Thermodynamics of Hydrochloric Acid in 1,2-Dimethoxyethane–Water Mixtures

Standard Potentials and Activity Coefficients

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The cell, H_2(1 atm) | HCl (m), 1,2-dimethoxyethane (X), Water (Y) | AgCl–Ag, was studied at 0°, 15°, 25°, and 35° C. at solvent compositions of 8.68, 17.81, 46.52 and 67.03 weight % of 1,2-dimethoxyethane. The standard potentials were evaluated by means of a curve fitting program, and activity coefficients were calculated. Within the limits of experimental error, the activity coefficients follow the same trends as in other solvent systems. Primary and secondary medium effects as defined by Owen are also tabulated.

THE ultimate purpose of this research program is to determine the effect of the solvent on the thermodynamics of chemical equilibria. This paper is a report of the study of the cell, H_2 (1 atm.) | HCl (m), Organic (*X*), Water (*Y*) | AgCl-Ag, in which the organic solvent is 1,2-dimethoxyethane or more commonly, monoglyme. It describes the evaluation of the standard potentials and mean activity coefficients on the molal scale at several compositions of solvent.

The revised version of the IBM 7.0.002 polynomial curve fitting program was used in evaluation of the standard potentials. The program assumed that a set of experimental data can be fitted to a polynomial of the form:

$$y = A_0 + A_1x + A_2x^2 + A_3x^3 + \ldots A_{15}x^{15} \qquad (1)$$

The coefficients are determined by the least squares technique and the resulting equations solved by a modified Gaussian elimination technique.

Such a program is theoretically sound and yields excellent results as was shown in an earlier paper (*4*).

EXPERIMENTAL

Monoglyme in the bulk was obtained from the Ansul Co., Marinette, Wis. Sodium wire was added to remove as much water as possible; it was then refluxed overnight with lithium aluminum hydride and then distilled through a 5-foot heated column keeping only the middle fraction.

Preparation of the solutions and other experimental details have been described (*3*). Density data required for calculation was obtained experimentally and from a technical data sheet issued by the Ansul Co.

The cells were first brought to equilibrium at one of the higher temperatures and then the temperature was lowered. Periodically a cell was rechecked, either by remaking the solution or by returning the cell to a former temperature. A cell was considered to be at equilibrium if readings taken over a half-hour period differed by 0.1 mv. or less. The electromotive forces were reproducible to ±0.1 mv. for the 8.68 and 17.81% monoglyme systems, to ±0.5 mv. for the 46.52% monoglyme system, and to ±0.8 mv. for the 67.03% monoglyme systems. Solutions containing 88.80% monoglyme were also studied, but the reproducibility was very poor. The electromotive force values were converted to values corresponding to a hydrogen gas pressure of 1 atm. using Raoult's law to calculate the

Table I. Values for E_{obsd} in Volts

m	0° C.	15° C.	25° C.	35° C.
IN 8.68% MONOGLYME				
0.0973		0.3491	0.3481	0.3458
0.0778		0.3597	0.3593	0.3569
0.0584		0.3731	0.3729	0.3716
0.03888		0.3916	0.3919	0.3912
0.01944		0.4237	0.4256	0.4263
0.00972		0.4562	0.4590	0.4602
0.00777		0.4671	0.4700	0.4714
0.00583		0.4806	0.4841	0.4863
0.003890		0.4999	0.5041	0.5072
0.001940		0.5337	0.5393	0.5434
IN 17.81% MONOGLYME				
0.0998		0.3431	0.3411	0.3381
0.0798		0.3538	0.3521	0.3495
0.0598		0.3667	0.3656	0.3635
0.03895		0.3863	0.3860	0.3848
0.01942		0.4184	0.4192	0.4194
0.00971		0.4512	0.4530	0.4538
0.00777		0.4614	...	0.4650
0.00582		0.4757	0.4780	0.4797
0.003880		0.4950	0.4983	0.5002
0.001980		0.5270	0.5312	0.5345
IN 46.52% MONOGLYME				
0.1043	0.3313	0.3241	0.3187	0.3123
0.0833	0.3413	0.3343	0.3286	0.3224
0.0625	0.3531	0.3464	0.3414	0.3355
0.0416	0.3692	0.3639	0.3594	0.3542
0.02080	0.3990	0.3949	0.3914	0.3870
0.01040	0.4268	0.4244	0.4218	0.4183
0.00828	0.4395	0.4372	0.4347	0.4328
0.00624	0.4511	0.4497	0.4484	0.4462
0.00417	0.4681	0.4679	0.4669	0.4655
0.002080	0.4996	0.5010	0.5009	0.5003
IN 67.03% MONOGLYME				
0.1073	0.3059	0.2935	0.2847	0.2743
0.0858	0.3146	0.3026	0.2942	0.2844
0.0643	0.3252	0.3135	0.3054	0.2965
0.0428	0.3414	0.3307	0.3226	0.3140
0.02141	0.3650	0.3553	0.3499	0.3420
0.01069	0.3925	0.3838	0.3792	0.3720
0.00856	0.4019	0.3942	0.3885	0.3814
0.00642	0.4139	0.4066	0.4013	0.3951
0.00428	0.4311	0.4248	0.4198	0.4132
0.002140	0.4611	0.4554	0.4512	0.4462

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Table II. E° Values in Volts

Systems	0° C.	15° C.	25° C.	35° C.	Deg. Eq.
8.68		0.2209	0.2155	0.2089	2
17.81		0.2158	0.2090	0.2009	2
46.52	0.2053	0.1905	0.1794	0.1680	3
67.03	0.1688	0.1449	0.1262	0.1099	4

Table IV. Primary Medium Effects of Monoglyme-Water Mixtures on Hydrochloric Acid

X = weight % of Monoglyme

X	0° C.	15° C.	25° C.	35° C.
8.68	0.086	0.067	0.058	0.055
17.81	0.114	0.112	0.113	0.121
46.52	0.292	0.336	0.362	0.385
67.03	0.672	0.761	0.814	0.872

Table III. Mean Activity Coefficients of Hydrochloric Acid in Monoglyme-Water Mixtures

X = % of Monoglyme

m	0° C.	15° C.	25° C.	35° C.
X = 8.68				
0.1		0.776	0.774	0.771
0.05		0.813	0.812	0.811
0.02		0.864	0.864	0.864
0.01		0.898	0.898	0.896
0.005		0.924	0.924	0.923
0.002		0.951	0.950	0.948
0.001		0.965	0.964	0.962
X = 17.81				
0.1		0.766	0.765	0.761
0.05		0.811	0.805	0.794
0.02		0.865	0.858	0.847
0.01		0.898	0.893	0.881
0.005		0.924	0.920	0.913
0.002		0.950	0.947	0.944
0.001		0.963	0.962	0.960
X = 46.52				
0.1	0.659	0.652	0.641	0.637
0.05	0.714	0.712	0.705	0.705
0.02	0.794	0.793	0.786	0.783
0.01	0.844	0.844	0.837	0.833
0.005	0.885	0.885	0.879	0.874
0.002	0.925	0.024	0.919	0.916
0.001	0.946	0.945	0.942	0.939
X = 67.03				
0.1	0.51	0.47	0.43	0.43
0.05	0.59	0.54	0.50	0.49
0.02	0.72	0.67	0.61	0.60
0.01	0.81	0.76	0.69	0.68
0.005	0.88	0.83	0.76	0.76
0.002	0.94	0.89	0.84	0.83
0.001	0.96	0.93	0.88	0.88

Table V. Values of Secondary Medium Effect of Monoglyme-Water Mixtures on Hydrochloric Acid

X = weight % of Monoglyme

m	0° C.	15° C.	25° C.	35° C.
X = 8.68				
0.1		−0.01458	−0.01297	−0.00936
0.05		−0.01156	−0.00994	−0.00538
0.02		−0.00734	−0.00609	−0.002320
0.01		−0.00481	−0.00400	−0.000727
0.005		−0.003444	−0.002490	−0.000014
0.002		−0.001974	−0.001283	−0.000260
0.001		−0.001444	−0.001010	−0.000263
X = 17.81				
0.1		−0.01747	−0.01773	−0.01946
0.05		−0.01056	−0.01371	−0.01962
0.02		−0.00500	−0.00869	−0.01531
0.01		−0.00255	−0.00592	−0.01133
0.005		−0.001540	−0.003890	−0.00820
0.002		−0.000599	−0.002191	−0.00533
0.001		−0.000411	−0.001660	−0.00383
X = 46.52				
0.1	−0.0898	−0.0917	−0.0934	−0.0895
0.05	−0.0705	−0.0702	−0.0704	−0.0655
0.02	−0.0475	−0.0467	−0.0463	−0.0423
0.01	−0.0347	−0.0335	−0.0331	−0.0297
0.005	−0.0251	−0.0241	−0.0234	−0.0208
0.002	−0.0163	−0.0153	−0.0147	−0.0131
0.001	−0.0117	−0.0109	−0.0106	−0.00926
X = 67.03				
0.1	−0.245	−0.258	−0.267	−0.276
0.05	−0.195	−0.209	−0.224	−0.237
0.02	−0.135	−0.146	−0.161	−0.173
0.01	−0.0998	−0.1081	−0.120	−0.130
0.005	−0.0727	−0.0790	−0.0880	−0.0954
0.002	−0.0473	−0.0511	−0.0573	−0.0625
0.001	−0.0339	−0.0367	−0.0413	−0.0450

vapor pressure of the solvent components. The converted values of e.m.f. have been termed E_{obsd} (*1*) and are tabulated in Table I. The plots of the polynomial and the experimental data are not reproduced here as they are of a similar nature as those presented earlier (*3*).

CALCULATION AND RESULTS

The e.m.f. of the cell studied is expressed by Equation 2:

$$E = E^\circ - \frac{2RT}{F} \ln \gamma_{\pm} m \tag{2}$$

where m is the molal concentration and $\gamma_{\pm}$ is the mean activity coefficient. In the case of hydrochloric acid, the molality can be substituted for the mean molality. Rearrangement of Equation 2 yields:

$$E + \frac{2RT}{F} \ln m = E^\circ - \frac{2RT}{F} \ln \gamma_{\pm} \tag{3}$$

Equation 3 can further be expressed by Equation 4 where A_1, A_2, A_3, etc., are constants composed of a number of other constants, the temperature, the dielectric constant of the system and one adjustable parameter, the ion-size parameter.

$$E + \frac{2RT}{\mathrm{F}} \ln m = E^\circ + A_1 m^{1/2} + A_2 m + A_3 m^{3/2} + \dots \tag{4}$$

Equation 4 is obtained from Equation 3 using the extended term of the Debye-Hückel equation for the activity coefficient (*4*).

The standard potentials were evaluated using the IBM 7.0.002 polynomial curve fitting program. The left hand side of Equation 3 was taken as ordinate and $m^{1/2}$ as the abscissa. The curve fitting program gives results which are in excellent agreement with the results of linear extrapolations (*4*). The standard potentials were evaluated from the first term of the polynomial. The degree of polynomial used for extrapolation purposes was determined by comparing the graphs and the trends in the values of the activity coefficients. The standard potentials are listed in Table II. The values should be good to ±0.2 mv. for the 8.68 and 17.81% monoglyme systems, to ±0.6 mv. for the 46.52% monoglyme system, and for the 67.03% monoglyme system to ±1.0 mv.

Table III contains the values of mean activity coefficients calculated from Equation 3. The activity coefficients in this case are referred to unity at infinite dilution in the mixed solvent system and are defined by Harned and Owen (*1*). The activity coefficients were evaluated using E_{obsd} values as calculated from the polynomials used for extrapolations. The values were then smoothed with respect to temperature. The values of primary and secondary medium effects as defined by Owen (*2*) are tabulated in Tables IV and V.

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Electronic Effects in the Ferrocene Ring System by Proton Magnetic Resonance Spectroscopy

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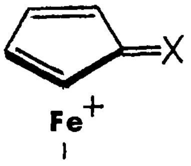
Results of a proton magnetic resonance study of the chemical shifts of ring protons of representative monosubstituted ferrocene compounds are reported. The substituents cover a span from strongly electron-donating groups to strongly electron-withdrawing. Some relationships appear to exist between the ring-proton chemical shifts in these compounds and those reported for the corresponding monosubstituted benzene compounds. The chemical shifts recorded were precisely measured. As such, they serve to revise the data reported while this work was in progress.

RECENTLY, estimates of electronic effects in metallocene ring systems have been forthcoming from PMR spectroscopy (*3, 4, 8, 10, 14*). In the case of the ferrocene ring system, abundant data are available to illustrate the deshielding effect of substituents containing a carbonyl group attached to the ring (*9, 12, 13*); however, substituent effects in the PMR spectra of other types of monosubstituted ferrocenes (particularly those containing electron-donating substituents) had not been reported at the time this work was initiated. A possible representation of resonance contribution to the ferrocene ring system of an electron-withdrawing group is shown in structure I; that of an electron-donating group is in structure II. Electron withdrawal, represented by the extreme formal-charge structure I, suggests deshielding of the substituted ring protons. Likewise, electron donation as in formal-charge structure II suggests shielding of the substituted ring protons will be observed. Structure II is, however, rendered less satisfactory than I because of the necessity of placing a negative formal charge on the iron atom.



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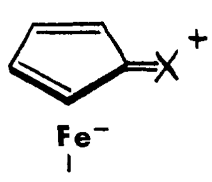

II

The results of a PMR study are reported for several representative monosubstituted ferrocene compounds; the substituents cover a span from strongly electron-donating groups (—NH_2) to strongly electron withdrawing (—CHO). A rough, nonlinear correlation is shown between the chemical shifts of protons at the 2 and 3 positions and the chemical shifts of protons at, respectively, the ortho and para positions of the corresponding benzene compounds (*15*).

The compounds employed were either commercial samples (acetylferrocene and carbomethoxyferrocene) or were pre-

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