Activity Coefficients of Sulphuric Acid in Aqueous Propylene Glycol and Aqueous Propan-1-ol at 25°.

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Electromotive force measurements have been made on the cell H_2 (1 atm.)|H_2SO_4(m), alcohol (x%), H_2O (100 − x%)|Hg_2SO_4–Hg at 25° c, with propan-1-ol and also propylene glycol as the organic part of the solvent. Values of x of 5, 10, and 20 were used, and the acid concentration (molal) was varied between 0·05 and 1·00. Standard potentials were computed by a graphical extrapolation method and are plotted against the reciprocal of the dielectric constant of the solvent giving smooth curves for each alcohol. Mean ion-activity coefficients were also calculated and are recorded.

The electromotive force between a mercury–mercurous sulphate electrode and a hydrogen electrode in sulphuric acid solutions in water has been measured by Brønsted (*Z. phys. Chem.*, 1910, **68**, 693), Lewis and Lacey (*J. Amer. Chem. Soc.*, 1914, **36**, 804), and Randall and Cushman (*ibid.*, 1918, **40**, 393), and the results are critically surveyed by Harned and Hamer (*ibid.*, 1935, **57**, 27). As noted in an earlier paper (French and Hussain, *J.*, 1955, 2211) relatively few data exist for solutions in organic and aqueous-organic media. It was thought desirable to extend the measurements on ethylene glycol systems reported in the last paper to propylene glycol– and propan-1-ol–water mixtures.

In this way further information may be obtained concerning the effect of change of solvent, as denoted by its dielectric constant, on the mean-ion activity coefficient of the solute.

Experimental.—Electromotive forces were measured with the apparatus described earlier (French and Hussain, *loc. cit.*) and were reproducible to within ±0·05 mv. The cells containing the solutions under investigation were kept in an air thermostat at 25° ± 0·02° during measurement.

Propylene glycol was purified by the method of Smyth and Walls (*J. Amer. Chem. Soc.*, 1931, **53**, 2116), and was finally distilled at 4 mm.; it had b. p. 62°/4 mm., d_4^{25} 1·0327, n_D^{25} 1·4315 (lit., d_4^{25} 1·0328, n_D^{25} 1·43143).

Propan-1-ol, purified according to Lund and Bjerrum's directions (*Ber.*, 1931, **64**, 210) and finally fractionated, had d_4^{25} 0·7996, n_D^{25} 1·3835 (lit., d_4^{25} 0·7993, 0·7999, 0·79985; n_D^{25} 1·3833, 1·3834).

Results and Discussion.—In all cases equilibrium was slowly attained and this was particularly marked in the case of 20% propylene glycol where constant values were obtained only after 30 hr. The mean e.m.f. of three solutions measured concurrently and agreeing generally to within 0·05 mv was taken as that of the solution under investigation. All these results were corrected to 1 atm., by using the measured vapour pressure of the corresponding sulphuric acid solutions. The resulting e.m.f. values are given in the Table (where *d* is the density and ε the dielectric constant) together with the mean ion-activity coefficients ($\gamma_{\pm}$).

Molality	d_4^{25}	E.m.f.	$\lambda_{\pm}$	$\lambda_{\pm}'$	d_4^{25}	E.m.f.	$\lambda_{\pm}$	$\lambda_{\pm}'$
	10% Propan-1-ol ($E°$ 0·6065), vap. press. 30·71 mm.				20% Propan-1-ol ($E°$ 0·6011), vap. press. 34·19 mm.			
0·05	0·9879	0·7473	0·3261	0·4087	0·9715	0·7425	0·3210	0·4629
0·1	0·9909	0·7305	0·2522	0·3161	0·9745	0·7260	0·2463	0·3552
0·2	0·9969	0·7136	0·1955	0·2451	0·9804	0·7092	0·1905	0·2747
0·3	1·0028	0·7037	0·1686	0·2112	0·9862	0·6991	0·1651	0·2380
0·4	1·0087	0·6962	0·1536	0·1924	0·9922	0·6916	0·1504	0·2168
0·5	1·0147	0·6901	0·1439	0·1803	0·9979	0·6857	0·1403	0·2021
0·6	1·0207	0·6853	0·1358	0·1702	1·0038	0·6810	0·1320	0·1903
0·7	1·0266	0·6809	0·1305	0·1636	1·0097	0·6761	0·1284	0·1852
0·8	1·0326	0·6770	0·1264	0·1584	1·0157	0·6724	0·1238	0·1784
0·9	1·0386	0·6734	0·1233	0·1546	1·0217	0·6689	0·1205	0·1738
1·0	1·0445	0·6703	0·1203	0·1508	1·0276	0·6659	0·1172	0·1690
	5% Propylene glycol ($E°$ 0·6092), vap. press. 23·4 mm.				10% Propylene glycol ($E°$ 0·6068), vap. press. 23·00 mm.			
		$\varepsilon_{25} = 76{\cdot}9$				$\varepsilon_{25} = 74{\cdot}8$		
0·05	1·0074	0·7502	0·3244	0·3791	1·0107	0·7483	0·3203	0·3983
0·1	1·0103	0·7338	0·2483	0·2901	1·0137	0·7318	0·2458	0·3056
0·2	1·0162	0·7168	0·1831	0·2255	1·0198	0·7153	0·1886	0·2345
0·3	1·0221	0·7065	0·1681	0·1964	1·0257	0·7050	0·1643	0·2042
0·4	1·0281	0·6992	0·1523	0·1780	1·0316	0·6977	0·1488	0·1851
0·5	1·0340	0·6933	0·1420	0·1660	1·0375	0·6918	0·1388	0·1726
0·6	1·0399	0·6882	0·1351	0·1579	1·0434	0·6867	0·1320	0·1642
0·7	1·0457	0·6837	0·1301	0·1522	1·0494	0·6825	0·1262	0·1570
0·8	1·0516	0·6799	0·1257	0·1469	1·0550	0·6787	0·1219	0·1516
0·9	1·0574	0·6763	0·1228	0·1432	1·0607	0·6751	0·1190	0·1479
1·0	1·0634	0·6733	0·1193	0·1395	1·0665	0·6722	0·1154	0·1435
	20% Propylene glycol ($E°$ 0·6013), vap. press. 22·21 mm.							
		$\varepsilon_{25} = 71{\cdot}1$						
0·05	1·0193	0·7430	0·3185	0·4569				
0·1	1·0223	0·7267	0·2432	0·9488				
0·2	1·0283	0·7101	0·1871	0·2683				
0·3	1·0340	0·6998	0·1629	0·2337				
0·4	1·0399	0·6923	0·1485	0·2129				
0·5	1·0457	0·6865	0·1380	0·1980				
0·6	1·0514	0·6819	0·1296	0·1859				
0·7	1·0572	0·6775	0·1246	0·1786				
0·8	1·0630	0·6740	0·1193	0·1712				
0·9	1·0689	0·6703	0·1168	0·1675				
1·0	1·0747	0·6673	0·1136	0·1629				

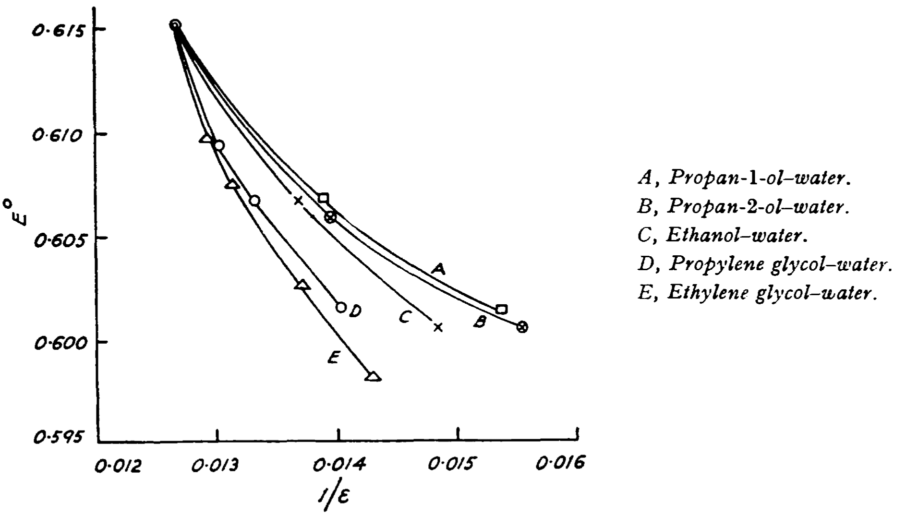
The value of the standard potential (shown in the Table) for each solvent medium was computed by Land and Crockford's method (*J. Amer. Chem. Soc.*, 1950, **72**, 1895), as described by French and Hussain (*loc. cit.*). As in the case of ethylene glycol the plots of ΔE against $m^{\frac{1}{2}}$ were linear for concentrations greater than 0·16m. At lower concentrations smooth curves closely resembling those of ethylene glycol and with a similar curvature were obtained. Graphical extrapolation to zero acid concentration was therefore effected as before.

The activity coefficients were calculated from the equation

$$E = E_0 - \frac{3RT}{2F} \ln (4^{\frac{1}{3}} m\gamma_{\pm})$$

Again the activity coefficients γ 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 γ' 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 $E°$ obtained by Harned and Hamer (*loc. cit.*) was employed.

Curves obtained by plotting γ and γ' against $m^{\frac{1}{2}}$ fall respectively below and above the same curves for systems in pure water, but resemble them closely and show the same tendency towards a minimum in each medium.



Finally it may be noted that if $E°$ for each solvent medium is plotted against the reciprocal of the dielectric constant of that solvent, then a smooth curve is obtained for each aqueous organic medium. All curves have, of course, a common origin at the $E°$ value for pure water. The curves for the systems investigated by the present authors together with those for ethanol and propan-2-ol obtained by Crockford and Wideman (*J. Phys. Chem.*, 1946, **50**, 418) and Land and Crockford (*loc. cit.*) are shown in the Figure. It will be observed that the curves for the monohydric alcohols are close together, particularly for the isomeric propanols, and are distinct from the curves for the dihydric alcohols.

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