THE ACTIVITY COEFFICIENTS OF SULPHURIC ACID IN ACETONE-WATER MIXTURES

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The work on the activity coefficient of H_2SO_4 in acetone-water mixture was conducted on the cell. Pt,H_2 (1 atm.) | H_2SO_4 (m), acetone (X%), H_2O (100−X%) Hg_2SO_4 | Hg. The electromotive forces were measured at eleven different molalities ranging from 0.5 to 1.00m at $32\pm.05°C$. To find the standard potentials, extrapolation method was used. Better extrapolation was obtained by plotting ΔE against the square root of molality, as described by Land and Crockford,[1] where ΔE is the difference between the measured e.m.f. for various acid molalities for a given acetone-water mixture and the corresponding values of Harned and Hamer [2] in water corrected to 32°C. Standard potentials were obtained by subtracting ΔE at zero molality from the standard potential of water at 32°C., and the values found were 0.5674, 0.5572, 0.5051 and 0.4654 volt at 32°C. for 5,10,20 and 40% acetone, respectively. The mean ion activity coefficients were calculated with the help of the equation:

$$E = E° - \frac{3\,RT}{2\,F} \ln \left(4^{1/3} \, m \, \gamma_\pm \right)$$

and the values were found to be lower than those in aqueous solutions at the corresponding molalities.

Introduction

Moore and Felsing [3] attempted to measure the electromotive forces on the cell H_2 (Pt.) | HCl AgCl | Ag, using 10% acetone in water as the solvent. They were unable to get steady and reversible hydrogen electrode in the medium using platinum electrodes coated with platinum black. D. Feakins and C.M. French [4] investigated the same cell and claimed stability and reproducibility of the electrode when a bare platinum electrode is used. They reported that the surface should be cleaned by polishing the electrode (e.g. by rubbing it with an abrasive or with round end of a glass rod) or by treatment with 50% aqua regia or preferably by a combination of these two methods. It is evident that rigid control of several conditions is necessary to obtain a steady and reversible hydrogen electrode in the acetone-water mixtures. The present investigation was designed to find the requisite conditions for a steady and reproducible hydrogen electrode in the said solvent when hydrochloric acid is replaced by sulphuric acid. Consequently the cell under investigation was

Pt. H_2 (1 atm.) | H_2SO_4 (m), acetone (X%), H_2O (100—X%) Hg_2SO_4 | Hg.
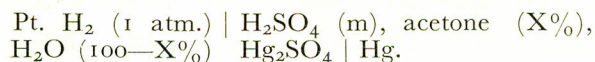
However a considerable data about the activity coefficients of sulphuric acid in water-organic solvents (except acetone) is available in literature. The worth mentioning work in this connection is of Y.S. Przeborwskii, V.G. Georgievskii and N.D. Filippowa,[5] Shibata and Oda,[6] McDougall Blumer,[7] Crockford and Wideman,[8] Land and and Crockford [1] and French and Hussain.[9]

Experimental

Materials.—100% sulphuric acid was obtained by adding a calculated quantity of oleum (containing 65% free SO_3) to concentrated sulphuric acid as described by Lange.[10] On account of the hygroscopic nature of the acid, it was considered desirable to prepare it frequently in small quantities for the experimental work.

Analar acetone was further purified by shaking it with silver oxide, then filtered, dried over freshly ignited potassium carbonate and distilled through an efficient fractionating column as described by Werner.[11] The middle fraction thus obtained was used.

Analar mercury supplied by the B.D.H. was further purified by passing repeatedly through dilute nitric acid column containing mercurous nitrate and subsequently distilled under vacuum.

Mercurous sulphate needed for the preparation of the electrode was prepared by adding mercurous nitrate in water containing a few drops of concentrated nitric acid and the resulting solution was poured into electrically stirred dilute (1 to 6%) sulphuric acid. Mercurous sulphate thus obtained was preserved in 3M. H_2SO_4 until used

For the purification of hydrogen and for the preparation of hydrogen electrode the procedure adopted was the same as already described by F. Hussain and S.S. Haque.[12]

Mercury-mercurous sulphate electrode was obtained by the method used by French and Hussin.[9]

Procedure.—For the measurement of the electromotive force, a Pye-Precision Vernier potentiometer was used. As there is a considerable change in electromotive force with respect to the variation of temperature, a Cambridge Weston standard cell was employed 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 device enabled to measure the e.m.f., to the fifth place of decimal.

The filling procedure and the cell design has been described by F. Hussain and S.S. Haque.[12] A mean value of the triplicate reading in each run was taken and a maximum deviation was of the order of ± 0.05mv.

In making a measurement, the cell solution was first saturated with hydrogen, and then forced into the cells under hydrogen pressure. The flow of hydrogen through the liquid was then started.

Results and Discussion

The readings were reproducible to within ±0.05 mv. During the whole work, exposure to bright light was avoided as far as possible, since such exposure causes a darkening of the mercurous sulphate, and the e.m.f. values obtained with its use are somewhat higher and less reliable. Moreover, the experimental work has shown that gold plating of hydrogen electrode before platinizing it as mentioned by Popoff, Kunz and Snow [13] is

not essential. The platinized hydrogen electrodes were kept in conductivity water in the darkness till used. The time required for equilibrium for 5 and 10% acetone was 3 to 5 hours while for 20 and 40% acetone it was 6 to 8 hours. At the low percentages of acetone, the equilibrium stability was much longer as compared to the higher ones. In case of higher acetone values, if the filled cells were not allowed to stand overnight, difficulty was experienced in getting three concordant readings in each run. The observations have shown that a platinized electrode functions properly to obtain a steady and reversible hydrogen electrode and the conditions of using bare and polished platinum electrode, as in the case of hydrochloric acid, are not essential.

The electromotive force and density values at definite molalities given in the Table I (where d is the density, and $\gamma\pm$ mean ionic activity coefficients) were read from large curves obtained by plotting the square root of the molality against the corresponding values. In the case of electromotive forces, before drawing the graph, the values were corrected to one atmosphere pressure of dry hydrogen. The electromotive forces are compared with similar data (converted to 32°C.) for water, obtained by Harned and Hamer as in Fig. I.

Standard potentials were obtained by extrapolation method. The best results were obtained by plotting the values of ΔE (Table 2) against the square root of molality as described by Land and Crockford.[1] ΔE denotes the difference between

TABLE I

m	5% Acetone $E^\circ = .5674$ volt.			10% Acetone $E^\circ = .5572$ volt.			20% Acetone $E^\circ = .5051$ volt.			40% Acetone $E^\circ = .4654$ volt.		
	d_4^{32}	E	$\gamma_\pm$	d_4^{32}	E	$\gamma_\pm$	d_4^{32}	E	$\gamma_\pm$	d_4^{32}	E	$\gamma_\pm$
0.05	0.9939	0.7126	0.3206	0.9857	0.7024	0.3206	0.9704	0.6676	0.2044	0.9391	0.6399	0.1507
0.10	0.9958	0.6958	0.2426	0.9882	0.6882	0.2277	0.9736	0.6558	0.1386	0.9423	0.6271	0.1042
0.20	1.0011	0.6782	0.1945	0.9939	0.6726	0.1687	0.9760	0.6426	0.0970	0.9482	0.6122	0.0958
0.30	1.0062	0.6685	0.1616	0.9985	0.6634	0.1420	0.9800	0.6345	0.07884	0.9535	0.6023	0.06671
0.40	1.0123	0.6621	0.1426	1.0040	0.6563	0.1276	0.9845	0.6286	0.06868	0.9570	0.5955	0.05809
0.50	1.0175	0.6549	0.1370	1.0098	0.6502	0.1191	0.9902	0.6240	0.06172	0.9612	0.5907	0.05249
0.60	1.0239	0.6518	0.1234	1.0159	0.6451	0.1129	0.9960	0.6199	0.05709	0.9656	0.5854	0.05003
0.70	1.0307	0.6484	0.1158	1.0214	0.6409	0.1076	1.0020	0.6162	0.05375	0.9705	0.5816	0.04723
0.80	1.0379	0.6453	0.1094	1.0280	0.6374	0.1007	1.0078	0.6123	0.05293	0.9758	0.5781	0.04516
0.90	1.0445	0.6425	0.1042	1.0342	0.6330	0.1000	1.0134	0.6081	0.05132	0.9810	0.5742	0.04432
1.00	1.0520	0.6412	0.09692	1.0423	0.6318	0.09499	1.0202	0.6068	0.04891	0.9869	0.5723	0.04186
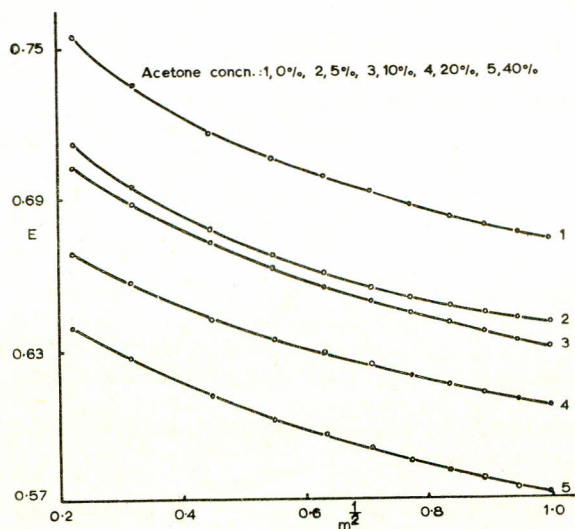
Fig. 1.— H_2SO_4 in acetone-water mixtures.

TABLE 2.

m	5% Acetone ΔE	10% Acetone ΔE	20% Acetone ΔE	40% Acetone ΔE
0.05	0.0417	0.0518	0.0866	0.1143
0.10	0.0411	0.0487	0.0811	0.1098
0.20	0.0410	0.0466	0.0766	0.1098
0.30	0.0406	0.0457	0.0746	0.1068
0.40	0.0394	0.0452	0.0729	0.1060
0.50	0.0402	0.0449	0.0711	0.1044
0.60	0.0382	0.0449	0.0701	0.1046
0.70	0.0371	0.0446	0.0693	0.1039
0.80	0.0362	0.0441	0.0692	0.1034
0.90	0.0353	0.0439	0.0689	0.1028
1.00	0.0362	0.0438	0.0688	0.1023

the electromotive forces for various acid molalities and the corresponding values of Harned and Hamer[2] in water converted to 32°C.

The curves obtained in this way were almost linear in the range of molality greater than 0.2m. However, smooth curves were obtained at lower molalities and the extrapolation could be done with great precision. The value of ΔE at zero molality was then subtracted from the standard potential of water at 32°C.

The activity coefficients were calculated with the help of the equation:—

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

The calculation of $\gamma_\pm$ was made on the basis of a reference state of unit activity coefficient of a solute at infinite dilution in the solvent.

The values of $-\log \gamma_\pm$ have been plotted against the square root of molality and are compared with those of water in Fig. 2.
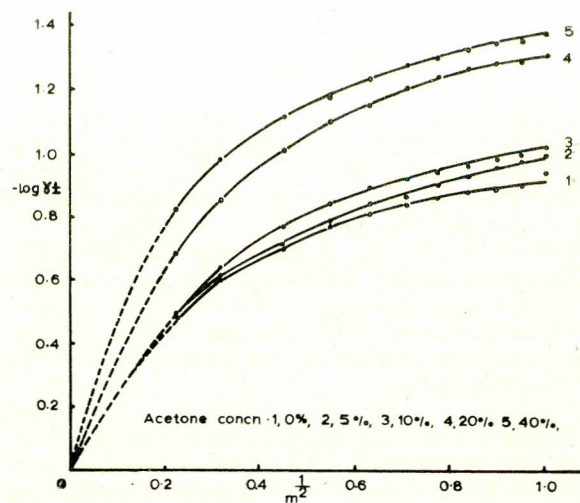
Fig.2.— H_2SO_4 in acetone-water mixtures.

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