608. *E.m.f. Measurements in Acetone–Water Mixtures: the Cell* $H_2(Pt)|HCl|AgCl–Ag$.

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Standard potentials of the cell $H_2(Pt)|HCl|AgCl–Ag$ in 5, 10, 20, and 40% solutions of acetone in water are reported, and their relation to the dielectric constant of the solvent discussed. Activity coefficients of hydrochloric acid in these mixtures are given for the range 0·003—0·1M. Some comments are made on the hydrogen electrodes used in the work.

THE properties of the cell $H_2(Pt)|HCl|AgCl–Ag$ have been examined in mixtures of water with alcohols, glycols, glycerol, dioxan, glucose, and fructose. (Standard potentials are listed, with references, by Robinson and Stokes.[1] For recent work see Harned and Allen [2] and Claussen and French.[3,4]) The present work was undertaken partly to remedy the lack of measurements in ketone–water mixtures, in particular for comparison of the standard potentials in acetone–water mixtures with those in the other solvents, where the organic components are mainly hydroxylic. The results of measurements in 5, 10, 20, and 40% solutions (w/w) of acetone in water are now presented.

Moore and Felsing [5] attempted to measure e.m.f.'s in the above cell, using a 10% solution of acetone in water. They were unable, however, to obtain steady and reversible hydrogen electrode potentials in this medium. Our early experiences with the conventional platinum-black electrodes substantially confirmed this and it was found necessary to develop a modified form of hydrogen electrode for use in ketone–water mixtures.[6]

EXPERIMENTAL

E.m.f.'s were measured by using a Pye Precision Vernier potentiometer, in conjunction with a high-sensitivity galvanometer. Three cells based on Harned and Morrison's design [7] were measured concurrently in each experiment, and were immersed in a water thermostat at 25° ± 0·05°.

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 cell liquid was then started, and the electrodes inserted in place of ground-glass stoppers. This procedure, although open to the objection that momentary contamination of cell solution with air occurs, is unlikely to cause error, since the solutions do not oxidise, and the hydrogen-electrode compartment is rapidly cleared of air by the hydrogen stream.

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[1] Robinson and Stokes, "Electrolyte Solutions," Butterworths Scientific Publications, London, p. 457.
[2] Harned and Allen, *J. Phys. Chem.*, 1954, **58**, 191.
[3] Claussen and French, *Trans. Faraday Soc.*, 1955, **51**, 708.
[4] *Idem, ibid.*, p. 1124.
[5] Moore and Felsing, *J. Amer. Chem. Soc.*, 1947, **69**, 1076.
[6] Feakins and French, *Chem. and Ind.*, 1954, 1107.
[7] Harned and Morrison, *Amer. J. Sci.*, 1937, **33**, 161.

Hydrogen electrodes were prepared from sheets of platinum foil 2·5 × 0·8 cm.^{2}, mounted in standard cone joints. Before use the foil was polished with the rounded end of a glass rod on a plate glass sheet, warmed in 50% aqua regia until the polish was just destroyed, warmed in concentrated nitric acid to remove adsorbed chlorine, and then washed successively in tap-water, conductance water, and the cell solution, and introduced into the cell immediately.

Silver–silver chloride electrodes were prepared by Brown's method [8] (for details see Claussen and French [3]).

Vapour-pressure measurements were made by the static method described by Hovorka and Dreisbach.[9] Densities were measured in a density bottle with ground-on cap.

Hopkin and Williams's "AnalaR" acetone was purified by Werner's method.[10] It was shaken with silver oxide, filtered, dried (ignited K_2CO_3), and distilled through a 3-ft. column packed with Fenske helices. Substantial head and tail fractions were rejected; n_D^{20} 1·3591 (lit.,[11] n_D^{20} 1·35916), d_4^{20} 0·7903 (lit.,[12] d_4^{20} 0·7906), b. p. (760 mm.) 56·2° (lit.,[13] 56·2°).

DISCUSSION

Although the essential features of our unplatinised hydrogen electrodes have already been discussed,[6] some further points may be of interest.

Everett and Rasmussen [14] successfully used a platinum-black electrode in pure acetone solutions of hydrochloric acid, and found no reduction after 24 hours' passage of hydrogen. Reduction of acetone in aqueous acid solution in the presence of platinum black has been demonstrated by Foresti,[15] and the present authors checked the possibility by hydrogenation at atmospheric pressure. In a typical experiment, a 40% solution of acetone in water, containing about 0·1M-hydrochloric acid, was shown to effect reduction at a slow but definite rate equivalent to about 1% per hour at 25°, in the presence of platinum black. Such reduction would explain the erratic results found in aqueous acetone with platinised electrodes. The bare electrodes were perfectly satisfactory, except in the higher acid concentrations of the 40% mixtures, where even the bare platinum appeared to cause some reduction. Apart from this, the bare electrodes would appear to be sufficiently active to act as hydrogen electrodes, but not to reduce the acetone.

The readings in the high acid concentrations of the 40% mixture (0·01—0·1M) were difficult to obtain. As is usual with hydrogen electrodes, apparently identical treatment resulted in slight variations of activity among electrodes, and some results were obtainable with the less active ones. Although the value given for the standard potential is considered reliable, the activity coefficients in the higher acid concentrations must be regarded as less trustworthy. The limit of usefulness of the bare electrode, as here described, is probably reached in the 40% mixture.

The catalytic activity of oxidised platinum is well known, but that polishing alone will impart considerable activity to a platinum foil [6] does not appear to be generally known. It is usually assumed that polishing, if anything, increases the overpotential, yet we could readily realise the reversible hydrogen potential at polished electrodes. Such electrodes were only slightly less sensitive than the etched electrodes.

This behaviour is not unreasonable in view of the properties of a polished surface, which may be considered as highly amorphous and of greater surface energy than an unpolished one. Both on steric grounds, since such a surface might contain an assortment of atomic spacings, and energetically, one might expect the various hydrogen-electrode processes to be facilitated. Various authors [16,17] studying the anodic oxidation of platinum and other metals postulated a more or less oxidised surface which, on initial reduction, was in an amorphous form and which slowly reverted to a more ordered state, losing its activity.

[8] Brown, *J. Amer. Chem. Soc.*, 1934, **56**, 646.
[9] Hovorka and Dreisbach, *ibid.*, p. 1664.
[10] Werner, *Analyst*, 1933, **58**, 335.
[11] Tomonari, *Z. phys. Chem.*, 1936, *B*, **32**, 202.
[12] Grunert, *Z. anorg. Chem.*, 1927, **164**, 257.
[13] Griffiths, *J.*, 1952, 1326.
[14] Everett and Rasmussen, *J.*, 1954, 2812.
[15] Foresti, Atti XXVII Riunione, Bologna, Soc. ital. Progresso Sci., 1939, **5**, 346—352.
[16] Bowden, *Proc. Roy. Soc.*, 1929, *A*, **125**, 446.
[17] Butler and Drever, *Trans. Faraday Soc.*, 1936, **32**, 427.

Butler and Drever [17] considered that anodic oxidation affected only the surface layer of atoms in platinum, but that the effect was more far-reaching in palladium, where definite oxides were formed. Be this as it may, the amorphous Beilby layer is usually considered to be of the order of 50 Å thick, and the disturbing effects of polishing to extend much deeper. Furthermore, we have found that after being repeatedly etched, without intermediate polishing, an electrode became too inactive to enable the reversible potential to be obtained. Visually the foil had a rough, somewhat crystalline appearance, in contrast to the filmy grey surface of an electrode which had been polished before being etched. This perhaps suggests that the oxidation process is concerned primarily with an amorphous, or partly amorphous layer, and will not occur so readily when this has been removed, in this case by repeated action of aqua regia.

It is noteworthy that, in the earlier stages of this work, gold-plated electrodes were used on which to deposit the platinum black. Completely satisfactory electrodes for use in acetone–water mixtures could not be obtained in this way, but their activity in the reduction of acetone was greatly reduced, compared with that of electrodes prepared without the preliminary gold-plating. Furthermore, a more satisfactory electrode was obtained if the platinum foil was kept highly polished. Earlier workers (*e.g.*, Britton [18]) attached importance to the nature of the electrode surface in connection with measurements in reducible systems. More recently Ives and his co-workers [19, 20] have shown that the electrode base may play an important part in the hydrogen-electrode processes.

The results of e.m.f. measurements in hydrochloric acid solutions of different molalities in the four solvents are given in Table 1, which also includes values of the total vapour pressure for each solvent mixture, found in this work, compared with the figures given in International Critical Tables, and the dielectric constants given by Allbright [21] and Åkerlöf.[22] Åkerlöf's values have been used for calculation. The value for the 5% solution was obtained by interpolation between the values for the 10% solution and pure water.

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

$$E = E_m^\circ - 2(\boldsymbol{RT}/\boldsymbol{F}) \ln m\gamma_\pm \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

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

The extended Debye–Hückel theory gives

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

where $M_{xy} = 100/[X/M_x + (100 - X)/M_y]$, where X is the weight % of acetone, and M_x and M_y are the molecular weights of acetone and water, respectively. The other symbols have their usual meaning.

Substituting this expression in equation (1), and rearranging, we have :

$$E_m^\circ = E + 2k \log_{10} m - 2kAc^{\frac{1}{2}}/(1 + \mathring{a}Bc^{\frac{1}{2}}) - 2k \log_{10}(1 + 0{\cdot}002M_{xy}m) + 2kB'm \quad . \quad . \quad (3)$$

where $2k = 2 \times 2{\cdot}3026\boldsymbol{RT}/\boldsymbol{F} = 0{\cdot}1183$.

If we substitute a quantity E_0' for the first four terms on the right-hand side of (3) we obtain

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

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

A value of 4·3 Å being used for the ionic parameter $\mathring{a}$, straight lines were obtained over the concentration range 0·003—0·1M, in all cases. The standard potentials and values of

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[18] Britton, " Hydrogen Ions," Chapman and Hall, London, 1932, 2nd. edn., p. 34.

[19] Hills and Ives, *J.*, 1951, 305.

[20] Cousens, Ives, and Swaroopa, *J.*, 1955, 3482.

[21] Allbright, *J. Amer. Chem. Soc.*, 1937, **59**, 2098.

[22] Åkerlöf, *ibid.*, 1932, **54**, 4125.

B' were obtained from these lines, which were plotted by the method of least squares. It is then clear that for each solvent concentration, the experimental values of the activity coefficients may be represented by equation (2) with the appropriate value of B'. This is a more expeditious method of obtaining "smoothed" activity coefficients than the usual procedure of smoothing the activity coefficients calculated directly for each reading against the molality, and is justifiable since the graph of E_0' versus m is a straight line. 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 ±0·1 mv or better. The values of A, B, B' are given, together with the activities at rounded concentrations calculated from (2), for the four solvent mixtures, in Table 2.

TABLE 1.

Molality (m)	E.m.f. (v) (E)	Molality (m)	E.m.f. (v) (E)	Molality (m)	E.m.f. (v) (E)	Molality (m)	E.m.f. (v) (E)
5% *Acetone.* ε = 75·9 (interpolated); V. p. = 47·7 ± 0·1 mm.; $E_m°$ = 0·2190 v.				10% *Acetone.* ε = 73·1,[21] 73·0;[22] V. p. = 69·4 ± 0·1 mm. (lit. 65 ± 4 mm.); $E_m°$ = 0·2156$_5$ v.			
0·004022	0·5058$_5$	0·02202	0·4224$_5$	0·003257	0·5132	0·02425	0·4147
0·004887	0·4963	0·03326	0·4024$_5$	0·004143	0·5012	0·02933	0·4055
0·005022	0·4949$_5$	0·04250	0·3905$_5$	0·005234	0·4897$_5$	0·04128	0·3890$_5$
0·005894	0·4870	0·06640	0·3692	0·006687	0·4777	0·05372	0·3765
0·007121	0·4777	0·08142	0·3594	0·007203	0·4741	0·06733	0·3656$_5$
0·008311	0·4701	0·1046	0·3472	0·007828	0·4698$_5$	0·08060	0·3570
0·009292	0·4645$_5$	0·1106	0·3447$_5$	0·009255	0·4617	0·1023	0·3455
0·01356	0·4461$_5$			0·01306	0·4431$_5$		
20% *Acetone.* ε = 67·6,[21] 67·0;[22] V. p. = 105·7 ± 0·1 mm. (lit. 104 ± 4 mm.); $E_m°$ = 0·2079$_5$ v.				40% *Acetone.* ε = 55·7,[21] 54·6;[22] V. p. = 155·5 ± 0·1 mm. (lit. 149 ± 4 mm.); $E_m°$ = 0·1859$_5$ v.			
0·003194	0·5070	0·01546	0·4296$_5$	0·003238	0·4856$_5$	0·01201	0·4224$_5$
0·004141	0·4940$_5$	0·02977	0·3980$_5$	0·004081	0·4742$_5$	0·02023	0·3976
0·006162	0·4745$_5$	0·4139	0·3825$_5$	0·005000	0·4645	0·03917	0·3668
0·006609	0·4712	0·05754	0·3666$_5$	0·005868	0·4566$_5$	0·06385	0·3445$_5$
0·007021	0·4682$_5$	0·07327	0·3553$_5$	0·006717	0·4503$_5$	0·08311	0·3327
0·008210	0·4605$_5$	0·09591	0·3424$_5$	0·007689	0·4436	0·1074	0·3207$_5$
0·009432	0·4535$_5$	0·1289	0·3282$_5$	0·008718	0·4376	0·1166	0·3172
0·01097	0·4463$_5$						

TABLE 2.

Acetone (%)	0	5	10	20	40
A		0·5328	0·5638	0·6425	0·8733
B		0·3340	0·3404	0·3559	0·3943
B'		0·14$_0$	0·15$_0$	0·17$_2$	0·10$_4$
Density (d_0)		0·9902	0·9837	0·9696	0·9366
m = 0·002	$\gamma_\pm$ = 0·9521	0·950	0·948	0·941	0·922
0·005	0·9285	0·926	0·924	0·913	0·885
0·01	0·9048	0·901	0·896	0·884	0·848
0·02	0·8755	0·871	0·865	0·850	0·797
0·05	0·8304	0·825	0·817	0·799	0·734
0·1	0·7964	0·789	0·780	0·758	0·679

It has been noted [23,4] that, if the standard potential is plotted against $1/\varepsilon$ for different organic solvent–water mixtures, three definite families of curves are obtained: for the monohydric alcohols, the glycols and glycerol, and the sugars. The plot of $E_m°$ against $1/\varepsilon$ for acetone–water mixtures is virtually a straight line, as with, *e.g.*, the sugars and glycerol. The 5% and 10% acetone values fall effectively on the same smooth curve as the results for aqueous *iso*- and *n*-propanol. There is, however, considerable deviation from this curve with the values for the 20% and 40% acetone solutions.

A plot of $E_N° - 0{\cdot}05915 \log N_w$ against $1/\varepsilon$, where $E_N° = E_m° - 0{\cdot}1183 \log (1000/M_{xy})$, which demonstrates a close relation between the monohydric alcohols,[3] shows that for acetone–water mixtures, the curve lies considerably above those for the alcohols, even at low acetone concentrations.

The salting-out coefficients are of the order usually found in this type of system except

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[23] Crockford, U.S. Bur. Stand., 1951, Circ. No. 514.

that for the 40% solution the value is low. In view of the experimental difficulties experienced with this solution, it would be wrong to attach too much significance to this value, in the absence of confirmation by studies in, say, a quinhydrone cell.

A more complete discussion of the standard potentials obtained here will be undertaken later in conjunction with the results for other similar systems now being studied.

Thanks are due to Dr. M. F. Ansell for suggesting, and to the late Mr. M. E. Selleck for assisting with, the hydrogenation experiments. We are indebted to the University of London and the Chemical Society for grants which have partially defrayed the cost of the investigation. One of us (D. F.) thanks the D.S.I.R. for a maintenance allowance received during the early part of the investigation.

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[*Received, February 28th,* 1956.]