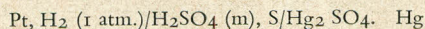# THE THERMODYNAMICS OF SULPHURIC ACID IN ALCOHOLS FROM ELECTROMOTIVE FORCE MEASUREMENTS

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Electromotive orce measurements have been made on the cell

$$Pt, H_2 \text{ (1 atm.)}/H_2SO_4 \text{ (m), S}/Hg_2 SO_4. \ Hg$$

where 'S' stands for organic solvents like methanol and *n*-propanol. The molality of the acid was varied from 0.022 to 4.00M. Standard potentials have been evaluated by the application of Debye–Hueckel limiting equation with a linear term. Mean ionic activity coefficients were calculated on the assumption that the acid acts as a uni-bivalent electrolyte. The values of the standard potentials were found to be 0.3754 and 0.2687 at 32°C. for methanol and *n*-propanol, respectively. The values of mean ionic activity coefficients were found to be much lower than those in aqueous solutions at the corresponding molalities.

Introduction

Much stress has been laid upon the measurements of activity coefficients of sulphuric acid in water-alcoholic mixtures, but no data in this connection so far are available in pure anhydrous alcohols except that in ethanol given by Scholl, Hutchinson and Chandlee.[1]

Bronsted[2] first studied the electromotive force of the cell Pt, H_2 (1 atm.)/H_4SO_4 (m) H_2O/Hg_2SO_4. Hg at various temperatures and over a wide range of concentration. In order to review the work of Bronsted,[2] Lewis and Lacey[3] again studied the same cell, and found that the activity is not equal to the concentration except at infinite dilution. Randal and Cushman[4] carried out similar measurements with the main idea of finding the free energy of dilution of H_2SO_4. Upto 1923 the thermodynamic studies of the above mentioned cell did not attract much attention due to the lack of theoretical development of the subject. The determination of activity coefficients, which has previously been regarded as purely emperical quantities received an impetus after the work of Debye and Hueckel.

In a critical survey of the previous determinations of activity coefficients measured by different methods, Harned and Hamer[5] undertook a thorough investigation with the help of the above mentioned cell, but they could not study it below 0.05M. of H_2SO_4 due to the solubility of Hg_2SO_4. Work worth mentioning about the e.m.f. measurements is that of McDougal and Blumer,[6] in aqueous acetic acid, of Shibata and Oda[7] in methanol-water mixtures, of Crockford and Wideman[8] in ethanol-water mixtures, of Land and Crockford[9] in aqueous propan-2-ol and of French and Hussain[10] in ethylene glycol-water mixtures. The present investigation was designed to extend the thermodynamic properties of the solute from the aqueous to non-aqueous solvents by e.m.f.

measurements with the help of the following cell:

$$Pt, H_2 \text{ (1 atm.)} / H_2SO_4 \text{ (m) alcohol}/Hg_2SO_4.Hg$$
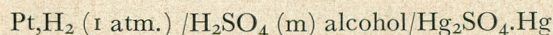
Experimental

Materials.—Sulphuric acid 100% was obtained by mixing concentrated sulphuric acid and fuming sulphuric acid containing 65% free sulphur trioxide as described by Lange.[11] The acid thus obtained was analysed gravimetrically by the barium sulphate method. As sulphuric acid is hygroscopic in nature, the 100% sulphuric acid was prepared in small quantities for the experimental work.

AnalaR methyl alcohol was further purified by the method of Lund and Bjerrum[12] as outlined by Weisberger.[13] The distillate from magnesium methoxide was further distilled over 2,4-dinitrophenylhydrazine in an atmosphere of nitrogen to remove aldehydes and ketones. The finally fractionated product had d_4^{25} 0.7865, n_D^{25} 1.3275 (Lit.[14,15] d_4^{25} 0.78662, 0.78654, 0.7866; n_D^{25} 1.3276).

n-Propanol was the analytical reagent supplied by the B.D.H. It was further dried and redistilled until a constant value in refractive index was obtained (n_D^{25} 1.3834).

AnalaR mercury supplied by the B.D.H. was further purified by passing repeatedly through dilute nitric acid column containing mercurous nitrate which was dried at 110°C. and filtered. Mercurous sulphate was prepared by the reduction of mercuric sulphate by formaldehyde at 50° to 55°C.

$$2HgSO_4 + H_2O + HCHO \xrightarrow{H_2SO_4} Hg_2SO_4 + HCOOH + H_2SO_4$$
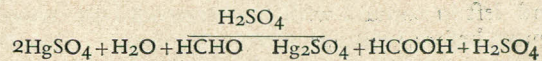
The mercurous sulphate obtained was preserved in 3M H_2SO_4.

Hydrogen supplied by the British Oxygen Company was purified through passage successively through concentrated silver nitrate, potassium permanganate in concentrated sulphuric acid and a solution of pyrogallol in concentrated potassium hydroxide.

Preparation of Electrodes.—The hydrogen electrode consisting of a centimeter square of platinum foil was welded at one end with 0.5 mm. thick platinum wire. To remove the coating of platinum black the platinum electrode was first cleaned by making it the anode in 6m. hydrochloric acid. The cleaned electrode was platinized by the method of Popoff, Kunz and Snow,[16] and kept in conductivity water in dark till used.

For the preparation of the mercury-mercurous sulphate electrode, mercurous sulphate stored in 3M. H_2SO_4 was separated by suction and washed several times with the solution of which the e.m.f. was to be measured; it was then made into a thin paste with the same solution and of such consistency that it flowed readily from a 5mm. diameter tube. This paste was transfered to one of the limbs of the cell so that it covered the mercury electrode to a depth of about 1 cm. In all these operations exposure to bright light was avoided as far as possible, since such exposure causes a darkening of the Hg_2SO_4 and the e.m.f. values obtained under such conditions are somewhat higher and less reliable.

Apparatus and Procedure.—The apparatus employed in this investigation is shown in Fig. 1. The external saturator and the hydrogen supply line was connected to the glass tripod separately. The connection between the hydrogen supply line and the top of the tripod was made with the help of the rubber pressure tubing. The external saturator and the hydrogen supply line were also connected together via a solution flask. This device was sufficient to saturate the solution externally as well as in the cell. Moreover, the internal, external saturators and the cell could be filled with the solution by the hydrogen pressure only. Purified hydrogen after bubbling through the external saturator was allowed to pass through the solution in the flask whose e.m.f. was to be measured for two hours. As hydrogen is four times more soluble[17,18] in alcohols than in water, this time was sufficient for the removal of oxygen from the solution. The saturated solution was then drawn into the cell (previously swept with hydrogen) by the pressure of hydrogen and left in contact with the electrodes for several hours before readings were commenced. For the purpose of accuracy a triplicate reading was taken in each run and the mean of the three readings

was regarded as the measured electromotive force at the given molality.

Electromotive forces were measured by a Pye-precision Vernier Potentiometer. A Cambridge Weston Standard Cell with a built-in thermometer was used as the working standard. The balance point was observed by using a lamp and scale-arrangement in conjunction with a high sensitivity mirror galvanometer. This arrangement enabled the measurement to be made with an accuracy of 0.01 mv. The time required for equilibrium was 2-3 hours in the case of dilute solutions and 6-8 hours in the case of concentrated solutions.

Results and Discussion

The values of the electromotive forces given in the table at definite molalities were read from large curves obtained by plotting the square root of the molality against the measured electromotive force corrected to one atmosphere pressure of dry hydrogen. The density values were also obtained by a similar procedure. These e.m.f. data are compared with similar data for solution in pure water obtained by Harned and Hamer[5] in Fig. 2

Values of the standard potential for the two solvent media were obtained as follows. The electromotive force of the cell under investigation may be expressed by the equation

$$E = E^o - \frac{3RT}{2F} \ln m_\pm \gamma_\pm \qquad (1)$$

E^o is the standard potential in the solvent in question, and γ and m are the mean activity coefficient and molality of the acid respectively. The rational mean activity coefficient $f_\pm$ is related to $\gamma_\pm$ according to the equation:

$$a_\pm = m_\pm \gamma_\pm = f_\pm N_\pm S \qquad (2)$$

where $a_\pm$ is the mean activity and $N_\pm$ is the mean mole fraction of the acid and S is a constant factor. From this we find that:

$$\log \gamma_\pm = \log f_\pm + \log N_\pm - \log m_\pm + \log S \qquad (3)$$

$$\log \gamma_\pm = \log f_\pm - \log (1 + .001 \, \nu m \, M) + \log .001 \, M + \log S \qquad (4)$$

where M is the molecular weight of the solvent and ν is the number of ions produced by the dissociation of one molecule of the electrolyte. According to equation (4) when m approaches zero, then log .001 M + log S also approaches zero. So at infinite dilution equation (4) reduces to:
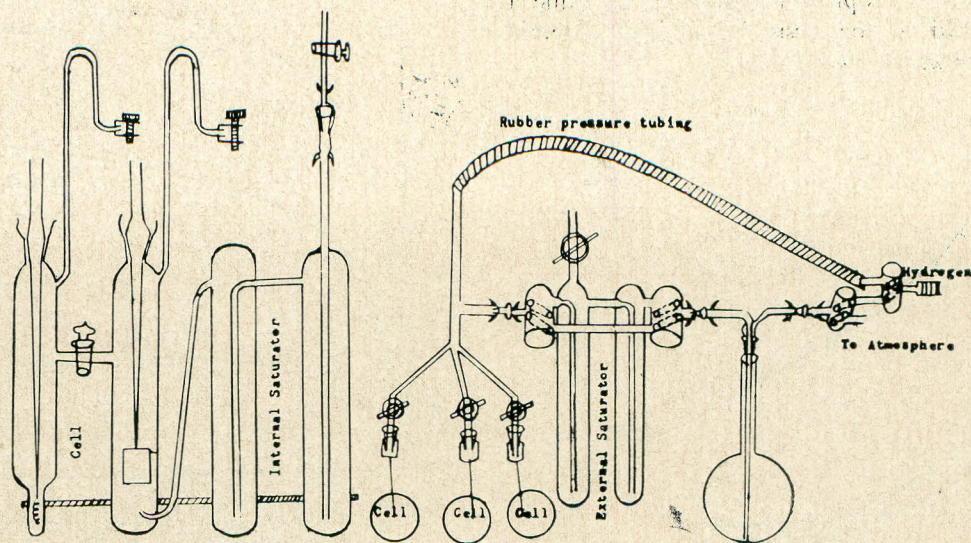
Fig 1.—Design of the apparatus.

$$\log \gamma_{\pm} = \log f_{\pm} - \log (1 + 0.001\, \nu_m\, M) \quad (5)$$

The Debye Hueckel limiting equation with a linear term, in the case of sulphuric acid can be written as:

$$\log f_{\pm} = -\frac{6.322 \times 10^{6}}{(D\,T)^{3/2}} \sqrt{C} + BC = -\mu \sqrt{C} + BC, \quad (6)$$

where D is the dielectric constant of the solvent, T is the absolute temperature and $C = m\, d_o$

where d_o is the density of the pure solvent.

Combining equations (1), (5) and (6) we obtain the desired equation for the extrapolation

$$E + \frac{2.303 \times 3RT}{2F} \left[\log m\, 4^{1/3} - \mu \sqrt{C} - \log (1 + .003\, m\, M) \right] = E' = E° - B'm \quad (7)$$

TABLE I.

Methanol E°=0.3754, D=30.0   n-propanol E°=0.2687, D=19.1

m	$\frac{32}{d_4}$	$\frac{E}{32}$	3×10	$\frac{32}{d_4}$	$\frac{E}{32}$	3×10
0.002				0.7940	0.6106	41.90
0.004	0.7825	0.6283	257.8	0.7942	0.6085	28.45
0.005	0.7833	0.6274	211.1	0.7946	0.6080	23.05
0.01	0.7852	0.6246	113.3	0.7966	0.6047	12.53
0.05	0.7922	0.6127	30.64	0.8035	0.5940	3.289
0.10	0.7978	0.6040	19.11	0.8091	0.5876	1.934
0.20	0.8055	0.5951	11.70	0.8175	0.5790	1.175
0.30	0.8123	0.5848	10.36	0.8243	0.5734	0.9243
0.40	0.8185	0.5808	8.602	0.8303	0.5685	0.7865
0.50	0.8235	0.5762	7.734	0.8360	0.5648	0.6864
0.60	0.8290	0.5724	7.098	0.8415	0.5620	0.6170
0.70	0.8335	0.5690	6.631	0.8465	0.5588	0.5883
0.80	0.8388	0.5661	6.244	0.8520	0.5562	0.5360
0.90	0.8440	0.5642	5.826	0.8573	0.5540	0.5040
1.0	0.8455	0.5626	5.461	0.8625	0.5518	0.4795
2.0	0.8913	0.5476	3.994	0.9110	0.5364	0.3543
3.0	0.9293	0.5369	3.493	0.9493	0.5267	0.3026
4.0	0.9668	0.5308	3.058	0.9383	0.5192	0.2740

If the left hand side of equation (7) which we represent by E' is plotted against m, its value at zero m would be the desired standard potential E^0, as is shown in Fig. 3.
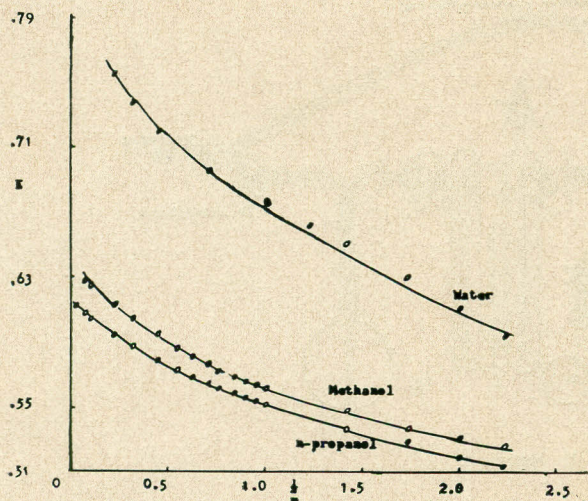

Fig 2.—Electromotive force (E) versus square root of the molality $(m)^{\frac{1}{2}}$ for various solvents.
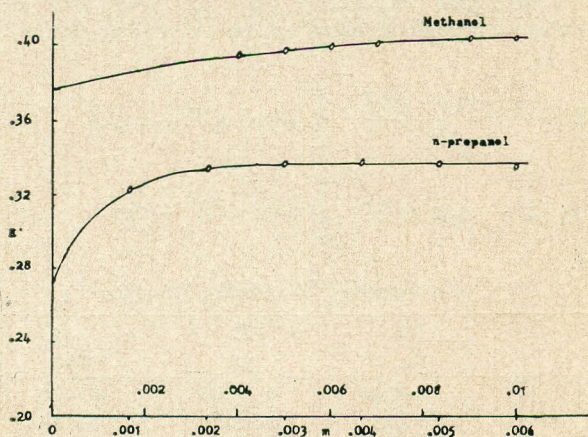

Fig. 3.—Plots of function E' against the molality (m).

The values of the dielectric constants of the pure solvents required for the computation of the limiting slopes μ were taken from the literature. The values of the densities, and dielectric constants given in the table when combined with the electromotive force data made possible the computation of the left side of equation (7). Values of all fundamental constants employed in these computations were those adopted by the International Critical Tables.

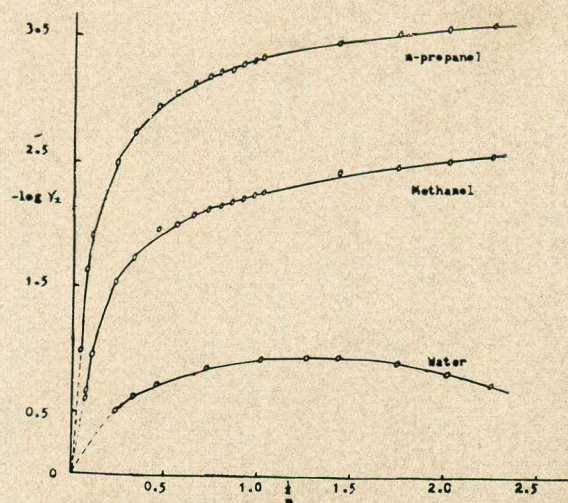The activity coefficients were calculated from the equation:

Fig. 4.—Plot of - log $\gamma\pm$ against the square root of the molality of the acid in different media.

$$E = E^0 - \frac{3RT}{2F} \ln 4^{\frac{1}{3}} m \gamma\pm$$

Plots of - log $\gamma\pm$ against the square root of molality of the acid shown in Fig. 4 give curves which show a similar shape to that obtained for pure water. For solvents of low dielectric constants, association into ion pairs becomes an appreciable one. Such an association into ion pairs lowers the values of the activity coefficients. Consequently the low values of $\gamma\pm$ in n- propanol whose dielectric constant at the experimental temperature is 19.1 is due to the considerable association of the ions only.

References

1. A.W. Scholl, A.W. Hutchinson and G.C. Chandlee, J. Am. Chem. Soc., **57**, 2542 (1935).
2. J. N. Bronsted, Z. Physik. Chem., **68**, 693 (1910).
3. G. N. Lewis and W. N. Lacey, J. Am. Chem. Soc., **36**, 804 (1914).
4. Randal and Cushman, ibid., **40**, 393 (1918).
5. H.S. Harned and W.J. Hamer, ibid, **57**, 27 (1935).
6. F. H. MacDougal and D.R. Blumer, ibid., **55**, 2236 (1933).
7. Shibata and Oda, J . Chem. Soc. (Japan) **52**, 590 (1931).
8. H.D. Crockford and S.D. Wideman, J. Phy. Chem., **50**, 418 (1946).
9. J. E. Land and H.D. Crockford, J. Am. Chem. Soc., **72**, 1895 (1950).
10. C. M. French and Ch. F. Hussain, J. Chem. Soc., 2211 (1955).

11. N.A. Lange, *Handbook of Chemistry* (Handbook Publishers Inc., 1956) p. 1149.

12. H. Lund and J. Bjerrum, Berdeut. Chem. Ges., **64**, 210 (1931).

13. A. Weisberger, *Technique of Organic Chemistry* (Interscienec Publishers, New York, 1955), Vol. VII, second edition, p. 334.

14. J. Timmermans, *Physicochemical Constants of Pure Organic Compounds* (Elsevier Publishing Co., Inc., 1950), p. 304.

15. G.W.C. Kaye and T.H. Laby, *Physical and Chemical Constants* (Longmans, Green and Co., 1956), p. 124.

16. S. Popoff, A. Kunz and R .D. Snow, J. Phy. Chem., **32**, 1056 (1928).

17. *International Critical Tables* (McGraw-Hill Book Co., Inc., New York and London, 1928), Vol. III, p.262.

18. N. A. Lange, *Handbook of Chemistry* (Handbook Publishers, Inc., 1956), p. 1092.