439. *E.m.f. Measurements in Ethyl Methyl Ketone–Water Mixtures with the Cell* $H_2(Pt)|HCl|AgCl–Ag$. *With an Appendix on Triethylene Glycol–Water Systems.*

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Standard potentials of the cell $H_2(Pt)|HCl|AgCl–Ag$ in 10% and 20% ethyl methyl ketone solutions in water are recorded. As with acetone solutions,[1] reversible and reproducible hydrogen-electrode potentials were unobtainable with platinum-black electrodes, but completely satisfactory results were obtained with unplatinised electrodes.[1, 2] E.m.f. measurements in the same cell with aqueous solutions of triethylene glycol were not entirely satisfactory, but in view of certain features of interest the results are recorded and discussed briefly in the Appendix.

Measurements of e.m.f. in the cell $H_2(Pt)|HCl|AgCl–Ag$ in aqueous acetone solutions have been reported.[1] These are now extended to solutions of 10 and 20% (w/w) of ethyl methyl ketone in water, and the results, including the standard potentials of this cell in these solvents, recorded.

Certain features in the behaviour of glucose solutions,[3] and to some extent glycerol [4, 5, 6] and fructose [7] solutions, led us to attempt e.m.f. measurements in triethylene glycol solutions to see whether these features were general for solutions where the organic constituent is of relatively high molecular weight. The results of this work are also reported.

Experimental

Cell measurements (at 25°), preparation of electrodes, and the measurement of vapour pressures and densities were as described earlier.[1] The dielectric constants of the pure solvent mixtures were determined with a radiofrequency bridge.

B.D.H. " Laboratory Reagent " ethyl methyl ketone was shaken with saturated potassium carbonate solution to remove acids,[8] separated, and dried (ignited K_2CO_3, then ignited Na_2SO_4). It was then fractionated 2 or 3 times with rejection of substantial head (containing aldehydes) and tail fractions. The final product only slowly restored the colour to Schiff's reagent : n_D^{20} 1·3785 (lit.,[9] n_D^{20} 1·37850), d_4^{20} 0·8054 (lit.,[10] d_4^{20} 0·8053), b. p. 79·6°/760 mm. (lit.,[11] 79·6°).

Triethylene glycol (B.D.H.) was dried ($CaSO_4$) for one week, and then repeatedly and very slowly distilled at 0·2—0·5 mm. with rejection of substantial head and tail fractions. The colourless liquid thus obtained was stored in a vacuum desiccator over P_2O_5 which was changed every time the desiccator was opened. Care was taken throughout to minimise contact of the liquid with moist air : n_D^{15} 1·4574 (lit.,[12] n_D^{15} 1·4578), d_4^{15} 1·1274 (lit.,[12] d_4^{15} 1·1274), b. p. 120—122°/0·5 mm. (lit.,[11] 115—117°/0·1 mm.).

Discussion of Ethyl Methyl Ketone Systems.—The results of e.m.f. measurements in hydrochloric acid solutions of different molalities (*m*) in the two solvent mixtures are given in Table 1, together with values of the total vapour pressures (v.p.) and dielectric constants of the two solvent mixtures

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If E_m° is the standard potential of the cell on the molal scale, then

$$E = E_m^\circ - 2\,(\boldsymbol{RT}/\boldsymbol{F})\ln m\gamma_\pm$$

where $\gamma_\pm$ is the mean molal activity coefficient and E is the observed e.m.f. corrected to 760 mm. pressure.

Following the procedure outlined earlier,[1] we can obtain a quantity E_0' which is related to standard potential by the equation

$$E_m^\circ = E_0' + 2kB'm$$

As before, the plot of E_0' against molality should yield a straight line of negative slope $-2kB'$, from which the salting-out constant B' can be determined. Extrapolation to zero molality will give E_m°.

TABLE 1.

Molality (m)	E.m.f. (E) (v)	Molality (m)	E.m.f. (E) (v)	Molality (m)	E.m.f. (E) (v)	Molality (m)	E.m.f. (E) (v)
10% Methyl Ethyl Ketone : $\varepsilon = 71{\cdot}9$; V. p. $= 69{\cdot}4 \pm 0{\cdot}1$ mm.; $E_m^\circ = 0{\cdot}2153_5$ v.				20% Methyl Ethyl Ketone : $\varepsilon = 74{\cdot}9$; V. p. $= 93{\cdot}9 \pm 0{\cdot}1$ mm. $E_m^\circ = 0{\cdot}2078$ v.			
0·003455	$0{\cdot}5102_5$	0·01141	$0{\cdot}4512_5$	0·003125	$0{\cdot}5083_5$	0·01738	0·4242
0·004677	0·4951	0·02154	$0{\cdot}4203_5$	0·005136	0·4837	0·04000	0·3844
0·006591	0·4784	0·04586	0·3840	0·006423	0·4726	0·05940	$0{\cdot}3656_5$
0·006886	$0{\cdot}4760_5$	0·06705	$0{\cdot}3658_5$	0·008077	0·4614	0·08020	$0{\cdot}3514_5$
0·007307	$0{\cdot}4731_5$	0·08710	0·3535	0·01023	0·4499	0·1054	$0{\cdot}3386_5$
0·008361	0·4665	0·1139	$0{\cdot}3406_5$				
0·009869	$0{\cdot}4583_5$						

A value of 4·3 Å being used for the ionic parameter $\mathring{a}$, straight lines (plotted by the method of least squares) were obtained over the concentration range 0·003—0·1m in both cases. The standard potentials and values of B' were obtained from these lines. Only in a few cases are the deviations of individual points from the straight lines as great as 0·2 mv. The standard potentials are probably accurate to at least ±0·1 mv.

Activity coefficients in the range 0·003—0·1m are obtained from the equation

$$\log_{10}\gamma_\pm = -Ac^{\frac{1}{2}}/(1 + \mathring{a}Bc^{\frac{1}{2}}) + B'm - \log_{10}(1 + 0{\cdot}002M_{xy}m) \tag{1}$$

by employing the appropriate experimental values of B'. $M_{xy} = 100/[X/M_x + (100 - X)/M_y]$ where X is the weight percentage of the ketone, and M_x and M_y are the molecular weights of the ketone and water respectively.

The values of A, B, and B', the densities of the pure solvent mixtures (d_0) and the activity coefficients at rounded acid concentrations calculated from eqn. (1) are given in Table 2.

TABLE 2.

Methyl ethyl ketone (%)	10	20			0	10	20
A	0·5779	0·6740	$m =$ 0·002m	$\gamma_\pm =$	0·9521	0·947	0·939
B	0·3436	0·3617	0·005m		0·9285	0·920	0·908
B'	$0{\cdot}14_4$	$0{\cdot}15_1$	0·01m		0·9048	0·894	0·878
d_0	0·9844	0·9703	0·02m		0·8755	0·862	0·842
M_{xy}	19·46	21·18	0·05m		0·8304	0·813	0·787
			0·1m		0·7964	0·774	0·744

The standard potentials will be discussed in detail in the following paper, but there are a few points which may be noted. The plot of E_m° against $1/\varepsilon$ gives a curve which is closely related to one on which the results for propanol solutions and for 5% and 10% acetone solutions lie. As is usually the case when comparing solutions of homologous series, the E_m° values for ethyl methyl ketone solutions are higher, for isodielectric mixtures, than those for acetone solutions. This is also true for the E_N° against $1/\varepsilon$, and $E_N^\circ - k\log N_w$ against $1/\varepsilon$ plots. Here the ethyl methyl ketone curve shows a closer relation to the curve for the monohydric alcohols than it does to that for acetone. These considerations indicate that little further progress can be made with plots of this sort.

On the other hand, the $E_m°$ values of 10% and 20% solutions respectively of the two ketones differ only slightly. The generally close similarity between the solutions (both show strong positive deviations from Raoult's law, and the vapour pressures of the two 10% solutions are identical) is also interesting. Both these facts support the contention that the stoicheiometry of the solvent mixture, and to some extent its thermodynamic properties, are the major factors in determining $E_m°$. Up to concentrations of 20% (w/w) solutions of both ketones obey fairly closely the same simple stoicheiometric relation.

APPENDIX

Considerable and unexpected experimental difficulty was experienced in the measurement of e.m.f. in aqueous triethylene glycol solutions. This arose principally from the behaviour of the silver–silver chloride electrodes. These were prepared as described earlier,[9] but even when carefully washed between runs became, after the second or third time of use, 0·2—0·3 mv negative to a freshly prepared electrode. After a few more runs the electrodes exhibited deviations often amounting to 2 mv or more. This effect was particularly marked in the more concentrated acid solutions of the 20% glycol–water mixtures. At least one freshly prepared electrode was therefore used for each run, and no electrode was used more than 3 times.

The behaviour of the hydrogen electrodes was fairly satisfactory in these solutions. "Activated" electrodes (*i.e.*, the unplatinised electrodes described earlier [1,2]) were not uniformly successful, some showing a tendency to failure. Agreement between platinum-black electrodes was also often poor, and the best electrodes for these systems were very thinly plated grey ones, obtained by platinising from solutions containing no lead.[10]

Even with these precautions, cell agreement was often poor (three cells differing from the mean by more than 0·05 mv), and led to the rejection of many unsatisfactory runs. It was believed however, that the electrode behaviour, and the anomalous results discussed below, could not be ascribed to solvent impurity since most of the e.m.f. measurements were reproducible between different batches of glycol, as also were the physical constants.

Measurements in both the 10% and 20% solvent mixtures were made over the acid concentration range 0·003—0·1m. The 10% solution was studied in greater detail than the 20% solution, where repeated lack of agreement between the three cells would have necessitated a very large number of trials.

The results are shown in Table 3 where, in addition to the observed e.m.f. at each concentration, are given the appropriate values of E_0', computed on the basis of an $\mathring{a}$ value of 4·3 Å.

TABLE 3.

Molality (10^3m)	E(v)	E_0'	Molality (10^3m)	E(v)	E_0'	Molality (10^3m)	E(v)	E_0'
10% Triethylene glycol : ε = 73·0; V. p. = 23·4 (± 0·1) mm; $E_m°$ = 0·2161$_5$ v.								
3·175	0·5160$_5$	0·2170	7·864	0·4707$_5$	0·2165	51·27	0·3790$_5$	0·2149
4·016	0·5044$_5$	0·2170$_5$	9·182	0·4628$_5$	0·2162	53·12	0·3774	0·2152
5·174	0·4917$_5$	0·2169	10·28	0·4573	0·2161$_5$	61·30	0·3707	0·2149$_5$
5·410	0·4895	0·2169	13·48	0·4441$_5$	0·2162	69·59	0·3645$_5$	0·2147
6·074	0·4838$_5$	0·2169	18·01	0·4296$_5$	0·2157	80·43	0·3574$_5$	0·2143$_5$
6·203	0·4829	0·2170	33·17	0·4001	0·2154	91·09	0·3515$_5$	0·2142$_5$
6·789	0·4779$_5$	0·2165	39·95	0·3911	0·2152	98·43	0·3478	0·2140$_5$
20% Triethylene glycol : ε = 67·0; V. p. = 22·8 ± 0·1 mm.; $E_m°$ = 0·2094 v.								
3·515	0·5059	0·2114	6·116	0·4779$_5$	0·2107	39·22	0·3867$_5$	0·2086$_5$
3·603	0·5045$_5$	0·2113	7·126	0·4699$_5$	0·2101$_5$	64·11	0·3629	0·2076
5·246	0·4856$_5$	0·2108$_5$	8·322	0·4621$_5$	0·2099$_5$	84·25	0·3496$_5$	0·2070$_5$
5·419	0·4839	0·2108	10·69	0·4490$_5$	0·2090	96·43	0·3433$_5$	0·2068$_5$
5·966	0·4791$_5$	0·2107	17·82	0·4243$_5$	0·2088			

The plots of E_0' against molality are highly anomalous. Neither plot is the single straight line which is usually found : neither plot can be made a straight line over the whole concentration range by adjusting *å*. In the 10% solution a straight line relationship holds from about 0·02 to 0·1m. From 0·003 to 0·02m, E_0' falls off very rapidly with molality, dropping about 1·3 mv compared with a normal drop of about 0·4 mv. While the values of E_0' are sensibly constant over a very short range in the most dilute solutions, any extrapolation to obtain $E_m°$ in concentrations below 0·02m would be extremely unreliable. Extrapolation of the results in the higher concentrations yields an $E_m°$ value of $0{\cdot}2161_5$ v, and a salting-out constant B' of $0{\cdot}18_2$.

In the 20% solution there is again a very rapid drop in E_0' with increase in acid concentration in the region 0·003—0·01m. At higher concentrations the results lie on a straight line, which, on extrapolation to zero molality, yields an $E_m°$ value of 0·2094 v, but with rather less certainty than in the 10% mixture. The salting-out constant B' is $0{\cdot}22_8$.

The uncertainty with which these values are obtained, owing to the lack of reliable measurements in the very dilute solutions, prevents our calculating activity coefficients. Further, although the trends in the dilute solutions are systematic, they are probably of experimental origin.

The B' values for triethylene glycol solutions are high compared with those found for solutions of simpler substances (0·13—0·17). Such high values are found also with glycerol, glucose, and fructose solutions if an *å* value of 4·3 is employed.

Finally it is interesting that the $E_m°$ values for the 10% and 20% solutions agree well with those predicted by the stoicheiometric relation discussed in detail in the following paper (0·2162 and $0{\cdot}2095_5$ respectively). Considered on the basis of isodielectric mixtures, the $E_m°$ values, unlike those of glucose and to some extent glycerol solutions, are not anomalously low. Triethylene glycol solutions, and glycerol solutions generally, obey the stoicheiometric relationship fairly closely, whilst glucose solutions do not. Special reasons for the deviations in the latter systems are given in the following paper.

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