897. *Studies in Ion Solvation in Non-aqueous Solvents and their Aqueous Mixtures. Part I. The Cell* $H_2|HX|AgX$–Ag (X = Br,I) *in* 10% *and* 43·12% *Mixtures of Methanol and Water.*

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Standard e.m.f. values at 25° for the cells $H_2|HX|AgX$–Ag (X = Br, I) in 10% and 43·12% mixtures of methanol with water are reported. Conventional hydrogen electrodes proved unsatisfactory in the experimental cells and the modifications required are described.

This paper describes the determination of the standard e.m.f. values, at 25°, of the cells

$$H_2|HBr|AgBr\text{–}Ag \quad \text{(I)}$$

and

$$H_2|HI|AgI\text{–}Ag \quad \text{(II)}$$

in methanol–water mixtures containing 10% and 43·12% of methanol by weight, these concentrations being chosen for comparison with existing work in the field.

The methods used were those usual for the same determinations in aqueous solution. The standard e.m.f. of cell I could be directly determined by using hydrobromic acid solutions in the cell, but solutions of hydriodic acid are easily oxidised, and so the standard e.m.f. values of cell II were found by Owen's method.[1] In this, oxidation is inhibited by buffering the cell solutions to high pH values. Measurements on two cells are required:

$$H_2|HBO_2(m)NaBO_2(m)KCl(m)|AgCl\text{–}Ag \quad \text{(III)}$$

and

$$H_2|HBO_2(m)NaBO_2(m)KI(m)|AgI\text{–}Ag \quad \text{(IV)}$$

Some difficulty was at first found in obtaining reliable hydrogen electrode potentials in any of the three experimental cells, I, III, and IV, for when conventional platinised platinum electrodes were used their behaviour resembled that of electrodes used in solutions containing reducible material.[2] They were frequently irreversible; apparently steady e.m.f. values were often not the true equilibrium values and could not be reproduced in duplicate runs; and the electrode potentials varied with the rate of passage of hydrogen through the cell.

Others [3] have found similar trouble with alcohols or their aqueous solutions, and have usually ascribed it to the presence of oxidation products of the alcohols. One of us [4] had previously found no difficulty in using hydrogen electrodes in methanolic hydrochloric acid. The reduction effect was, however, present in hydrobromic acid solutions and was particularly serious in the buffer solutions. In these, because of the low hydrogen-ion concentrations, the exchange currents would have been smaller than in the acid solutions and the equilibrium at the electrode the more readily disturbed.

A short series of experiments, undertaken to determine what species in the solutions was being reduced, was inconclusive. However, whatever the cause of the trouble, it was easily eliminated. First, the "activated" hydrogen electrodes developed by Feakins and French [5] for use in acetone–water mixtures were found to behave reversibly in these solutions. These electrodes consist of platinum foils which have been given a low catalytic activity by polishing them and then etching the polished surfaces with dilute *aqua regia.*

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[1] Owen, *J. Amer. Chem. Soc.*, 1935, **57**, 1526.

[2] Scatchard, *J. Amer. Chem. Soc.*, 1926, **48**, 2026.

[3] Danner, *J. Amer. Chem. Soc.*, 1922, **44**, 2832; Moore and Felsing, *ibid.*, 1947, **69**, 1076; De Ligny and Wieneke, *Rec. Trav. chim.*, 1960, **79**, 268; Kanning and Campbell, *J. Amer. Chem. Soc.*, 1942, **62**, 517; Nonhebel and Hartley, *Phil. Mag.*, 1925, **50**, 729.

[4] Feakins, *J.*, 1961, 5308.

[5] Feakins and French, *Chem. and Ind.*, 1954, 1107; *J.*, 1956, 3168.

Secondly, platinised platinum electrodes with light deposits of " black " could be used under special conditions. Although the potentials of such electrodes varied with the rate of bubbling of hydrogen, a limiting rate, which was much faster than normal, though not inconveniently so, could be found above which no further change in potential was observed.

Each type of electrode was used in turn in a particular cell solution, the order of use being immaterial, and the two equilibrium e.m.f. readings normally agreed to within 0·1 mv. Their mean was taken as the e.m.f. of the cell.

EXPERIMENTAL

Measurements of e.m.f. were made with a Pye precision vernier potentiometer in conjunction with a sensitive galvanometer and a standard cell.

The experimental cell contained hydrogen and silver–silver halide compartments connected by a cross-piece. Two electrodes for each compartment were mounted with short poly(vinyl chloride) sleeves into adaptors made from standard cone joints, which fitted sockets on the heads of the cell compartments. Hydrogen was delivered to the hydrogen electrode compartment and nitrogen to the halide electrode compartment, through pre-saturators fused to them, and escaped through long capillary tubes. The cell and pre-saturators were immersed in a water-bath kept at 25° ± 0·01°.

For a measurement, the cell was filled with the solution, the electrode compartments were closed with stoppers, and the solution was then saturated with the gases. The stoppers were then replaced by the electrodes, the halide electrodes being shielded from direct light. This precaution was especially important with the bromide electrodes, whose potentials were very light-sensitive. The bias potential of two electrodes in the same compartment was normally $<0{\cdot}05$ mv for the halide electrodes and $<0{\cdot}02$ mv for the hydrogen electrodes. When the cell was at equilibrium (e.m.f. constant to $\pm 0{\cdot}02$ mv for 2 hr.) with one type of hydrogen electrode, the e.m.f. was recorded as the mean of those between the two independent combinations of electrodes in the cell, and the hydrogen electrodes were then replaced by ones of the other type, and the mean e.m.f. found in the same way. Equilibration times varied from 2 to 24 hr. depending on the nature of the cell solutions and the electrodes. The silver–silver iodide electrodes were particularly slow to equilibrate, normally requiring some 6 hr.

For the preparation of " activated " hydrogen electrodes see Feakins and French.[5] Platinised electrodes were made by cathodising platinum foils in a solution containing 2% of chloroplatinic acid and 2N with respect to hydrochloric acid, at a current density of 0·1 amp./cm.^{2} for 2 min. This produced a thin, large-grained deposit of " black " of fairly low catalytic activity.

All the silver–silver halide electrodes were thermal-electrolytic. Platinum wires, of diameter 0·02″ and length 11 cm., having one end sealed into glass tubes, were formed into compact helices, 0·6 cm. in diameter. These were filled and thinly coated with a paste made of silver oxide[6] and conductance water and then heated in a muffle furnace at 550—600° for 5 min. This was repeated once or twice to give a continuous, coherent, thin layer of silver on the outside of the spiral and a porous mass of it within. The electrodes were then anodised at 2 mA/electrode for 2 hr. in a 0·1N-solution of the appropriate halogen acid or potassium halide. All electrodes were prepared afresh for each run.

" AnalaR " hydrobromic acid was diluted to the composition of the constant-boiling mixture and distilled in an atmosphere of nitrogen. The middle third of the distillate was redistilled and this product was free from bromine.

Potassium chloride was precipitated by passing hydrogen chloride gas into a cold, saturated solution of the " AnalaR " salt, redissolved and reprecipitated in the same way, recrystallised twice from conductance water, dried at 110°, and kept in a desiccator over SiO_2 gel. It was free from bromide.

" AnalaR " potassium iodide was twice recrystallised from conductivity water at 60°, dried at 110°, and kept in a desiccator over SiO_2 gel.

" AnalaR " borax was used without further purification and was stored over a saturated solution of sodium bromide.

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[6] Ives and Janz, " Reference Electrodes," Academic Press, New York, 1961, p. 198.

Conductance water was as before.[4] Methanol was as before,[4] except that an atmosphere of nitrogen was maintained throughout the preparation. It contained $<0{\cdot}01\%$ of formaldehyde.

DISCUSSION

For cell I,

$$E = E^\circ_{\text{m}} - 2k \log m\gamma_\pm \tag{1}$$

where $k = 2{\cdot}3026\boldsymbol{R}T/\boldsymbol{F}$, E is the observed e.m.f. corrected to 760 mm. pressure, and E°_{m} and $\gamma_\pm$ are the standard e.m.f. and mean ion activity coefficient on the molal scale. From the extended Debye–Hückel theory we have

$$\log \gamma_\pm = \frac{-A\sqrt{c}}{1 + \mathring{a}B\sqrt{c}} + bm - \log\,(1 + 0{\cdot}002M_{xy}m), \tag{2}$$

where A and B are the Debye–Hückel constants appropriate to the solvent mixture, M_{xy} is the mean molecular weight of the solvent, and $\mathring{a}$ has been taken as 4·4, the value used in aqueous solutions. Substituting (2) in (1) and re-arranging we have

$$E^\circ_{\text{m}} = E + 2k \log m - \frac{2kA\sqrt{c}}{1 + \mathring{a}B\sqrt{c}} - 2k \log\,(1 + 0{\cdot}002M_{xy}m) + 2kbm. \tag{3}$$

Putting the first four terms on the right-hand side of (3) $= E^{\circ\prime}_{\text{m}}$, and rearranging gives

$$E^{\circ\prime}_{\text{m}} = E^\circ_{\text{m}} - 2kbm. \tag{4}$$

Table 1 gives values of E and $E^{\circ\prime}_{\text{m}}$ at various values of m in the two solvent mixtures, over a range of about 0·004—0·08m. Table 2 contains values of various properties, required in the calculations.

TABLE 1.

Molality of HBr (m)	E (v)	$E^{\circ\prime}_{\text{m}}$ (v)	Molality of HBr (m)	E (v)	$E^{\circ\prime}_{\text{m}}$ (v)
		10% *Methanol*			
0·004683	0·34601	0·06640	0·017953	0·27991	0·06615
0·004760	0·34521	0·06639	0·02559	0·26253	0·06580
0·004842	0·34434	0·06638	0·02750	0·25908	0·06578
0·005184	0·34105	0·06644	0·03465	0·24785	0·06558
0·005695	0·33647	0·06650	0·04619	0·23414	0·06550
0·009409	0·31163	0·06634	0·05687	0·22384	0·06502
0·012020	0·29943	0·06617	0·06371	0·21838	0·06485
0·015050	0·28843	0·06608	0·08971	0·20155	0·06405
0·017071	0·28231	0·06605			
		43·12% *Methanol*			
0·004304	0·34104	0·05588	0·016048	0·27716	0·05559
0·005775	0·33026	0·05594	0·03191	0·24477	0·05552
0·006271	0·32264	0·05593	0·03559	0·23937	0·05525
0·008147	0·30976	0·05568	0·05127	0·22223	0·05491
0·008923	0·30569	0·05600	0·07527	0·20444	0·05466
0·009765	0·30132	0·05600			

TABLE 2.

MeOH (wt. %)	Dielectric constant	Vapour press. (mm.)	Density	Mean mol. weight (M_{xy})
10	74·18 *	33·7 †	0·9799 ‡	18·84
43·12 §	59·40	66·0	0·9257	22·19

* Ref. 7. † Ref. 8. ‡ Ref. 9. § Ref. 10 (all constants).

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[7] Albright and Gosting, *J. Amer. Chem. Soc.*, 1946, **68**, 1061.

[8] Butler, Thomson, and Maclennan, *J.*, 1933, 674.

[9] Harned and Thomas, *J. Amer. Chem. Soc.*, 1935, **57**, 1666.

[10] Schwab and Ziegenbalg., *Z. Elektrochem.*, 1958, **62**, 172.

If equation (4) is obeyed the plots of $E^{\circ\prime}_{\mathrm{m}}$ against m should be straight lines for both solvent systems, and this was found to be true within the experimental error. Values of $E^{\circ\prime}_{\mathrm{m}}$ and b were found by the method of least squares. The accuracy of the E°_{m} values is better than 0·1 mv in both cases.

With b known, activity coefficients can be calculated from equation (2), and the constants required are listed in Table 3. Table 4 gives the mean ion activity coefficients of the acid at rounded molalities in the two solvent mixtures.

TABLE 3.

	A	*B*	*b*
10% Methanol	0·552	0·338	0·229
43·12% Methanol	0·770	0·378	0·162

TABLE 4.

m	0·005	0·01	0·02	0·05
10% Methanol, $\gamma_{\pm}$	0·925	0·901	0·872	0·830
43·12% Methanol, $\gamma_{\pm}$	0·899	0·866	0·827	0·767

For cells III and IV

$$E = E^{\circ}_{\mathrm{m}} - k \log a_{\mathrm{H}} a_{\mathrm{X}} \qquad (5)$$

and

$$a_{\mathrm{H}} = K a_{\mathrm{HA}} / a_{\mathrm{A}}, \qquad (6)$$

where K is the dissociation constant of boric acid in the particular solvent mixture, $\mathrm{A} = \mathrm{BO_2}$, and $\mathrm{X} = \mathrm{Cl}$ or I.

From equations (5) and (6) we may deduce that

$$E_{\mathrm{HX}} = E^{\circ}_{\mathrm{m,HX}} - \frac{k \log m_{\mathrm{HA}} m_{\mathrm{X}}}{m_{\mathrm{A}}} - k \log K - k \log \frac{\gamma_{\mathrm{HA}} \gamma_{\mathrm{X}}}{\gamma_{\mathrm{A}}}. \qquad (7)$$

Consider a pair of cells, III and IV, in which m has been made the same. In both, $m_{\mathrm{X}} = m$. m_{HA} and m_{A} differ slightly from m because of the hydrolysis of the borate ion, but they will have the same values in each cell. With the low ionic strengths ($\leqslant 0{\cdot}02$m), γ_{HA} and γ_{A} will have negligibly different values in the two solutions.

Thus

$$E^{\circ}_{\mathrm{m,HI}} = E^{\circ}_{\mathrm{m,HCl}} + E_{\mathrm{HI}} - E_{\mathrm{HCl}} - k \log \frac{\gamma_{\mathrm{Cl}}}{\gamma_{\mathrm{I}}}. \qquad (8)$$

The application of Guggenheim's equations [11] for activity coefficients shows that the last term of equation (8) is linear in m; thus we may put

$$E^{\circ\prime}_{\mathrm{m,HI}} = E^{\circ}_{\mathrm{m,HI}} + \lambda_1 m, \qquad (9)$$

where $E^{\circ\prime}_{\mathrm{m,HI}}$ is equivalent to the first three terms on the right-hand side of equation (8).

For aqueous solutions a calculation based on Guggenheim's equations suggests that, for $m = 0{\cdot}01$m, the activity coefficient term would be of the order of only 0·1 mv. Although this is small, and our data are not of the highest accuracy, we have nevertheless assumed non-zero λ_1 values for the methanolic solutions and have calculated $E^{\circ}_{\mathrm{m,HI}}$ values from equation (9) by the method of least squares. These are accurate to $\pm$ 0·1 mv in the case of the 10% solution, and $\pm 0{\cdot}15$ mv in the case of the 43·12% solution. Values of E_{HI}, E_{HCl}, and $E^{\circ\prime}_{\mathrm{m,HI}}$ at various molalities are shown in Table 5. The values of $E^{\circ}_{\mathrm{m,HCl}}$ used are listed in Table 6 along with the extrapolated values of $E^{\circ}_{\mathrm{m,HBr}}$ and $E^{\circ}_{\mathrm{m,HI}}$, with values for aqueous solutions for comparison.

Values for the pK of boric acid in the two solvent mixtures may be deduced if assumptions are made about the solvolysis of the borate ion. For aqueous solutions

$$\mathrm{BO_2^-} + \mathrm{H_2O} \rightleftharpoons \mathrm{HBO_2} + \mathrm{OH^-}$$

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[11] Guggenheim, *Phil. Mag.*, 1935, **19**, 588.

and it is easily shown that

$$\frac{m_{\mathrm{HA}}}{m_{\mathrm{A}}} = \frac{m + K_{\mathrm{w}}/K}{m - K_{\mathrm{w}}/K},$$

where K_{W} is the ionic product of water. Similar equations may be written for the methanolysis. Values of $m_{\mathrm{HA}}/m_{\mathrm{A}}$ have been found by calculating the total solvolysis with the ionic products for water [14] and methanol [15] appropriate to each *pure* solvent. The error in this procedure is likely to be negligible.

TABLE 5.

m	E_{HCl} (v)	E_{HI} (v)	$E^{\circ\prime}_{\mathrm{m,HI}}$ (v)	pK'	m	E_{HCl} (v)	E_{HI} (v)	$E^{\circ}_{\mathrm{m,HI}}$ (v)	pK'
		10% *Methanol*					43·12% *Methanol*		
0·003	0·91332	0·54398	−0·15399	9·282	0·003	0·90427	0·55980	−0·14867	9·460
0·004	0·90620	0·53682	−0·15403	9·284	0·0035	0·90056	0·55555	−0·14921	9·462
0·005	0·90052	0·53125	−0·15392	9·285	0·004	0·89725	0·55241	−0·14904	9·464
0·007	0·89216	0·52271	−0·15410	9·288	0·005	0·89138	0·54670	−0·14888	9·461
0·010	0·88304	0·51346	−0·15423	9·288	0·006	0·88690	0·54210	−0·14900	9·464
					0·007	0·88288	0·53810	−0·14898	9·462
					0·010	0·87396	0·52910	−0·14906	9·465

TABLE 6

Values of E°_{m} for cells $\mathrm{H_2|HX|AgX\text{–}Ag}$, in volts.*

Solvent	HCl	HBr	HI
Water	0·2224 †	0·0712 ¶	−0·15225 ‖
10% Methanol	0·21535 ‡	0·06655	−0·15385
43·12% Methanol	0·1958 §	0·0560	−0·1489

* To nearest 0·05 mv. † Mean of three recorded values.[12] ‡ Ref. 9. § Calc. from the data of Schwab and Ziegenbalg [10] for the calomel cell in the methanol solutions, and the above value for the silver chloride cell in aqueous solution. ¶ Mean of four recorded values.[13] ‖ Ref. 1.

Rearranging equation (7) and putting X = Cl, we have

$$\frac{E_{\mathrm{HCl}} - E^{\circ}_{\mathrm{m,HCl}}}{k} + \log\frac{m_{\mathrm{HA}}m}{m_{\mathrm{A}}} = \mathrm{p}K - \log\frac{\gamma_{\mathrm{HA}}\gamma_{\mathrm{Cl}}}{\gamma_{\mathrm{A}}}. \tag{10}$$

Putting the left-hand side of equation (10) equal to pK', and noting that the term in the activity coefficients should be linear in m, we have

$$\mathrm{p}K' = \mathrm{p}K - \lambda_2 m. \tag{11}$$

Values of pK' at various values of m, obtained from measurements on cell III, are shown in Table 5. The values of pK for the two solvent mixtures, obtained by using equation (11) with the method of least squares, are given in Table 7. They are accurate to ±0·002 pK unit.

TABLE 7.

Solvent	Water	10% Methanol	43·12% Methanol
pK	9·234	9·281	9·460

The values of E°_{m} obtained will be discussed, along with comparable thermodynamic data from the literature, in Part II.

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[12] Harned and Ehlers, *J. Amer. Chem. Soc.*, 1932, **54**, 1350; 1933, **55**, 2179; Bates and Bower, *J. Res. Nat. Bur. Stand.*, 1954, **53**, 283; Harned and Paxton, *J. Phys. Chem.*, 1953, **57**, 531.

[13] Harned, Keston, and Donelson, *J. Amer. Chem. Soc.*, 1936, **58**, 984; Owen and Foering, *ibid.*, p. 1575; Harned and Donelson, *ibid.*, 1937, **59**, 1280; Hetzer, Robinson, and Bates, *J. Phys. Chem.*, 1962, **66**, 1423.

[14] Harned and Robinson, *Trans. Faraday Soc.*, 1940, **36**, 973.

[15] Brière, Crochon, and Félici, *Compt. rend.*, 1962, **154**, 4458.

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