Redetermination of Standard Potential of Silver-Silver Bromide Electrode in Methanol–Water Mixtures at 25°C

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The standard emf, $E_m°$, of the cell, Pt, H_2 (1 atm)|HBr(m), methanol(X), water(Y)|AgBr, Ag, has been redetermined over a broad range of methanol concentrations in an attempt to resolve wide discrepancies in the literature. Though generally not in agreement with published values, the new set of $E_m°$ values is the most self-consistent and probably, the best so far.

Standard molal emf's, $E_m°$, of cells I and II in methanol–

$$\text{Pt, } H_2 \text{ (1 atm)}|\text{HBr}(m), \text{methanol}(X), \text{water}(Y)|\text{AgBr, Ag} \quad \text{(I)}$$

$$\text{Pt, } H_2 \text{ (1 atm)}|\text{HI}(m), \text{methanol}(X), \text{water}(Y)|\text{AgI, Ag} \quad \text{(II)}$$

water mixtures at 25°C have been determined by several workers, but agreement between them is frequently very poor. Recently, Feakins and Khoo (*2*) revised the values of $E_m°$ for cell II by use of cells III and IV, buffered to high pH, in an effort to resolve the discrepancies between the values of Feakins

$$\text{Pt, } H_2 \text{ (1 atm)}|HBO_2(m), NaBO_2(m), \text{KCl}(m), \text{methanol}(X), \text{water}(Y)|\text{AgCl, Ag} \quad \text{(III)}$$

$$\text{Pt, } H_2 \text{ (1 atm)}|HBO_2(m), NaBO_2(m), \text{KI}(m), \text{methanol}(X), \text{water}(Y)|\text{AgI, Ag} \quad \text{(IV)}$$

et al. (*3*, *4*) and McIntyre and Amis (*8*). The revised values agreed with those of Feakins and Watson (*4*) but not with those of Feakins and Tomkins (*3*) for 20.22 and 33.4% methanol. This was rationalized in terms of some fault present in the silver-silver chloride electrodes used by Feakins and Tomkins (*3*). Preference for the new data was then based on the better cell design and improved technique of cell manipulation.

Melton and Amis (*8*) have determined the $E_m°$ of cell I in methanol–water mixtures. Direct comparison of their values with those of Feakins et al. (*3*, *4*) is difficult except for 90% methanol where there is a difference of 5.5 mV between the two values. On interpolating from the data of Feakins et al, discrepancies of about 2 mV and 5 mV are noted for 30 and 60% methanol, respectively.

The $E_m°$ values of cells I and II—i.e., $E_{m,\text{HBr}}°$ and $E_{m,\text{HI}}°$—give, respectively, values of $\Delta G_t°$, the molar free energy of transfer of HBr and HI from water to the mixed solvents. In the case of HI, $\Delta G_t°$ shows marked inflections with a pronounced maximum and minimum in the region 0–50% when plotted against the volume fraction of methanol in the mixture (*2*). This type of behavior was held to be relevant to the "nonelectrolytic" effect of ion solvation in those systems (*1*). Assessment of the nonelectrolytic effect of HBr in these terms is now somewhat uncertain because of the existing discrepancy in the values of $E_{m,\text{HBr}}°$. In view of this, we have redetermined $E_{m,\text{HBr}}°$ in 10, 20.22, 30, 33.4, 43.12, 50, 60, 68.33, and 90%/(w/w) methanol at 25°C. Measurements in 30, 60, 68.33, and 90% methanol were made directly with cell I using hydrobromic acid. This is known to be normally trouble-free. Owen's buffer method (*10*) requires the use of cell V in conjunction with cell III. Data for cell III are already available

$$\text{Pt, } H_2 \text{ (1 atm)}|HBO_2(m), NaBO_2(m), \text{KBr}(m), \text{methanol}(X), \text{water}(Y)|\text{AgBr, Ag} \quad \text{(V)}$$

(*2*) for 10, 20.22, 33.4, 43.12, and 50% methanol. Since the previous values of $E_{m,\text{HBr}}°$ in these solvent mixtures were obtained from direct measurements with cell I (*3*, *4*), it was thought that application of Owen's method to these solvent mixtures should provide a convenient and independent check on the $E_{m,\text{HBr}}°$ values and also increase the internal consistency of the results.

EXPERIMENTAL

Merck's "pro analysis" methanol was refluxed for 3 hr with silver oxide, dried for 3 days in $CaSO_4$ (H & W Drierite) and distilled through a 3-ft column packed with Fenske helices, with considerable rejection of head and tail fractions. The product was free of aldehydes. Conductance water was deionized water redistilled over alkaline permanganate. Hydrobromic acid was the Analar reagent diluted to the composition of the constant-boiling point mixture and distilled twice, the middle third of the distillate being collected each time. The product free of bromine was analyzed gravimetrically as silver bromide. Merck's Suprapur potassium bromide was used without further purification as was Merck's "pro analysis" borax which was previously equilibrated over a saturated solution of sodium bromide.

Cylinder hydrogen gas was purified by passing it in turn over copper turnings at 450°C, potassium hydroxide pellets, and silica gel.

The silver–silver bromide electrodes were the thermal electrolytic type. Platinum spirals sealed in borosilicate glass tubes were thinly coated with silver oxide paste and heated to 550°C for 5 min. This was repeated until the spiral was coated with a continuous and coherent layer of silver. The electrodes were then bromidized in 0.1*M* KBr at 0.03 amp/electrode for about 1/2 hr in batches of three and aged in 0.1*M* KBr for two days. The bias emf between any two of these was <0.03 mV. The hydrogen electrodes were prepared by platinizing 1 cm^2 platinum foils in 2% chloroplatinic acid, 2*M* in hydrochloric acid. Previous observations (*3*, *4*) showed that some attention must be paid to the preparation and use of hydrogen electrodes in methanol–water media. In particular, among platinized platinum electrodes, only those which are very lightly platinized could be used in solvents containing high concentrations of methanol. On this basis, platinization was carried out for 2 min at a current density of 0.1 amp cm^{-2} for measurements in solvent mixtures containing 50% methanol or less, while for measurements in 68.33 and 90% methanol, the plating time and current density were reduced to 1 min and 0.02 amp cm^{-2}, respectively. Under these conditions, the hydrogen electrodes were highly satisfactory and showed no tendency toward irreversibility of the type experienced by previous workers (*3*, *4*).

The experimental cell, immersed in a water bath at 25 ±

0.01°C has been described (*7*). It is a modification of the one used by Feakins and Khoo (*2*) but is more compact and easier to manipulate. Compared with a conventional H-type cell, the new cell uses a much smaller volume of solution (25 ml) for an experiment. Further, cell-filling, washing, and draining operations on the cell are made with the cell in situ, therefore minimizing time consumed by these operations on previous cells and enables more measurements to be made within a given time.

The following experimental procedure was adopted, bearing in mind that the effects of adsorption of bromide by the silver-silver bromide electrode could be large for a small cell like this. All measurements on any particular cell, I or V, were made in one continuous sequence in decreasing order of molality. Before such a series of measurements was started, the silver-silver bromide electrode was immersed overnight in the most concentrated solution of the series. The cell was filled with this solution and its emf read at 3–5 min intervals until equilibrium (emf constant to ±0.01 mV for $^1/_2$–1 hr) was reached. The cell was then drained and refilled with this solution. The equilibrium emf obtained agreed to within ±0.01 mV of the previous value. This solution was flushed out of the cell, which was then washed twice and filled with the next solution. The emf was read as before. Three successive fillings of the cell with this new solution then normally gave emf readings which agreed to within ±0.01 mV of each other. Since only one electrode of each kind was employed in any measurement, it was important to check their behavior in the experimental cell. In the case of the hydrogen electrode, this was done by replacing one electrode by another in the course of an experiment and subjecting them intermittently to a wide range of flow rates of hydrogen through the solution. In all cases, the equilibrium emf remained constant to within ±0.01 mV. The behavior of the silver-silver bromide electrode was tested by comparing its potential, after a sequence of measurements, with those of aged and unused ones having intercomparison emf's less than 0.03 mV. The bias emf normally remained <0.03 mV but in the very rare cases where it exceeded 0.03 mV, the whole sequence of measurements was repeated.

Cell emf measurements were recorded with a Pye precision vernier potentiometer (Scientific Instrument Centre, Cambridge, Catalogue 7565) having a certified absolute accuracy of ±0.02%. This was used in conjunction with a sensitive Pye Cambridge galvanometer (Catalogue 7904/S, sensitivity 0.14 mm/μV) and a Cambridge Weston standard cell thermostated at 25 ± 0.02°C and certified to read 1.01857 V at 20°C with a temperature correction of −0.00004 V for a 1°C rise in temperature between 15 and 25°C.

Table I. Properties of the Solvent Mixtures (*3, 4, 8*) at 25°C

Weight, %, methanol (X)	Dielectric constant	Vapor pressure mm Hg	Density, g/ml	M_{xy}[a]
10	...	33.7	0.9799	...
20.22	...	44.5	0.9646	...
30	64.36	53.5	0.9491	20.74
33.4	...	57.8	0.944	...
43.12	...	66.0	0.9257	...
50	...	71.8	0.9125	...
60	49.88	80.2	0.8887	24.44
68.33	47.9	88.0	0.8714	25.69
90	37.91	111.8	0.8156	29.73

[a] $M_{xy} = 100/[X/M_x + (100 - X)/M_y]$
where M_{xy} = mean mol wt of solvent
M_x = mol wt of methanol
M_y = mol wt of water

Table II. Emf, *E/V*, of Cell Pt, H_2 (1 atm)|HBr(*m*), Methanol (*X*), Water (*Y*)|AgBr, Ag at 25°C

m/Mol kg^{-1}	E/V	m/Mol kg^{-1}	E/V
X = 30% Methanol		X = 60% Methanol	
0.002903	0.36297	0.002987	0.34969
0.004528	0.34107	0.004896	0.32595
0.006199	0.32576	0.006968	0.30910
0.009663	0.30432	0.010738	0.28832
0.012674	0.29113	0.013947	0.27610
0.017266	0.27633	0.017237	0.26612
0.020260	0.26867	0.024938	0.24895
0.027853	0.25357	0.031157	0.23932
X = 68.33% Methanol		X = 90% Methanol	
0.003153	0.33892	0.003685	0.27840
0.006730	0.30278	0.006338	0.25337
0.009626	0.28578	0.008541	0.23950
0.011781	0.27634	0.013864	0.21778
0.016379	0.26089	0.018563	0.20472
0.021367	0.24856	0.025493	0.19090
0.028314	0.23595	0.033345	0.17985

RESULTS AND DISCUSSION

All emf's listed were corrected to a hydrogen pressure of 1 atm in the standard manner (*5*) using the vapor pressure data shown in Table I which also includes other relevant properties of the solvent mixtures. The corrections to the experimentally observed emf's range from about 0.00070 V in 10% methanol to about 0.00220 V in 90% methanol.

Table II gives the data for cell I at 25°C for measurements in 30, 60, 68.33, and 90% methanol. The emf of this cell, E, is given by Equation 1 where $k = 2.3026\ RT/F$, R being the gas constant, T the absolute temperature and F the Faraday, and m is the molality; $\gamma_\pm$ the mean ionic activity coefficient, is given by Equation 2, in which d is the solvent density

$$E = E_{m,\mathrm{HBr}}^\circ - 2\,k \log (m\,\gamma_\pm) \tag{1}$$

$$\log \gamma_\pm = -\frac{A\sqrt{(dm)}}{1 + \mathring{a}B\sqrt{(dm)}} + bm - \log(1 + 0.002\,M_{xy}m) \tag{2}$$

A and B are Debye-Huckel constants (*11*), b is a variable parameter, and $\mathring{a}$ is the ion-size parameter which is given the value 4.4 Å (*4*). Equations 1 and 2 lead to Equation 3:

$$E + 2\,k \log m - \frac{2\,kA\sqrt{(dm)}}{1 + \mathring{a}B\sqrt{(dm)}} - 2\,k\ \log(1 + 0.002\,M_{xy}m) = E_{m,\mathrm{HBr}}^\circ - 2\,kbm \tag{3}$$

Putting the terms on the left-hand side of Equation 3 equal to $E_m^{\circ\prime}$, we get Equation 4. $E_{m,\mathrm{HBr}}^\circ$ and b are determined from a least-squares plot of $E_m^{\circ\prime}$ against m.

$$E_m^{\circ\prime} = E_{m,\mathrm{HBr}}^\circ - 2\,kbm \tag{4}$$

If E_{HBr} and E_{HCl} are, respectively, the emf's of cells V and, III at the same value of m, Equation 5 follows, where k is the factor 2.3026 RT/F and γ_x denotes the molal activity coefficient of species X. The term log $(\gamma_{\mathrm{Cl}}/\gamma_{\mathrm{Br}})$ can be expected to be linear in m, so that we write Equation 6, where λ is a variable parameter. Plots of ΔE vs. m give $E_{m,\mathrm{HBr}}^\circ - E_{m,\mathrm{HCl}}^\circ$ on extrapolation to $m = 0$, and $E_{m,\mathrm{HBr}}^\circ$ was then obtained from published values (*3, 4*) of $E_{m,\mathrm{HCl}}^\circ$. The data required for Equation 6 are given in Table III and the $E_{m,\mathrm{HBr}}^\circ$ are summarized in Table IV.

$$E_{\mathrm{HBr}} - E_{\mathrm{HCl}} = E_{m,\mathrm{HBr}}^\circ - E_{m,\mathrm{HCl}}^\circ + k \log (\gamma_{\mathrm{Cl}}/\gamma_{\mathrm{Br}}) \tag{5}$$

$$E_{\mathrm{HBr}} - E_{\mathrm{HCl}} = E_{m,\mathrm{HBr}}^\circ - E_{m,\mathrm{HCl}}^\circ = \Delta E = E_{m,\mathrm{HBr}}^\circ - E_{m,\mathrm{HCl}}^\circ + \lambda\,m \tag{6}$$

Table III. Emf Data at 25°C for Cells Containing Borax

m/Mol kg^{-1}	E_{HBr}/V	$\Delta E/V$	m/Mol kg^{-1}	E_{HBr}/V	$\Delta E/V$
10% Methanol			20.22% Methanol		
0.00300	0.76258	−0.14912	0.00300	0.76141	−0.14725
0.00400	0.75576	−0.14919	0.00400	0.75455	−0.14704
0.00500	0.75030	−0.14929	0.00500	0.74889	−0.14726
0.00700	0.74201	−0.14969	0.00700	0.74029	−0.14780
0.01000	0.73265	−0.14993	0.01000	0.73150	−0.14776
$E_{m,HBr}° - E_{m,HCl}° =$ −0.1487 V (±0.1 mV)			$E_{m,HBr}° - E_{m,HCl}° =$ −0.1468 V (±0.1 mV)		
33.4% Methanol			43.12% Methanol		
0.00300	0.76162	−0.14306	0.00300	0.76157	−0.14124
0.00400	0.75473	−0.14330	0.00400	0.75533	−0.14087
0.00500	0.74951	−0.14305	0.00500	0.74987	−0.14101
0.00700	0.74150	−0.14301	0.00700	0.74219	−0.14072
0.00900	0.73532	−0.14315	0.01000	0.73319	−0.14085
$E_{m,HBr}° - E_{m,HCl}° =$ −0.1432 V (±0.1 mV)			$E_{m,HBr}° - E_{m,HCl}° =$ −0.1412 V (±0.1 mV)		
50% Methanol					
0.00400	0.75519	−0.13902			
0.00500	0.74956	−0.13885			
0.00700	0.74136	−0.13902			
0.00900	0.73540	−0.13874			
0.01500	0.72237	−0.13927			
$E_{m,HBr}° - E_{m,HCl}° =$ −0.1388 V (±0.1 mV)					

Table IV. Values of $E_m°/V$ at 25°C

Weight, %, meth-anol	HCl (*3*, *4*)	HBr		
		This work	Refs. *3* and *4*	Ref. *9*
10	0.21535	0.0667 ±0.2 mV)	0.06655	...
20.22	0.2089	0.0621 ±0.2 mV)	0.0634	...
30	...	0.0589 (±0.1 mV)	...	0.0582
33.4	0.2010	0.0578 (±0.2 mV)	0.0585	...
43.12	0.1958	0.0546 (±0.4 mV)	0.0560	...
50	0.1907	0.0519 (±0.2 mV)	0.0538	...
60	...	0.0455 (±0.1 mV)	...	0.0436
68.33	...	0.0372 (±0.1 mV)	0.0385	...
90	...	−0.0183 (±0.1 mV)	−0.0171	−0.0226

For the 10% mixture, the new $E_{m,HBr}°$ value is in good agreement with that of Feakins and Watson (*4*), but for the rest of the solvent systems, the $E_{m,HBr}°$ values are lower than those of Feakins et al. Further, there is no consistent difference between the different sets of $E_{m,HBr}°$ values. Thus, the differences between the results reported here and those of Feakins et al. range from 0.1 mV for the 10% mixture to 1.9 mV for the 50% mixture. We are informed by Feakins that the value 0.0634 V for $E_{m,HBr}°$ in 20.22% methanol is definitely in error and must be considered withdrawn. The discrepancies between the results reported here and elsewhere could be ascribed either to some unsuspected fault present in the silver–silver bromide electrodes used by the other workers or to some undetectable malfunctioning of their hydrogen electrodes.

First, Feakins and Khoo (*2*) suspected that the silver–silver chloride electrodes used by Feakins and Tomkins (*3*) were not of high accuracy and subsequently established that the electrodes were indeed faulty. Since their measurements with the silver–silver bromide electrodes were made at about the time of the work with their silver–silver chloride electrodes, it is possible that some hitherto unknown fault might also be present in their silver–silver bromide electrodes. Further, Feakins and Tomkins found some tendency for their hydrogen electrodes to behave irreversibly. In the present work, no problem of this sort was encountered. This could be ascribed to the much smaller cell used in the present work, the design of which is probably well suited to measurements of the sort in which some reaction appears to occur at the hydrogen electrode which thus depletes the surrounding solution of hydrogen (*4*). Since a smaller volume of solution is used, it is relatively easier to keep the solution saturated with hydrogen, and this is further aided by the fact that the hydrogen is delivered through a sintered glass frit instead of through the usual bubbler so that the solution is thoroughly agitated and the gas is dispersed to all parts of it. It is therefore concluded that the results obtained here are more reliable than those obtained by Feakins et al. (*3*, *4*).

Second, it is noted that while the electrodes used in this work were prepared by the thermal electrolytic method, those used by Melton and Amis (*9*) were prepared differently by Keston's method (*6*). However, it is unlikely that the dissimilarity of electrodes in itself could account for the large discrepancies in the $E_{m,HBr}°$ values. Table IV shows that the $E_{m,HBr}°$ values obtained by Melton and Amis are all lower than the corresponding values obtained in this work. It is known (*5*) that when a hydrogen electrode functions improperly, it generally assumes a positive rest potential which thus results in a cell emf that is lower than the correct one. This may account for the difference between the present results and and those of Melton and Amis, since the possibility of errors arising from this source was minimized, if not eliminated, in the present work, by replacing one electrode by another in the experimental cell on several occasions, as noted earlier. Incidentally, an examination of the Melton and Amis data for 60% methanol at 25°C showed uncertainties in their emf values in their HBr solutions of molalities 0.00875 and 0.00996 mol kg^{-1}.

We are satisfied that the set of $E_{m,HBr}°$ values reported here for the methanol–water system at 25°C, though not completely definitive, is the best so far. It is certainly the most self-consistent.

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LITERATURE CITED

(1) Andrews, A. L., Bennetto, H. P., Feakins, D., Lawrence, K. G., Tomkins, R. P. T., *J. Chem. Soc.* (*A*), **1968,** p 1486.
(2) Feakins, D., Khoo, K. H., *ibid.*, **1970,** p 361.
(3) Feakins, D., Tomkins, R. P. T., *ibid.*, **1967,** p 1458.
(4) Feakins, D., Watson, P., *J. Chem. Soc.*, **1963,** p 4686.
(5) Ives, D. J. G., Janz, G. J., "Reference Electrodes," Academic Press, London, New York, 1961.
(6) Keston, A. S., *J. Amer. Chem. Soc.*, **57,** 1671 (1935).
(7) Khoo, K. H., *J. Chem. Soc.* (*A*), **1971,** p 1177.
(8) McIntyre, J. M., Amis, E. S., *J. Chem. Eng. Data*, **13,** 371 (1968).
(9) Melton, S. L., Amis, E. S., *ibid.*, p 429.
(10) Owen, B. B., *J. Amer. Chem. Soc.*, **57,** 1526 (1935).
(11) Robinson, R. A., Stokes, R. H., "Electrolyte Solutions," Chap. 9, Butterworths, London, 1959.

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