[CONTRIBUTED FROM THE VENABLE CHEMISTRY LABORATORY, UNIVERSITY OF NORTH CAROLINA, CHAPEL HILL, N. C., AND THE DEPARTMENT OF CHEMISTRY, ALABAMA POLYTECHNIC INSTITUTE, AUBURN, ALA.]

The Activity Coefficients of Sulfuric Acid in Aqueous 2-Propanol Solutions at 25°

BY J. E. LAND AND H. D. CROCKFORD

An exhaustive study of the activity coefficients of sulfuric acid in pure water has been made by Harned and Hamer.[1] Studies concerned with the determination of sulfuric acid activities by electromotive force measurements in acetic acid solutions have been made by McDougall and Blumer,[2] in methanol solutions by Shibata and Oda,[3] and in ethanol solutions by Crockford and Wideman.[4] The study of such systems not only establishes the activity coefficients of the acid in the various solutions but also adds to the knowledge of the effect of changing dielectric constant on the activity.

The investigation reported on in this paper was concerned with the activity coefficients of sulfuric acid in 2-propanol solutions at 25°. It was hoped that similar studies could be made with 1-propanol solutions but no satisfactory results could be obtained. This is in line with the experiences of other investigators. Moore and Felsing[5] in their study of the activity of hydrochloric acid in 1-propanol solutions likewise were unable to secure satisfactory results.

The cell used in the studies was H_2, H_2SO_4, 2-propanol, Hg_2SO_4, Hg. Five, ten and twenty weight per cent. solutions of 2-propanol were studied. The sulfuric acid molalities reported on range from 0.05 to 1.0 *m*. Beyond this concentration equilibrium was very slow and in general the results were unsatisfactory. Results were also erratic for higher concentrations of alcohol. Readings below 0.05 *m* acid cannot be obtained with such a cell because of the solubility of the mercurous sulfate.

Experimental Procedure

For the potential measurements a Leeds and Northrup Type K-2 potentiometer calibrated by the Bureau of Standards was employed. The standard cell was properly checked against cells certified by the Bureau of Standards. Temperatures were accurate to ±0.02°.

The cells employed were H-shaped, one arm containing the mercury–mercurous sulfate electrode and the other the hydrogen electrode. The two arms were connected with a stopcock. The purification of the hydrogen and the technique of making a determination were the same as those used by Crockford and Wideman.[4]

All reagents and chemicals employed were carefully purified and where necessary analyzed by acceptable methods. The 2-propanol was refluxed with calcium oxide for eight hours and the dried alcohol fractionated through a packed column according to the method employed by Langdon and Keyes[6] and Lebo.[7] The density of the purified product was 0.77229 at 35°.

The equipment used and the techniques employed were checked by a series of measurements with aqueous sulfuric acid. The results obtained agreed with those of Harned and Hamer.[1]

The mean of at least four sets of readings (usually not more than 0.05 mv. apart) was taken as the electromotive force of a particular combination. All electromotive force readings were corrected to 1 atmosphere of dry hydrogen. For this correction the vapor pressures of sulfuric acid–2-propanol–water solutions as determined by Crockford, Land and Bailey[8] were employed. Constancy of potential was very slow, particularly in the more concentrated acid solutions and in the higher percentages of 2-propanol. For the more dilute solutions twenty-four to forty-eight hours were necessary. Above four molal values of 20% 2-propanol solutions constancy of potential in individual solutions required as much as fourteen days. Once equilibrium was established the value obtained remained constant for several hours.

Data and Results

Table I gives a summary of the results obtained. The values of *E* given were determined from large curves prepared by plotting the square root of the molality against the corrected electromotive force. In Fig. 1 the electromotive force–molality data are plotted together with the data of Harned and Hamer[1] for pure water for comparison purposes. The density values given were also obtained from large plots. The activity

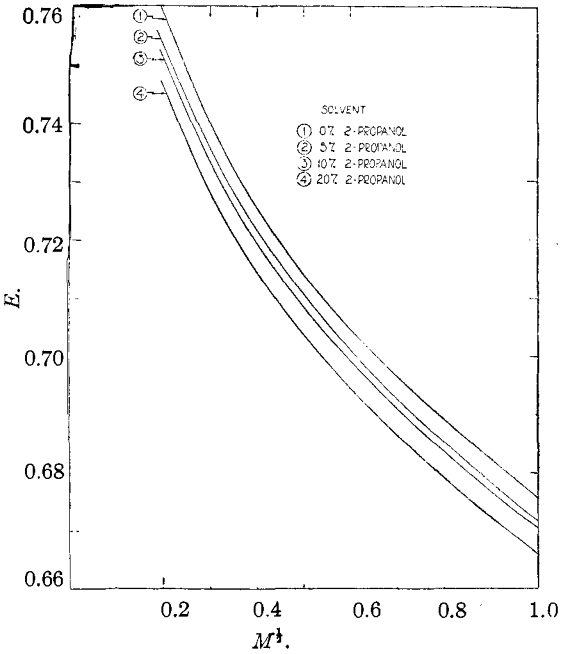

Fig. 1.—Solvent 2-propanol: 1, 0%; 2, 5%; 3, 10%; 4, 20%.

---

(1) Harned and Hamer, THIS JOURNAL, **57**, 27 (1935).

(2) McDougall and Blumer, *ibid.*, **55**, 2236 (1933).

(3) Shibata and Oda, *J. Chem. Soc.* (*Japan*), **52**, 590 (1931).

(4) Crockford and Wideman, *J. Phys. Chem.*, **50**, 418 (1946).

(5) Moore and Felsing, THIS JOURNAL, **69**, 1076 (1947).

(6) Langdon and Keyes, *Ind. Eng. Chem.*, **35**, 459 (1943).

(7) Lebo, THIS JOURNAL, **43**, 1005 (1921).

(8) Crockford, Land and Bailey, *Journal of the Alabama Academy of Science*, in press (1950).

TABLE I

ACTIVITY COEFFICIENTS OF SULFURIC ACID IN 2-PROPANOL SOLUTIONS AT 25°

	2-Propanol concentrations											
	5%				10%				20%			
Molality	Density	E	y	y^*	Density	E	y	y^*	Density	E	y	y^*
0.05	0.9912	0.7492	0.322	0.389	0.9836	0.7470	0.323	0.412	0.9690	0.7414	0.322	0.473
.10	0.9940	.7327	.247	.298	0.9870	.7304	.248	.317	.9717	.7249	.249	.366
.20	1.0030	.7162	.190	.229	0.9928	.7140	.190	.243	.9771	.7091	.188	.276
.30	1.0065	.7057	.166	.200	0.9984	.7040	.164	.209	.9826	.6990	.163	.239
.40	1.0122	.6981	.152	.184	1.0040	.6966	.149	.190	.9876	.6918	.147	.216
.50	1.0180	.6922	.141	.170	1.0095	.6908	.139	.177	.9929	.6862	.136	.200
.60	1.0237	.6872	.134	.162	1.0148	.6856	.132	.169	.9980	.6811	.129	.189
.70	1.0297	.6828	.129	.156	1.0202	.6812	.127	.162	1.0032	.6767	.124	.182
.80	1.0352	.6788	.125	.150	1.0255	.6774	.123	.157	1.0083	.6728	.120	.176
.90	1.0410	.6753	.122	.147	1.0308	.6741	.119	.152	1.0133	.6693	.117	.172
1.00	1.0463	.6720	.119	.144	1.0360	.6709	.116	.148	1.0182	.6661	.114	.167
	E^0 = 0.6079 volt				E^0 = 0.6058 volt				E^0 = 0.6004 volt			

coefficients were calculated from the equation

$$E = E^0 - 3RT/2F \ln (4^{1/3} m y_{\pm})$$

The activity coefficients were calculated on the basis of a reference state of unit activity coefficient for the acid at infinite dilution in the given solvent. The activity coefficients, y^*, were calculated on the basis of a reference state of unit activity coefficient for the solute at infinite dilution in pure water. For this purpose the E^0 obtained by Harned and Hamer[1] was employed.

In order to obtain the standard potentials for the three 2-propanol solutions, E was plotted against log m for the three 2-propanol solutions and for the data of Harned and Hamer in pure water. The values of ΔE, the difference between the measured E for various molalities of acid in a given 2-propanol solution and the value for the same molality in pure water, obtained from the E–log m plots were plotted against the square root of the molality. The resulting curves were essentially straight lines over a sufficient concentration range to permit accurate extrapolation to zero molality. This extrapolated value of ΔE was then subtracted from the value of E^0 for pure water in order to obtain the standard cell potential for the particular 2-propanol concentration. Table I gives the three values of E^0 so obtained.

Plots of y and y^* against the square root of the molality of the acid give curves which show a similar shape to that obtained for pure water. The same typical minima is indicated from the data given in Table I. The data obtained for higher molalities than those given in the table while erratic, showed the existence of the minimum with the curve sharply rising at higher molalities.

Summary

1. Electromotive force measurements have been made at 25° with cells consisting of a hydrogen electrode and a mercury–mercurous sulfate electrode in sulfuric acid solutions of aqueous 2-propanol. The 2-propanol solutions contained 5, 10, and 20% alcohol and the acid concentrations upon which data are reported varied from 0.05 m to 1.00 m.

2. From the electromotive force values obtained the activity coefficients of the acid have been calculated.

RECEIVED OCTOBER 19, 1949