a_i can be calculated.

Values for the dielectric constant of aqueous glucose mixtures are not reported in the literature but values for aqueous sucrose, mannitol, glycerol, and ethylene glycol mixtures are given by Harned and Owen (" Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., 1943, p. 118), and mixtures containing the same percentage of water by weight show values of dielectric constant very close together. Since these substances contain polar groups similar to those in glucose, we might expect water–glucose mixtures to have dielectric constants of approximately the same values. If this reasoning is correct the dielectric constants (D) of water–glucose mixtures should be approximately as follows : 50% glucose 64·0, 40% glucose 67·5, 32% glucose 70·0, 25% glucose 72·0, 15% glucose 74·8. These values being used for the calculation of A and B in each case, plots were made as described above, and satisfactory straight lines were obtained intercepting the axis at zero concentration at the following values for E_0 :

Glucose in solution, %	15	25	32	40	50
E_0, volts	0·2074	0·1964	0·1885	0·1788	0·1634

These values correspond very closely (within ±0·1 mv.) with the values which would be suggested by the plot of $E + (2\boldsymbol{RT}/\boldsymbol{F}) \ln m$ against $m^{\frac{1}{2}}$.

These results therefore suggest that : (*a*) The standard electrode potentials of the silver–silver chloride electrode in water–glucose mixtures are as given above. (*b*) The values of the dielectric constant of water–glucose mixtures are very close to those suggested. (*c*) Because straight lines are obtained, the mean activity coefficients of hydrochloric acid in such solutions are adequately described by equation (3), and the Gronwall, La Mer, and Sandved extension terms (*Physikal. Z.*, 1928, **29**, 358) need not be included even in the solution of lowest dielectric constant considered. This supports Harned and Morrison's statement (*Amer. J. Sci.*, 1937, **33**, 161 ; *J. Amer. Chem. Soc.*, 1936, **58**, 1908) that in the calculation of activity coefficients of hydrochloric acid in dioxan–water mixtures the Gronwall, La Mer, and Sandved extension terms play a significant part only in solutions of dielectric constant less than 60.

The Mean Activity Coefficients of Hydrochloric Acid in Water–Glucose Mixtures.—Insertion of the values for E_0 given above in equation (2) leads to evaluation of the mean activity coefficients of hydrochloric acid at the various concentrations concerned. These have been evaluated, and from the graphs the values at rounded concentrations are given in the following table, the values for the activity coefficients in pure water, included for comparison, being obtained from Shedlovsky and MacInnes (*J. Amer. Chem. Soc.*, 1936, **58**, 1930).

Mean activity coefficients (reported as $-\log_{10}\gamma_{\pm}$*) of* HCl *in water–glucose mixtures at* 25°.

	Glucose, %.					
m.	0.	15.	25.	32.	40.	50.
0·1	0·0989	0·1162	0·1188	0·1264	0·1285	0·1345
0·09	—	0·1130	0·1156	0·1223	0·1252	0·1305
0·08	—	0·1094	0·1124	0·1183	0·1212	0·1272
0·07	—	0·1045	0·1076	0·1134	0·1165	0·1216
0·06	—	0·0996	0·1030	0·1078	0·1117	0·1164
0·05	0·0807	0·0936	0·0965	0·1010	0·1046	0·1096
0·04	—	0·0870	0·0898	0·0938	0·1075	0·1030
0·03	—	0·0788	0·0815	0·0846	0·0875	0·0934
0·02	0·0578	0·0675	0·0709	0·0728	0·0752	0·0807
0·01	0·0434	0·0506	0·0521	0·0550	0·0568	0·0612
0·005	0·0323	0·0350	0·0365	0·0324	0·0404	0·0431

The Distance of Closest Approach of Ions.—The slope of the graphs in which $E - E_\rho + (2\boldsymbol{RT}/\boldsymbol{F}) \ln m - 0{\cdot}1183\ Am^{\frac{1}{2}}$ is plotted against $[E - E_\rho + (2\boldsymbol{RT}/\boldsymbol{F}) \ln m - E_0]m^{\frac{1}{2}}$ equals $-\ \beta a_i$. By using the values of D listed above, values of β have been obtained which lead to the following values for the distance of closest approach of ions :

Glucose solution, %	15	25	32	40	50
Distance of closest approach, A.	4·9	5·3	4·95	5·3	6·2

These values correspond closely to the value of 5·3 A. for hydrochloric acid in water determined by Harned and Ehlers (*J. Amer. Chem. Soc.*, 1932, **54**, 1350), suggesting that the presence of glucose in the solution does not affect the distance of closest approach of ions, and also that the ions are solvated in such mixtures completely by water molecules and that the glucose molecules do not take part in or interfere with such solvation.

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