

*Standard Potentials of Mercury–Mercurous Sulphate Electrodes in  
Ethylene Glycol–Water Mixtures at 25°.*

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The electromotive force of the cell Pt, H<sub>2</sub> (1 atm.)|H<sub>2</sub>SO<sub>4</sub>(*m*), ethylene glycol (*X*%), H<sub>2</sub>O (100 – *X*%)|Hg<sub>2</sub>SO<sub>4</sub>|Hg was measured at 25° for *X* values of 5, 10, 20, and 30. Standard potentials were computed in each case by extrapolation, and the mean ion activity coefficients of sulphuric acid were calculated for the various acid molalities from 0.05 to 1.00 used in this work.

A DETAILED investigation of the activity coefficient of sulphuric acid in water has been made by Harned and Hamer (*J. Amer. Chem. Soc.*, 1935, 57, 27). Relatively few data, however, exist for the activity coefficient of sulphuric acid in other solvents. Notable exceptions are the e.m.f. measurements in aqueous acetic acid (McDougal and Blumer, *ibid.*, 1933, 55, 2236), in methanol–water mixtures (Shibata and Oda, *J. Chem. Soc. Japan*, 1931, 52, 590), in ethanol–water mixtures (Crockford and Wideman, *J. Phys. Chem.*, 1946, 50, 418), and in aqueous propan-2-ol (Land and Crockford *J. Amer. Chem. Soc.*, 1950, 72, 1895). The present investigation was designed to extend this range of solvents and to provide information on the effect of change of solvent, as denoted by its dielectric constant, on the activity coefficient of the solute.

#### EXPERIMENTAL

Ethylene glycol was purified by the method of Smyth and Walls (*ibid.*, 1931, 53, 2116) and finally distilled at 4 mm.: it had b. p. 68°/4 mm.,  $d_4^{25}$  1.10985,  $n_D^{25}$  1.43057 (lit.;  $d_4^{25}$  1.10987, Gibson and Loeffler, *ibid.*, 1941, 63, 898;  $n_D^{25}$  1.43055, Smyth and Walls, *loc. cit.*).

Water used for the preparation of solutions was obtained by passing distilled water through a four-foot column packed with "Biodeminrolit" ion-exchange resin.

Mercury was purified by washing it with dilute nitric acid, dilute sodium hydroxide, and water, and subsequent distillation *in vacuo*. Some of this mercury was then used for the electrolytic preparation of mercurous sulphate by Hulett's method (*Phys. Rev.*, 1911, 32, 257). The mercurous sulphate was then washed by suction with 3*M*-sulphuric acid and then 8 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 5-mm. diameter tube. This paste was transferred to 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 mercurous sulphate, and the e.m.f. values obtained with its use are somewhat higher and less reliable. The hydrogen electrode consisted of platinum foil 0.4 × 2.5 cm. first cleaned by making it the anode in 6*M*-hydrochloric acid, then plating it for 3 min. in gold cyanide solution (Clark, *J. Phys. Chem.*, 1928, 32, 1056). This electrode was then platinized by the method of Popoff, Kuntz, and Snow (*ibid.*, p. 1056). H-Shaped cells were employed, the two limbs being connected *via* a stop-cock. Hydrogen purified by passage over heated copper turnings was passed first through the solution in a saturator and then through the solution to be measured for 2 hr. The latter solution was then drawn into the cell previously filled with hydrogen and left in contact with the electrodes for several hours before readings were commenced.

Electromotive forces were measured by using a Tinsley two-dial thermoelectric-free potentiometer, and a high-sensitivity mirror galvanometer in conjunction with a lamp and scale. Readings were reproducible to within ±0.05 mv. The experimental e.m.f. values were corrected to 1 atm. pressure of dry hydrogen, the measured vapour pressures of the corresponding solutions of sulphuric acid in ethylene glycol–water mixtures being used for this purpose.

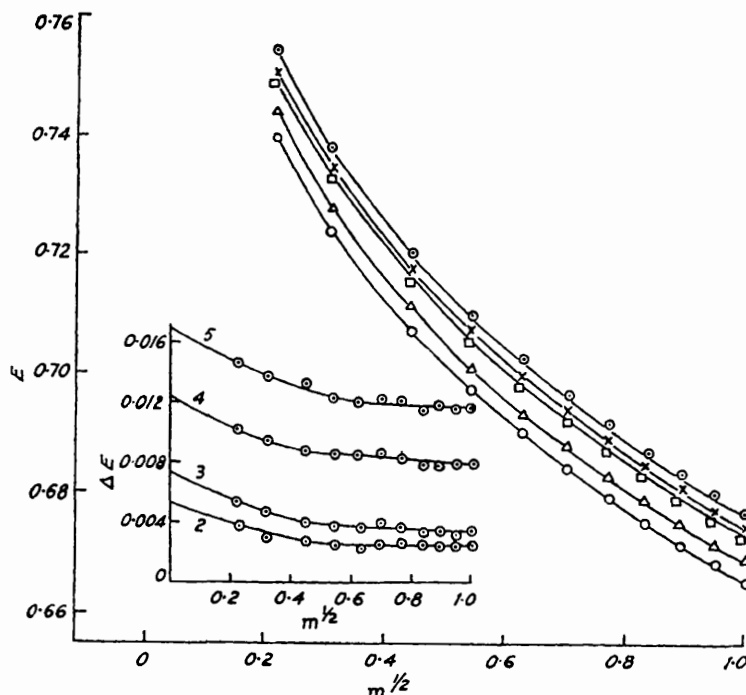
#### RESULTS AND DISCUSSION

In addition to the solutions for which results are given in this paper, measurements were also attempted on solutions of higher glycol content and both greater and smaller

acid concentration. For solutions containing more than 30% of ethylene glycol or of acid concentration greater than 1.0m, the time taken for equilibrium to be established and steady values of e.m.f. to be obtained was so great (>120 hr.) as to render the results somewhat uncertain. Even in the case of 5% ethylene glycol equilibrium was reached only in 40–50 hr. Owing to the solubility of mercurous sulphate, solutions of acid concentration less than 0.05m could not be measured.

Values of the e.m.f. corrected to 1 atm. pressure for solutions of various acid molalities are given in the Table (where  $d$  is the density and  $\epsilon$  the dielectric constant) together with the mean ion activity coefficients ( $\gamma_{\pm}$ ). These e.m.f. data are compared with similar data for solutions in pure water (Harned and Hamer, *loc. cit.*) in the Figure.

Ethylene glycol concn.: (1,  $\odot$ ) 0, (2,  $\times$ ) 5%, (3,  $\square$ ) 10%, (4,  $\triangle$ ) 20%, (5,  $\circ$ ) 30%.



Values of the standard potential for the four solvent media were obtained by the procedure recommended by Land and Crockford (*loc. cit.*), as follows: The values of  $\Delta E$ , the difference between the measured e.m.f. for the various acid molalities for a given glycol-water mixture and the corresponding values of Harned and Hamer in pure water, were plotted against  $m^{1/2}$ . The curves thus obtained were nearly linear for concentrations having  $m^{1/2}$  greater than 0.4. At lower molalities smooth curves were obtained and extrapolation was accordingly effected to zero molality. The resulting value of  $\Delta E$  was then subtracted from the value of  $E^\circ$  for pure water, the difference representing the value of the standard potential in the aqueous glycol solvent. The latter values are also shown in the Table.

The activity coefficients were calculated from the equation

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

The activity coefficients  $\gamma$  were calculated on the basis of a reference state of unit activity coefficient of the solute at infinite dilution in the given solvent. The activity coefficients  $\gamma'$  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 value of  $E^\circ$  obtained by Harned and Hamer (*loc. cit.*) was employed.

Molality (m)	E.m.f. ( $E$ )				$\gamma_{\pm}$	$\gamma'_{\pm}$	E.m.f. ( $E$ )			
	$\alpha_1^{\pm}$	5% Ethylene glycol ( $E^\circ$ 0.6095), $\epsilon_{25} = 77.1$ D	$\gamma_{\pm}$	$\gamma'_{\pm}$			$\alpha_1^{\pm}$	10% Ethylene glycol ( $E^\circ$ 0.6077), $\epsilon_{25} = 75.6$ D	$\gamma_{\pm}$	$\gamma'_{\pm}$
0.05	1.0097	0.7505	0.3244	0.3761	1.0161	0.7490	0.3223	0.3911		
0.1	1.0127	0.7340	0.2490	0.2882	1.0191	0.7324	0.2480	0.3016		
0.2	1.0188	0.7170	0.1935	0.2273	1.0251	0.7158	0.1905	0.2345		
0.3	1.0249	0.7068	0.1681	0.1949	1.0310	0.7055	0.1659	0.2016		
0.4	1.0309	0.6995	0.1524	0.1766	1.0370	0.6983	0.1500	0.1823		
0.5	1.0369	0.6935	0.1421	0.1651	1.0429	0.6922	0.1406	0.1708		
0.6	1.0429	0.6884	0.1355	0.1570	1.0488	0.6872	0.1334	0.1620		
0.7	1.0488	0.6840	0.1302	0.1510	1.0547	0.6830	0.1275	0.1549		
0.8	1.0547	0.6802	0.1257	0.1457	1.0605	0.6793	0.1228	0.1491		
0.9	1.0606	0.6766	0.1227	0.1422	1.0664	0.6757	0.1199	0.1456		
1.0	1.0666	0.6736	0.1193	0.1384	1.0723	0.6727	0.1166	0.1417		
20% Ethylene glycol ( $E^\circ$ 0.6026), $\epsilon_{25} = 72.7$ D					30% Ethylene glycol ( $E^\circ$ 0.5982), $\epsilon_{25} = 69.9$ D					
0.05	1.0301	0.7441	0.3202	0.4411	1.0434	0.7397	0.3202	0.4978		
0.1	1.0330	0.7277	0.2451	0.3398	1.0462	0.7234	0.2444	0.3800		
0.2	1.0387	0.7110	0.1892	0.2622	1.0517	0.7067	0.1886	0.2931		
0.3	1.0445	0.7007	0.1646	0.2283	1.0573	0.6970	0.1617	0.2507		
0.4	1.0503	0.6933	0.1496	0.2075	1.0629	0.6898	0.1462	0.2272		
0.5	1.0559	0.6874	0.1395	0.1934	1.0686	0.6840	0.1359	0.2113		
0.6	1.0616	0.6827	0.1313	0.1821	1.0744	0.6790	0.1289	0.2004		
0.7	1.0673	0.6785	0.1255	0.1741	1.0802	0.6747	0.1236	0.1922		
0.8	1.0730	0.6748	0.1209	0.1677	1.0860	0.6709	0.1192	0.1879		
0.9	1.0788	0.6712	0.1180	0.1636	1.0917	0.6674	0.1162	0.1806		
1.0	1.0846	0.6681	0.1151	0.1596	1.0972	0.6644	0.1131	0.1757		

Plots of  $\gamma$  and  $\gamma'$  against the square-root of molality of the acid give curves which show a similar shape to that obtained for pure water. However, the  $\gamma$  values are lower than those for pure aqueous solutions, whereas the values of  $\gamma'$  are higher.

Finally, it may be observed that if  $E^\circ$  is plotted against the reciprocal of the dielectric constant for the four solvent media studied, and for water by using the data of Harned and Hamer (*loc. cit.*), a smooth curve is obtained.

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