[CONTRIBUTION FROM THE VENABLE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

Potential Studies with the Silver–Silver Chloride Electrode in Aqueous Solutions of Hydrochloric Acid and *d*-Glucose at 25°

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In continuation of work on activities being carried on in this Laboratory, the electromotive force measurements of cells

$$H_2/HCl(m),\ d\text{-glucose}(x),\ H_2O(y)/AgCl\text{-}Ag$$

at 25° in solutions containing 5, 10, 20 and 30% *d*-glucose by weight have been made. From these measurements the standard potentials of the cells and the ion size parameter in the various aqueous *d*-glucose solutions were obtained. The experimental activity coefficients of hydrochloric acid were determined at acid concentrations of 0.005 to 0.5 *m*.

Electromotive force measurements on cells of the above type using organic solvents, especially of the hydroxyorganic type, have been summarized by Harned and Owen.[1] Extensive work has been done in dioxane–water mixtures by Harned and co-workers.[2] Investigations in aqueous hydroxyorganic media include methanol–water solutions by Harned and Thomas[3]; ethanol–water solutions by Harned and Fleysher,[4] Harned and Calmon,[5] Scatchard,[6] and Patterson with Felsing[7]; propanol-2–water solutions by Harned and Calmon,[5] and Moore with Felsing[8]; and glycerol–water solutions by Lucasse.[9] Recent work at this Laboratory has involved studies in ethylene glycol–water mixtures by Knight, Masi and Roesel,[10] and an expansion of this work is soon to be published. However, it is thought that the research reported in this paper is the first wherein the organic media involve such a complex molecule as *d*-glucose, although Scatchard[11] has reported a few electromotive force measurements in sucrose solutions. The complexity of the *d*-glucose molecule may account for some of the abnormalities, such as large ion size parameter and non-linear Debye–Hückel relations, that were found in this investigation.

Experimental

The methods of purification of chemicals (except *d*-glucose), the preparation of the electrodes and the experimental procedure were essentially the same as those of Knight, Masi and Roesel.[10]

d-Glucose.—Merck Reagent Grade anhydrous dextrose was used. Analysis for water, acid (as acetic), chloride, etc., showed this reagent sufficiently pure for research use.

Densities.—Density measurements were made at 25° in a pycnometer of about 25-ml. capacity.

Vapor Pressures.—The vapor pressures of the solvent mixtures were assumed to obey Raoult's law[12] and were so calculated.

Dielectric Constants.—The dielectric constants of the *d*-glucose solutions were determined at the National Bureau of Standards[13] as earlier values were not in agreement.[14,15]

The electromotive force measurements, corrected to 1 atm. of hydrogen, are averages of three cells usually agreeing within ±0.05 mv. Such checks were readily obtainable in moderate acid concentration, but in acid ranges above 0.1 *m*., agreement between cells was not as good, although in all cases the cells agreed within ±0.1 mv.

Calculations and Results

The standard potentials were determined by the use of the function E', defined by the equation

$$E' = E + 0.1183 \log m - \frac{0.1183A\sqrt{c}}{1 + \mathring{a}B\sqrt{c}} - 0.1183 \log (1 + 0.002\, mM_{xy}) = E^\circ_m + f(m) \quad (1)$$

where E' is the apparent molal potential, E is the observed electromotive force corrected to 1 atm. of hydrogen, m is the molality, A and B are Debye–Hückel constants, $\mathring{a}$ is the ion size parameter in Å., c is the concentration in moles per liter and M_{xy} is the mean molecular weight of the solvent.

Table I[16] gives the observed electromotive force, molality and E' (for $\mathring{a}$ = 6.6 Å.) for each of the solutions and Table II shows the values used for the constants of equation (1) in each solution.

Empirical formulas for the densities of the various solutions are given

$$d(5\%\ d\text{-glucose}) = 1.0162 + 0.0173m$$
$$d(10\%\ d\text{-glucose}) = 1.0361 + 0.0173m$$
$$d(20\%\ d\text{-glucose}) = 1.0779 + 0.0162m$$
$$d(30\%\ d\text{-glucose}) = 1.1229 + 0.0153m$$

where d is the density of the respective *d*-glucose solutions of hydrochloric acid molality, m.

The data shown in Table I gives the molality of hydrochloric acid, the density of the solutions, the observed electromotive force, and the apparent molal potential (for $\mathring{a}$ = 6.6 Å.) of cells

$$H_2/HCl\ (m),\ d\text{-glucose}\ (x),\ H_2O\ (y)/AgCl\text{-}Ag$$

(1) Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, pp. 331–346.

(2) Harned, *et al.*, THIS JOURNAL, **58**, 1908 (1936); **60**, 336 (1938); **60**, 339 (1938); **60**, 2128 (1938); **60**, 2130 (1938); **60**, 2133 (1938); **61**, 44 (1939); **61**, 48 (1939); **61**, 49 (1939).

(3) Harned and Thomas, *ibid.*, **57**, 1666 (1935); **58**, 761 (1936).

(4) Harned and Fleysher, *ibid.*, **47**, 82 (1925).

(5) Harned and Calmon, *ibid.*, **61**, 1491 (1939).

(6) Scatchard, *ibid.*, **47**, 2098 (1925).

(7) Patterson with Felsing, *ibid.*, **64**, 1478 (1942).

(8) Moore with Felsing, *ibid.*, **69**, 1076 (1947).

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

(10) Knight, Masi and Roesel, THIS JOURNAL, **68**, 661 (1946).

(11) Scatchard, *ibid.*, **48**, 2026 (1926).

(12) Pozner and Amirkhanov, *J. Phys. Chem.* (*U. S. S. R.*), **15**, 1137 (1941).

(13) Private communication, The National Bureau of Standards, Washington 25, D. C., June, 1948.

(14) Furth, *Ann. Physik*, **70**, 63 (1923).

(15) Berliner and Ruter, *Kolloid Z.*, **47**, 251 (1929).

(16) Table I is not shown here but is available through American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., Document 2705, microfilm or photoprints, 50¢.

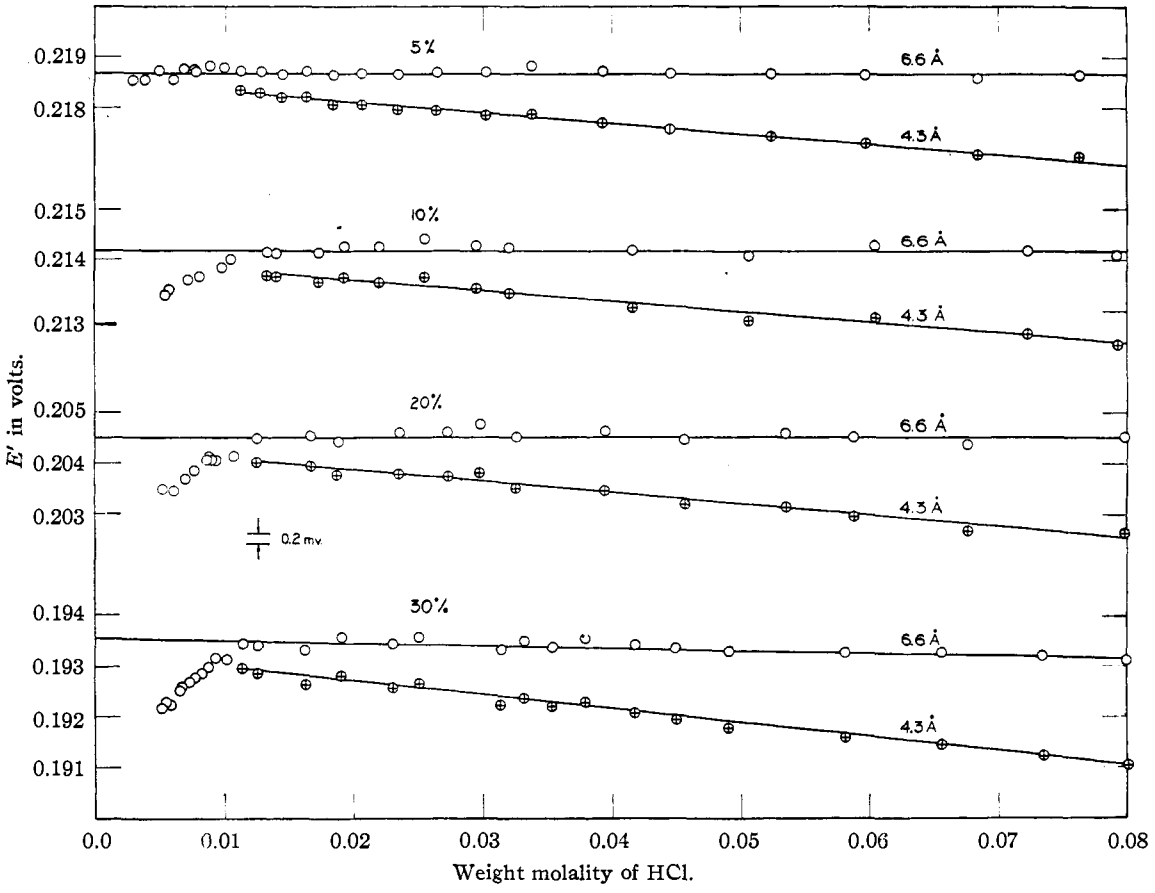

Fig. 1.—The molal electrode potentials of the silver–silver chloride electrode in aqueous *d*-glucose solutions: curve families from top to bottom are: 5% *d*-glucose; 10% *d*-glucose; 20% *d*-glucose; 30% *d*-glucose.

at 25° in solutions containing 5, 10, 20 and 30% *d*-glucose by weight.

TABLE II

CONSTANTS OF EQUATIONS (1) AND (5)

	A	*B*	M_{xy}	*å*, Å
5% *d*-Glucose	0.52044	0.33105	18.86	6.6
10% *d*-Glucose	.53383	.33386	19.81	6.6
20% *d*-Glucose	.56356	.33995	21.97	6.6
30% *d*-Glucose	.59868	.34687	24.68	6.6

TABLE III

STANDARD POTENTIALS OF THE CELLS
H_2/HCl (*m*), *d*-GLUCOSE (*x*), H_2O (*y*)/AgCl–Ag

	D	E^0_m	E^0_N	E^0_c
5% *d*-Glucose	77.3	0.21863	0.01468	0.21951
10% *d*-Glucose	76.1	.21419	.01271	.21601
20% *d*-Glucose	73.4	.20451	.00835	.20836
30% *d*-Glucose	70.5	.19355	.00336	.19951

Straight lines were obtained in the lower acid concentration ranges when E' was plotted against the weight molality, *m*, and from them the standard potentials, E^0_m, were obtained to within ±0.1 mv. The "extended form" of the Debye–Hückel expression for activity was not employed as the dielectric constants of the various solutions were too high to have appreciable effect on the E' values.[1] An *å* value of 4.3 Å. was first used as this was the value found by Harned and Ehlers[17] for aqueous solutions and is recommended by Harned and Owen[1] in solutions of higher dielectric constant ($D \geq 60$). However, it was necessary to employ an *å* value of 6.6 Å. to obtain lines of zero slope in the 5, 10 and 20% *d*-glucose solutions, and a slightly larger value is indicated for the 30% solution, as can be seen in Fig. 1 which shows the E' *vs.* *m* plot from 0.01 to 0.08 *m*. The average deviation of the points from these lines is between 0.05 and 0.1 mv.

Examination of Table I[16] and Fig. 1 will show that the E' *vs.* *m* plot is straight only between 0.01 and 0.08 *m*, except in 5% *d*-glucose. Below 0.01 *m* the E' values fall sharply with small changes in acid concentration, while above 0.08 *m* the values also decrease. Numerous readings were taken in an acid range of 0.003 to 0.01 *m*, but in every case the E' values were lower than in the 0.01 to 0.08 *m* limits and fell on a straight line with a large positive slope. Standard potentials determined from these lines would not be satisfactory for activity and similar calculations in acid

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

concentrations greater than 0.01 *m* and are not included here. The slope of the lines reported by Knight, Masi and Roesel[10] may indicate that similar results were obtained in certain ethylene glycol solutions.

The standard potentials at 25° on the *m*-, *c*- and *N*-scales are related by the equations

$$E^0_c = E^0_m + 0.1183 \log d_0 \quad (2)$$

$$E^0_N = E^0_m - 0.1183 \log (1000/M_{xy}) \quad (3)$$

where the *m*-, *c*- and *N*-subscripts refer to molal, molar and mole fraction concentration units, respectively, and d_0 is the density of the solvent. Table III gives the values of E^0_m, E^0_c and E^0_N for 5, 10, 20 and 30% *d*-glucose solutions as well as their dielectric constants.

In Fig. 2 values of E^0_m are plotted against the reciprocal of the dielectric constant of the medium. The origin of the plot on the left of the figure represents E^0_m for pure water. The curve is typical of plots of this type.

Activity Coefficients

The mean activity coefficients, $\gamma_\pm$, of hydrochloric acid in the various *d*-glucose solutions were computed from the electromotive force measurements and molalities given in Table I[16] and the standard potentials, E^0_m, given in Table II, by means of the equation

$$\log \gamma_\pm = (E^0_m - E)/0.1183 - \log m \quad (4)$$

The values of $\gamma_\pm$ were plotted against *m* on a large scale and from such plots the activity coefficients at rounded molalities were established and assembled in Table IV. For comparison, values of $\gamma_\pm$ for water are also listed.

TABLE IV

MEAN ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN *d*-GLUCOSE–WATER MIXTURES AT 25°

X = weight per cent. *d*-glucose in solvent

Molality	*X* = 0[a]	*X* = 5	*X* = 10	*X* = 20	*X* = 30
0.005	0.9285	0.929	0.942[b]	0.944[b]	0.941[b]
.01	.9048	.904	.907	.903	.897
.02	.8755	.877	.873	.867	.856
.05	.8304	.833	.829	.818	.811
.07		.816	.811	.801	.793
.1	.7964	.799	.794	.782	.774
.2	.7667	.769	.765	.750	.746
.3		.759	.753	.743	.739
.4		.758	.752	.743	.737
.5	.7571	.762	.753	.744	.743
.6		.768[c]	.761	.755	.753[c]
.7			.776	.777[c]	

[a] Harned and Owen, ref. 1, p. 340. [b] From non-linear portion of curves in Fig. 1. [c] Extrapolated values.

The experimental activity coefficients should be capable of representation by a Debye–Hückel equation of the type

$$\log \gamma_\pm = -\frac{A\sqrt{c}}{1 + \mathring{a}B\sqrt{c}} - \log (1 + 0.002\, mM_{xy}) + C'c \quad (5)$$

A "salting out" constant, C', in the linear term, $C'c$, was not necessary to fit experimental and calculated activity coefficients (within ±0.002) in the acid range of about 0.01 to 0.08 *m*, except in the case of the 30% medium, where a value of 0.04 was needed from 0.05 to 0.11 *m*. Since the relations between E' and *m* were not linear in all the *d*-glucose solutions of acid concentration greater than 0.08 *m*, it was impossible to match experimental and calculated activities with the linear term in equation (5). Fair agreement (±0.005) could be accomplished from approximately 0.08 to 0.5 *m* by substituting a quadratic term, $G'c^2$ for the $C'c$ term. A single value for G' of 0.15 in the 5, 10 and 20% solutions in the range of 0.08 to 0.5 *m* was satisfactory. In the 30% medium G' values of 0.22, 0.18 and 0.15 best reproduced the experimental activity coefficients in the ranges of 0.11 to 0.3 *m*, 0.3 to 0.4 *m* and 0.4 to 0.5 *m*, respectively.

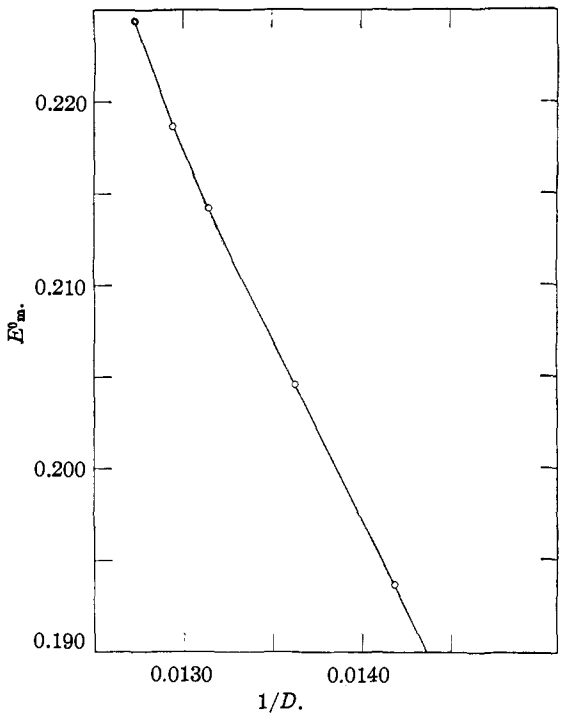

Fig. 2.—A plot of E^0_m *vs.* $1/D$ in aqueous *d*-glucose solutions. The origin of the plot represents E^0_m in pure water.

Harned and co-workers[3,4,5] as well as Felsing and co-workers[7,8] have attained linear relations between E' and *m* for methanol–, ethanol– and propanol-2–water mixtures in acid ranges up to 1 *m* and consequently could find $\mathring{a}$ and C' values suitable for calculating activity coefficients over the whole range of concentrations. In this work, in acid ranges above 0.08 *m* the E' *vs.* *m* plot changes from a straight line to a smooth curve reminiscent of similar plots reported by Harned and co-workers[2] in dioxane solutions and explains why the quadratic term $G'c^2$ is necessary to match experimental activities with the Debye–

Hückel expression for activity coefficient (equation 5).

Behavior of Cells

It was found that after the cells were filled and placed in the constant temperature bath, the time required to reach equilibrium (±0.03 mv. for at least two hours) was longer than most other reported work of this nature, especially in the higher *d*-glucose concentrations and in the higher hydrochloric acid concentrations. In the acid range of 0.01 to about 0.1 *m*, where most of the electromotive force readings were recorded, equilibrium times of 2 to 4, 4 to 6, 6 to 8 and 8 to 12 hours were required in the 5, 10, 20 and 30% *d*-glucose solutions, respectively. In the acid range above 0.1 *m* the electromotive force increased very rapidly for four to eight hours or longer until readings were suspended and the cells allowed to stand overnight. When readings were resumed next day the cells had stabilized and constant measurements could be obtained. This initial instability occurred even in solutions prepared several days prior to filling the cells and indicated some reaction occurred after the flow of hydrogen was begun. Scatchard[11] mentioned similar findings in sucrose solutions.

Acknowledgment is gratefully made to the National Bureau of Standards for the determination of the dielectric constants used in this investigation.

Summary

1. The values of the electromotive force at 25° of cells of the type H_2/HCl (*m*), *d*-Glucose (*x*), H_2O (*y*)/AgCl-Ag were determined for acid concentrations up to 0.5 *m* and for 5, 10, 20 and 30 weight per cent. *d*-glucose.

2. From the data obtained the standard potentials of the solutions were determined.

3. An ion size parameter for hydrochloric acid of 6.6 Å. is indicated in the solutions studied.

4. The mean activity coefficients of hydrochloric acid in these solvents are tabulated at rounded molalities to 0.5 *m*.

5. The activity coefficients may be calculated by a Debye–Hückel expression with a constant å and a linear or quadratic term added.

6. The behavior of the cells containing these solvents indicates possible reaction or rearrangement of the *d*-glucose molecule under conditions of the experiment.

CHAPEL HILL, NORTH CAROLINA RECEIVED JULY 8, 1949

[CONTRIBUTION FROM THE APPLIED SCIENCE RESEARCH LABORATORY OF THE UNIVERSITY OF CINCINNATI]

Studies of Fluorophosphoric Acids and their Derivatives. XIV. Preparation of Anhydrous Difluorophosphoric Acid[1]

BY WILLY LANGE[2] AND RALPH LIVINGSTON[3]

Formation of difluorophosphoric acid was first observed during the hydrolysis of phosphorus oxytrifluoride.[4a,c,5] Formation of the acid in small

$$POF_3 \xrightarrow{H_2O} H[PO_2F_2] \underset{HF}{\overset{H_2O}{\rightleftharpoons}} H_2[PO_3F] \underset{HF}{\overset{H_2O}{\rightleftharpoons}} H_3[PO_4] \quad (1)$$

quantities, together with orthophosphoric, monofluorophosphoric and a trace of hexafluorophosphoric acids, was noted also when phosphorus pentoxide was dissolved in a 40% hydrofluoric acid solution. However, both the di- and the hexafluorophosphoric acids are unstable in this system and undergo slow but complete hydrolysis at room temperature.[4b] During the preparation of phosphorus oxytrifluoride by heating a mixture of calcium fluoride and phosphorus pentoxide in the presence of traces of moisture and fractionating carefully the volatile reaction products, Tarbutton, *et al.*,[6] isolated small quantities of anhydrous difluorophosphoric acid formed probably by hydrolysis of phosphorus oxytrifluoride in accord with (I).

Investigations confirmed, as anticipated from the equilibrium reactions indicated in (I), that neither hydrogen fluoride nor water should be present in appreciable quantities at the end of the reaction in any practical method of preparing pure difluorophosphoric acid. This objective was achieved by allowing phosphorus oxytrifluoride to react with anhydrous monofluorophosphoric acid, in accordance with the equation

$$POF_3 + POF(OH)_2 \longrightarrow 2POF_2(OH) \quad (II)$$

Purification of the liquid product by distillation at 75-mm. pressure results in good yields (calculated on the basis of phosphorus oxytrifluoride absorbed) of pure difluorophosphoric acid.

Experimental

Starting Materials.—Anhydrous monofluorophosphoric acid[5] contained 18.7% F and 30.95% P as compared with

(1) A portion of a thesis by R. Livingston, submitted to the Faculty of the Graduate Department of Applied Science, College of Engineering and Commerce, University of Cincinnati, in partial fulfillment of the requirements for the degree of Doctor of Science, May, 1943.

(2) Present address: The Procter & Gamble Company, Cincinnati 17, Ohio.

(3) Present address: Monsanto Chemical Company, Clinton Laboratories, Oak Ridge, Tenn.

(4) (a) W. Lange, *Ber.*, **60**, 965 (1927); (b) **61**, 799 (1928); (c) **62**, 786 (1929).

(5) W. Lange and R. Livingston, THIS JOURNAL, **69**, 1073 (1947).

(6) G. Tarbutton, E. P. Egan, Jr., and S. G. Frary, *ibid.*, **63**, 1782 (1941).