Evaluation of the Standard Potential of the Cell Pt, H_2 (1 Atm.) | HCl (*m*), Tetrahydrofuran (*X*), Water (*Y*) | AgCl, Ag, Using Polynomial Curve-Fitting Program

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Electromotive force measurements were made on the cell Pt, H_2 (1 atm.) HCl (*m*), tetrahydrofuran (*X*), water (*Y*) | AgCl, Ag for 8.98, 18.21, 47.20, 73.03, and 89.00 weight % tetrahydrofuran at 0°, 15°, and 35° C. The values of the standard potential of the above cell in mixed solvents were evaluated by using polynomial curve-fitting technique.

GRAPHICAL EXTRAPOLATIONS (*2, 4, 5, 7*) of the e.m.f. data of the cell, Pt, H_2 (1 atm.) | HCl (*m*), tetrahydrofuran (*X*), water (*Y*) | AgCl, Ag, using the extended terms of the Debye-Hückel theory, derived by Gronwall, LaMer, and Sandved (*3, 8*), normally exhibit a high degree of error, especially along the curved segment of the plot—i.e., at the lower concentrations range which unfortunately is the region of greatest importance. Sen, Johnson, and Roy (*9*) have shown that the rearranged Nernst equation containing extended terms may be expressed as a polynomial in powers of $m^{1/2}$. The values of E^0 obtained by a polynomial curve fitting program are in excellent agreement with the best values of E^0 obtained by linear extrapolation. It has been shown theoretically, and substantiated by experimental data, that the coefficients of the polynomial are primarily functions of the dielectric constant of the solvent as long as the bulk dielectric constant of the solvent is not less than 18 (*9*), and hydrochloric acid concentration is low. The evidence (*9*) strongly suggests that under such conditions, the ion-size parameter is reasonably constant.

EXPERIMENTAL

Commercially available tetrahydrofuran (THF) obtained from the Fisher Scientific Co. was purified (*10*) by passing 100 to 200 ml. of THF through a column (10 × 2 cm.) containing 1 part of Celite to 3 parts of freshly activated alumina in a nitrogen atmosphere. The purified solvent was immediately stored over alumina; its purity was checked by gas chromatography.

A stock solution of hydrochloric acid was prepared from reagent grade acid by distilling twice in all-glass apparatus; each time only the middle fraction was collected. Hydrochloric acid was standardized following the normal procedure (*11*). Conductivity grade water prepared by double distillation in all-glass apparatus was used in all preparations. The conductivity of the freshly prepared water was less than 1×10^{-6} mho.

ELECTRODES

The hydrogen electrodes (*1, 6*) were prepared from a Sargent half-cell platinum electrode having a length of approximately 12 cm. and thickness of about 0.125 mm. The electrodes were replatinized as soon as the system showed any sign of instability. The finished electrodes were stored in water. The silver–silver chloride electrodes (*1*) were prepared by sealing a silver wire about 7 mm. long and 2 mm. in diameter in a flint glass tube. After cleaning the bases with warm 6*M* HNO_3, a thick paste of well-washed silver oxide was applied to each helix. The electrodes were then placed in a crucible furnace (500° C.) until a spongy surface of metallic silver had covered the helix surface. To make the surface smooth, the process was repeated using a slightly thinner paste for each additional coat. The electrodes then were electrolyzed in 1*M* HCl acid for 45 minutes at a current of 10 ma., using a platinum wire as the cathode and a silver electrode as the anode. A thick coating of AgCl was avoided. The completed electrodes were placed in 0.05*M* HCl acid overnight and then were stored in distilled water for use. The potentials of the electrodes were intercompared and those differing in potential by more than 0.1 mv. were rejected. Four out of 14 electrodes were found good. Two essential requirements for obtaining good AgCl electrodes are proper washing of the silver oxide, and the use of HCl acid solution of highest purity.

PROCEDURE

The cell was constructed to permit the use of two silver–silver chloride electrodes and two hydrogen electrodes. Ten solutions of hydrochloric acid in mixed solvents, in the concentration range of 0.1 to 0.001 molal, were prepared for each system. Five systems—8.98, 18.21, 47.20, 73.03, and 89.00% tetrahydrofuran—were studied at four different temperatures—0°, 15°, 25°, and 35° C. The cell was placed in a Sargent thermonitor controlled water bath thermostated at 15°, 25°, and 35° C., respectively, with a precision of ±0.01° C. A Styrofoam ice chest was used as the 0° C. bath and had an accuracy of the order of ±0.5° C. It was assumed that equilibrium was reached when the e.m.f. measurement taken by means of a Leeds and Northrup K-3 universal-type potentiometer over a period of a half hour agreed to ±0.1 mv. This usually required several hours after the initiation of hydrogen bubbling. Prior to introduction into the cell, Ultrapure hydrogen from Matheson Co., Inc., was passed first through a Deoxo catalytic purifier and then through a bubbling tower filled with a solution of composition identical to that present in the cell. Measurements of electromotive forces were rather difficult for low concentration of hydrochloric acid and high concentration of the organic solvent, since the galvanometer deflection was not large.

An Eppley standard cell having low temperature coefficient and a Rubicon galvanometer having a sensitivity of 0.004 μa. per mm. was used in conjunction with the potentiometer.

THEORY

On rearrangement the Nernst equation may be written as

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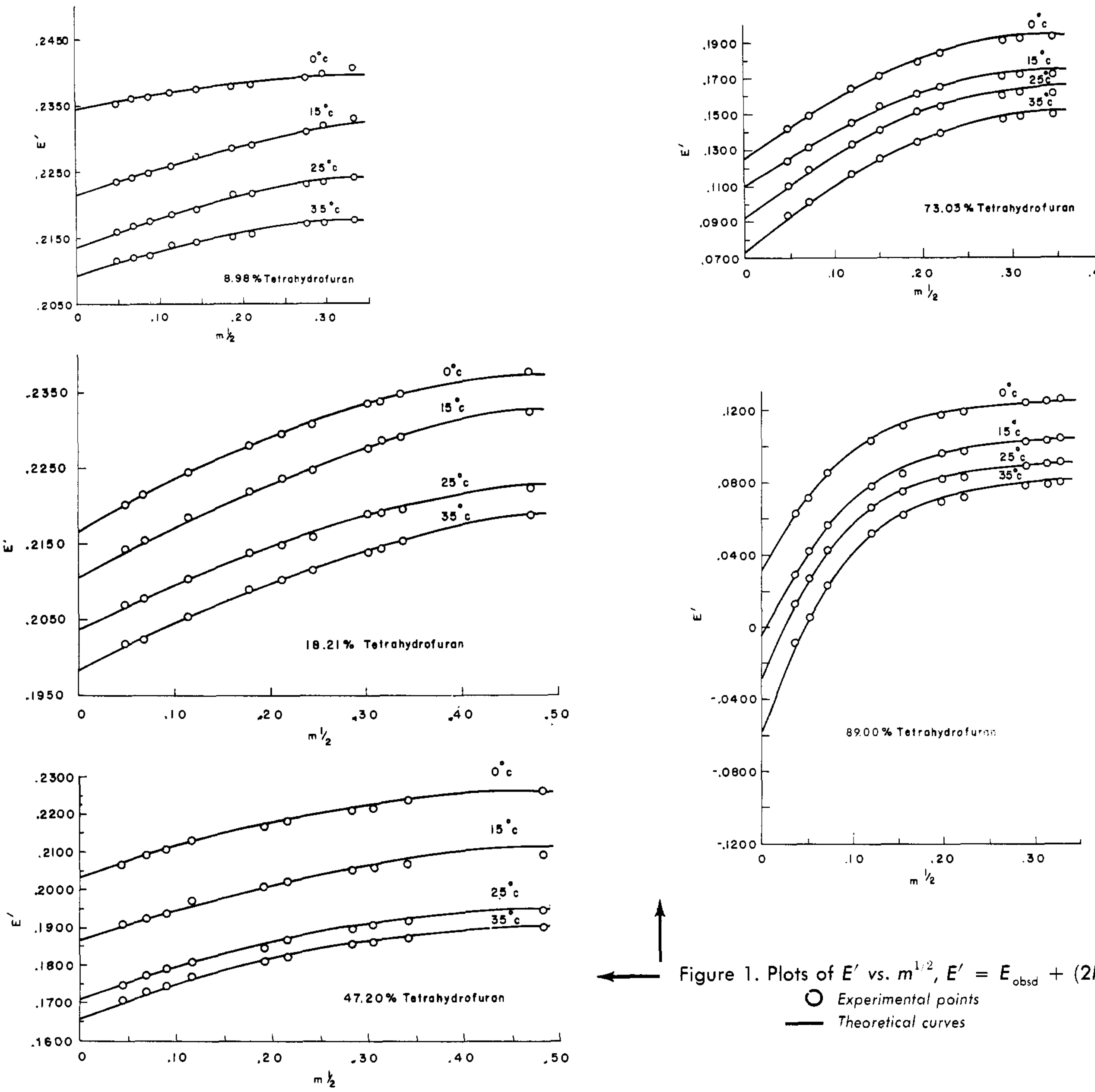

Figure 1. Plots of E' vs. $m^{1/2}$, $E' = E_{obsd} + (2RT/F) \ln m$

○ *Experimental points*

—— *Theoretical curves*

$$E_{obsd.} + \frac{2RT}{F} \ln m = E^0 - \frac{2RT}{F} \ln \gamma \pm \qquad (1)$$

in which E_{obsd} is the potential of the cell corrected to hydrogen pressure of 1 atm. (*4*). A plot of the left side of Equation 1 against some function of molality is evidently nonlinear. The polynomial curve-fitting program was used to eliminate the error encountered in normal graphical extrapolations and to avoid the necessity of knowing the correct values of the dielectric constant of the solvent and the mean distance of the closest approach of the ions involved in extended terms of the Debye-Hückel theory. This program is based on the assumption that a set of experimental data can be best fitted to a polynomial of the form

$$y = A_0 + A_1 x + A_2 x_2 + \ldots\ldots + A_{15} x^{15} \qquad (2)$$

The quantity $[E_{obsd} + (2RT/F) \ln m]$ in Equation 1 can be expressed as a polynomial series in $m^{1/2}$ of the form,

$$E_{obsd} + \frac{2RT}{F} \ln m = E^0 + A_1 m^{1/2} + A_2 m + A_3 m^{3/2} \qquad (3)$$

in which coefficients E^0, A_1, etc., are not arbitrary constants if the concentration is low and if the Gronwall, LaMer, and Sandved extention to the Debye-Hückel equation (*3, 4*) holds. The curve-fitting program only avoids their numerical computation. The proof (*9*) is based on the validity of the Debye-Hückel theory. It is evident from Equation 2 that the first approximation is of linear form, $y = A_0$ $A_1 X$. In these investigations, the second-degree equation was used for 8.98, 18.21, 47.20, and 73.03 weight % THF, whereas the third-degree equation was for 89.00%. The standard error calculated by the method of least squares, and the general nature of the curves obtained by plotting the experimental quantity E' which is equal to $[E_{obsd} + 2RT/F \ln m]$, against $m^{1/2}$, were the most useful criteria in deciding the degree of equation to use. There was a direct correlation between the degree of the equation (*9*) and the dielectric constant of the solvent.

With the method of least squares, a set of linear equations with the constants A_0, A_1, etc., was obtained. A modified Gaussian elimination technique was used to determine the values of the constants. The polynominal curve-fitting program computed the values of the coefficients, the standard error for the degree of equation specified, and the calculated value of the dependent variable, E'.

Table I. Values of m, E_{obsd} of Hydrochloric Acid in Tetrahydrofuran-Water Mixtures at Various Temperatures

X = wt. % of tetrahydrofuran

m = molality of hydrochloric acid

m	E_{obsd}			
	0° C.	15° C.	25° C.	35° C.
X = 8.98				
0.11140	0.34454	0.34199	0.33585	0.33352
0.08905	0.35479	0.35189	0.34665	0.34513
0.07679	0.35995	0.35706	0.35395	0.35223
0.04449	0.38459	0.38355	0.38155	0.38082
0.03519	0.39538	0.39464	0.39351	0.39276
0.02111	0.41897	0.41887	0.41753	0.41975
0.01299	0.44143	0.44140	0.44100	0.44445
0.00779	0.46475	0.46585	0.46582	0.46992
0.00462	0.48911	0.49115	0.49170	0.49756
0.00231	0.52094	0.52495	0.51900	0.53341
X = 18.21				
0.22588	0.30430	0.30331	0.29646	0.29502
0.11271	0.33769	0.33744	0.33162	0.32932
0.09940	0.34151	0.34333	0.33768	0.33553
0.09010	0.34511	0.34612	0.34252	0.33992
0.05960	0.36453	0.37764	0.36073	0.36124
0.04501	0.37655	0.38753	0.37410	0.37478
0.03560	0.38507	0.36482	0.38265	0.38596
0.01314	0.42894	0.43374	0.43240	0.43211
0.00467	0.47318	0.48181	0.48425	0.48689
0.00234	0.50377	0.51343	0.51822	0.52338
X = 47.20				
0.23414	0.29279	0.28645	0.28024	0.27097
0.11679	0.32363	0.31645	0.31084	0.30373
0.09339	0.33281	0.32704	0.32050	0.31553
0.08052	0.33942	0.33393	0.32727	0.32269
0.04665	0.36132	0.35669	0.34621	0.34745
0.03690	0.37191	0.36433	0.35386	0.36069
0.01362	0.41371	0.40799	0.40122	0.40492
0.00817	0.43685	0.43218	0.42561	0.42952
0.00484	0.46028	0.45686	0.44986	0.45587
0.00242	0.49028	0.48994	0.48406	0.48851
X = 73.03				
0.12050	0.29259	0.27773	0.26972	0.26236
0.09632	0.30214	0.28818	0.28023	0.27325
0.08305	0.30812	0.29355	0.28819	0.27912
0.04811	0.32682	0.31564	0.30709	0.30010
0.03806	0.33334	0.32397	0.31889	0.30745
0.02283	0.34995	0.34239	0.33654	0.32569
0.01404	0.36426	0.35669	0.35094	0.34348
0.00499	0.39945	0.39515	0.39127	0.38241
0.00250	0.42408	0.42756	0.42799	0.41121
X = 89.00				
0.10823	0.23065	0.21441	0.21824	0.19816
0.09817	0.23425	0.21834	0.20925	0.20234
0.08464	0.24032	0.22480	0.21596	0.20912
0.04904	0.26101	0.24681	0.23758	0.23159
0.03879	0.27015	0.25753	0.24915	0.24210
0.02326	0.28784	0.27168	0.26825	0.26178
0.01432	0.30286	0.28898	0.28426	0.27666
0.00509	0.33352	0.31790	0.31399	0.30369
0.00254	0.35278	0.33881	0.33357	0.32221
0.00130	0.37556	0.35919	0.35419	0.34169

Table II. Standard Potentials (E^0) of the Cell

H_2 (1 Atm.) | HCl (m), THF (X), Water (Y) | AgCl, Ag

X and Y are wt. percentages

X	0° C.	15° C.	25° C.	35° C.
0	0.23655	0.22857	0.22234	0.21565
8.98	0.23467	0.22160	0.21368	0.20933
18.21	0.21662	0.21062	0.20375	0.19828
47.20	0.20365	0.18662	0.17060	0.16572
73.03	0.12600	0.11163	0.09310	0.07330
89.00	0.03397	−0.00279	−0.02582	−0.05689

RESULTS AND DISCUSSION

The molalities of the various solutions of hydrochloric acid in mixed solvents were calculated from the volumetric data and the appropriate density data. The observed potentials, E_{obsd} of the cell in which X = 8.98, 18.21, 47.20, 73.03, and 89.00 are presented in Table I. Plots of E' [$=E_{obsd} + (2T/F) \ln m$] are presented in Figures 1 through 5. The experimental points are represented by circles, whereas the solid curves are calculated plots using the parameters of Equation 3 evaluated from the experimental data. The values of the standard potentials of the cells were determined by extrapolation of the polynomial to zero molality, and the E^0 values given in Table II were taken directly from the computer.

The errors in each system were estimated by two factors—the reproducibility of the cells, and the criteria for equilibrium. For 8.98 and 18.21% THF, the error in e.m.f. data was ±0.1 mv.; for 47.20, 73.03, and 89.00 the errors were estimated to be ±0.4, ±0.9, and ± several millivolts, respectively.

A thorough examination of the data listed in Table I shows that in each system and at every temperature, the value of E_{obsd} increases with the corresponding decrease in molality of hydrochloric acid. Furthermore, examination of the plots in Figure 1 shows that the curvature of the plot becomes more pronounced as the concentration of the tetrahydrofuran is gradually increased.

CONCLUSION

The curve-fitting technique permits us to evaluate the standard potential in mixed solvents with considerable elimination of some of the errors encountered in linear graphical extrapolations where a previous knowledge of the dielectric constant of the solvent and ion size parameter is required.

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LITERATURE CITED

(1) Bates, R.G., "Electrometric pH Determinations," Wiley, New York, 1954.

(2) Feakins, D., French, C.M., *J. Chem. Soc.* **1956**, p. 3168.

(3) Gronwall, T.H., LaMer, V.K., Sandved, K., *Physik. Z.* **29**, 358 (1929).

(4) Harned, H.S., Owen, B.B., "The Physical Chemistry of Electrolytic Solutions," 3rd ed., Reinhold, New York, 1958.

(5) Harned, H.S., Nestler, F.H.M., *J. Am. Chem. Soc.* **68**, 665 (1946).

(6) Ives, D.J.G., Janz, G.J., "Reference Electrode," Academic Press, New York, 1961.

(7) Knight, S.B., Masi, J.F., Roesel, D., *J. Am. Chem. Soc.* **68**, 661 (1946).

(8) LaMer, V.K., Gronwall, T.H., Grieff, L.G., *J. Phys. Chem.* **35**, 2245 (1938).

(9) Sen, B., Johnson, D.A., Roy, R.N., *Ibid.*, **71**, 1523 (1967).

(10) Silvermann, L., Bradshaw, W.G., Shideler, M.E., *Anal. Chem.* **31**, 1669 (1959).

(11) Vogel, A.I., "A Textbook of Quantitative Inorganic Analysis," 3rd ed., Wiley, New York, 1961.

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