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STANDARD POTENTIALS OF SILVER–SILVER BROMIDE ELECTRODE IN WATER–DIMETHYLFORMAMIDE MIXTURES AT DIFFERENT TEMPERATURES AND THE RELATED THERMODYNAMIC QUANTITIES

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ABSTRACT

Standard electrode potentials of silver–silver bromide electrode were determined in the temperature range 15–30°C in 10–60 weight% dimethylformamide–water mixtures by EMF measurements of the cell.

$Pt, H_2(g, 1\ atm)\,|HBr_{(m)}, DMF_{(x)}\text{–}water_{(y)}|AgBr\text{–}Ag$

The standard molal potential, ${}_{s}E^0_m$, in the various solvent mixtures has been expressed as a function of temperature. The primary medium effect, the mean molal activity coefficient and the various thermodynamic parameters for the transfer of HBr from water to these solvent mixtures at 25°C have been reported. The variation of the thermodynamic parameters with the solvent composition has been discussed.

INTRODUCTION

In continuation of the earlier investigations [1–5] from this laboratory on electrolyte–solvent and ion–solvent interactions in mixed aqueous amphiprotic solvents, the present work deals with the determination of standard potentials of silver–silver bromide electrode in water–DMF mixtures in the composition range 10–60 wt% DMF at different temperatures. The results obtained have been utilised for the evaluation of the thermodynamics of transfer of HBr and its ions from water to water–DMF mixtures. It may be mentioned that although a large body of data using Ag–AgBr electrodes in mixed aqueous amphiprotic solvents [4–8] are reported, only a few reports are available using Ag–AgBr electrodes in mixed aqueous aprotic solvents such as water–DMSO [9], water–acetonitrile [10] and water–acetone [11]. To our knowledge no such data have yet been reported on water–DMF mixtures. Thus results on the cell,

$$Pt,\ H_{2(g,1\ atm)}\,|HBr_{(m)},\ DMF_{(x)}\text{–}water_{(y)}\,|AgBr\text{–}Ag \qquad (1)$$

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in water–DMF mixtures in the composition range 10–60 wt% DMF in the temperature range 15–30°C are reported in this paper.

EXPERIMENTAL

The purification of the solvent is similar to that described earlier [12]. The Ag–AgBr and hydrogen electrodes were prepared according to the procedure of Hills and Ives [13].

The stock solutions of aqueous HBr were prepared from triply-distilled water and 47% aqueous HBr (Merck) which was freshly distilled twice before use. All solutions were prepared by weight. The strength of HBr in the experimental solution was determined by titration with aqueous NaOH which was previously standardised with a standard solution of potassium hydrogen phthalate. The experimental set-up and the procedure adopted in the EMF measurements are similar to those described earlier [1]. All measurements were made with a pair of hydrogen electrodes and two pairs of Ag–AgBr electrodes. The cells were thermostatted at each temperature with an accuracy of ±0.1°C. The electrodes were found to be stable over the complete range of solvent compositions and temperatures and the constancy of cell EMF within ±0.05 mV over a period of 30 min was considered as an adequate criterion of equilibrium in the EMF measurements. The physical constants of the solvent mixtures at various temperatures were reported earlier [14]. The Nernst equation has been found to be valid in all solvent compositions. The coating of the hydrogen electrode was observed to deteriorate with time from 60 wt% DMF onwards leading to a drift in the EMF values. This difficulty was overcome by giving a light coating on platinum electrodes. However, even this procedure failed from 70% DMF and hence EMF measurements were restricted up to 60 wt% DMF.

RESULTS AND DISCUSSION

The EMF data of cell (1) in the various solvent mixtures corrected to a partial pressure of one atmosphere of hydrogen are given in Table 1. The standard molal potentials, ${}_{\mathrm{s}}E^0_{\mathrm{m}}$, of the cell in the various solvent mixtures were determined by extrapolation of the function

$$E^{0\prime} = E + 2K \log m - 2KA'C^{1/2}/(1 + aB'C^{1/2}) - 2K \log(1 + 0.002mM_{xy}) = {}_{\mathrm{s}}E^0_{\mathrm{m}} - 2Kbm \quad (2)$$

to zero molality. Such a plot in 40 wt% DMF, which is typical of the results in these mixtures, is shown in Fig. 1. In eqn. (2)

$$K = RT \ln 10 \,|\, F \quad (3)$$

TABLE 1

EMF data of cell 1, corrected for 1 atm pressure of H_2, from 15 to 30°C in various water–DMF mixtures [a]

mHBr (mol kg^{-1})	E (V)			
	15°C	20°C	25°C	30°C
x = 10 wt%				
0.00912	0.32397	0.32593	0.32799	0.32924
0.01033	0.31687	0.31890	0.32065	0.32181
0.01244	0.30866	0.31044	0.31205	0.31321
0.01422	0.30221	0.30378	0.30551	0.30663
0.01833	0.29144	0.29283	0.29425	0.29502
0.02230	0.28027	0.28174	0.28283	0.28339
x = 20 wt%				
0.00918	0.33333	0.33463	0.33617	0.33722
0.01408	0.31159	0.31298	0.31401	0.31492
0.01612	0.30824	0.30939	0.31004	0.31087
0.01798	0.30391	0.30482	0.30571	0.30639
0.02025	0.29637	0.29788	0.29871	0.29939
0.02410	0.28881	0.28959	0.29031	0.29081
0.02573	0.28629	0.28703	0.28755	0.28795
x = 40 wt%				
0.00908	0.36117	0.36220	0.36171	0.36148
0.01011	0.35662	0.35712	0.35690	0.35649
0.01423	0.34029	0.34062	0.34009	0.33881
0.01628	0.33495	0.33480	0.33360	0.33233
0.01809	0.32755	0.32852	0.32827	0.32723
0.02019	0.32246	0.32239	0.32230	0.32177
x = 60 wt%				
0.00912	0.35100	0.35319	0.35560	0.35677
0.01017	0.34661	0.34858	0.35003	0.35119
0.01228	0.33659	0.33913	0.34132	0.34192
0.01329	0.33431	0.33501	0.33720	0.33825
0.01412	0.33025	0.33231	0.33314	0.33506
0.01614	0.32530	0.32684	0.32803	0.32919

[a] Weight% DMF.

m and c are the molality and molarity of HBr, respectively. A' and B' are the Debye–Huckel constants on the molality scale, a is the ion size parameter (Å), b is the coefficient occurring in the expression for the activity coefficient as a function of molality and M_{xy} is the mean molecular weight of the solvent mixture. In the determination of ${}_sE^0_m$, $a = 5$ Å was used in all compositions. Table 2 gives the ${}_sE^0_m$ values at the various temperatures and also ${}_sE^0_c$ and ${}_sE^0_N$ i.e., the ${}_sE^0$ values in molar and mole fraction scales, at 25°C calculated from,

$$ {}_sE^0_C = {}_sE^0_m + 2K \log d_0 \quad (4)$$

$$ {}_sE^0_N = {}_sE^0_m - 2K \log(1000/M_{xy}) \quad (5)$$

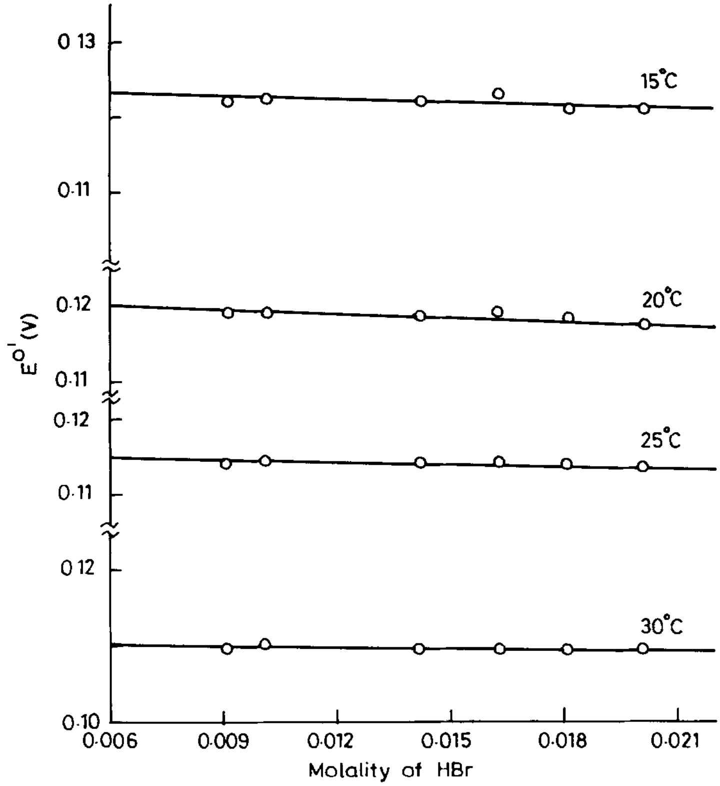

Fig. 1. Extrapolation of plot of $E^{0\prime}$ (V) against molality of HBr in water–DMF mixtures (40 wt% DMF) at various temperatures.

where d_0 is the density of the solvent. The standard error in E^0_m values is about ±0.2 mV in all the solvent mixtures at different temperatures. The ${}_sE^0_m$ can be expressed as a function of temperature according to

$$ {}_sE^0_m = {}_sE^0_{m,25^\circ C} + b(t-25) + c(t-25)^2 \tag{6}$$

where t is the temperature in °C and b and c are empirical coefficients. These data are summarised in Table 3. The standard deviations in ${}_sE^0_m$ calculated from eqn. (6) are found to be within ±0.2 mV. The stoichiometric mean molal activity coefficients of HBr, ${}_s\gamma_\pm$, referred to a value of unity at infinite dilution in the particular solvent and calculated according to the equation

$$\log {}_s\gamma_\pm = \left({}_sE^0_m - E\right)/2K - \log m \tag{7}$$

at 25°C in all solvent mixtures at rounded molalities of the acid are recorded in Table 4. The primary medium effect of HBr, defined as $\log {}_m\gamma_\pm$ in the various solvent mixtures at 25°C, calculated from

$$\log {}_m\gamma_\pm = \left({}_wE^0_m - {}_sE^0_m\right)/2K \tag{8}$$

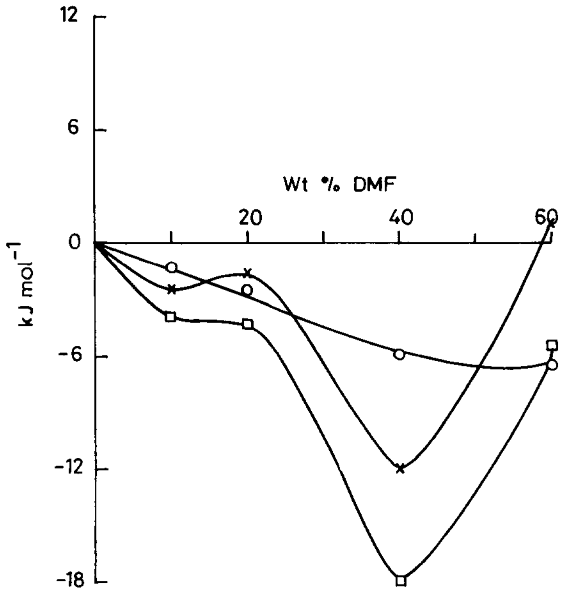

Fig. 2. Variation of the various thermodynamic quantities (mole fraction scale) of transfer of HBr in water–DMF mixtures. (×) $T\Delta S_t^0$, (□) ΔH_t^0, (○) ΔG_t^0.

TABLE 2

${}_sE_m^0$ At different temperatures and ${}_sE_N^0$ and ${}_sE_C^0$ at 25°C in various water–DMF mixtures

x [a] (wt%)	${}_sE_m^0$ (V)				${}_sE_C^0$	${}_sE_N^0$
	15°C	20°C	25°C	30°C		
10	0.08579	0.08319	0.08154	0.07759	0.08136	−0.12075
20	0.09445	0.09171	0.08893	0.08593	0.08873	−0.10902
40	0.12374	0.12033	0.11511	0.11039	0.11494	−0.07278
60	0.11044	0.10874	0.10702	0.10336	0.10666	−0.06838

[a] Weight% DMF.

TABLE 3

Coefficients of empirical equation ${}_sE_m^0 = {}_sE_{m,25°C}^0 + b(t-25) + c(t-25)^2$

x [a] (wt%)	${}_sE_{m,25°C}^0$	-10^4b	-10^6c
0	0.07107	4.917	2.7
10	0.08105	5.925	13.5
20	0.08890	5.798	2.6
40	0.11545	9.709	13.1
60	0.10673	5.572	19.6

[a] Weight% DMF.

TABLE 4

Mean molal activity coefficient (${}_{s}\gamma_{\pm}$) at rounded molalities of HBr and primary medium effects of HBr ($\log {}_{m}\gamma_{\pm}$) in various water–DMF mixtures at 25°C

x [a] (wt%)	mHBr (mol kg^{-1})					
	0.01	0.012	0.014	0.015	0.02	$\log {}_{m}\gamma_{\pm}$
10	0.924	0.908	0.893	0.887	0.858	−0.089
20	0.879	0.866	0.856	0.850	0.825	−0.151
40	0.893	0.884	0.877	0.874	0.869	−0.372
60	0.865	0.853	0.845	0.841	0.825	−0.304

[a] Weight% DMF.

is also given in the same table; ${}_{w}E^{0}_{m}$ and ${}_{s}E^{0}_{m}$ in eqn. (8) represent the standard EMFs of cell (1) on the molal scale in water and solvent, respectively. The primary medium effect is a measure of the free energy change associated with the transfer of 1 mol of HBr from water to the given solvent at infinite dilution according to

$$\mathrm{HBr(water)} = \mathrm{HBr(water\text{–}DMF)} \tag{9}$$

The standard free energy change, ΔG^{0}_{t}, for the process given by eqn. (9) was calculated on the mole fraction scale for the various solvent mixtures at 25°C by using

$$\Delta G^{0}_{t} = F\left({}_{w}E^{0}_{N} - {}_{s}E^{0}_{N}\right) \tag{10}$$

where ${}_{w}E^{0}_{N}$ and ${}_{s}E^{0}_{N}$ represent the standard EMFs of cell (1) on the mole fraction scale. The transfer process (eqn. 9) is associated with the transfer of charged species, H^{+} and Br^{-}, from water to the mixed solvent at infinite dilution. It is generally accepted [15] that ΔG^{0}_{t} consists of an electrostatic part, $\Delta G^{0}_{t(el)}$ and a non-electrostatic part $\Delta G^{0}_{t(nonel)}$. While the former arises due to the difference in the dielectric constants of the solvents, the latter reflects the contributions of solvation and other specific ion–solvent interactions which depend on the basicity of the solvent. Thus

$$\Delta G^{0}_{t} = \Delta G^{0}_{t(el)} + \Delta G^{0}_{t(nonel)} \tag{11}$$

The electrostatic contribution in all the solvent mixtures has been calculated by employing Born equation

$$\Delta G^{0}_{t(el)} = \left(Ne^{2}/2\right)\left(\frac{1}{r_{H^{+}}} + \frac{1}{r_{Br^{-}}}\right)\left(\frac{1}{D_{S}} - \frac{1}{D_{W}}\right) \tag{12}$$

The numerical values of $r_{H_3O^{+}}$ and $r_{Br^{-}}$ are taken as 2.76 and 1.95 Å, respectively. The value of $\Delta G^{0}_{t(nonel)}$ can be calculated by utilising eqn. (11). The standard entropy of transfer, ΔS^{0}_{t}, was calculated from

$$\begin{aligned}\Delta S^{0}_{t} &= \left[-(\mathrm{d}/\mathrm{d}T)F\left({}_{w}E^{0}_{N} - {}_{s}E^{0}_{N}\right)\right]\\ &= \left[(b_{s} - b_{w}) - 2(c_{s} - c_{w})(t - 25) + (K_{w} - K_{s})\right]\end{aligned} \tag{13}$$

TABLE 5

Standard thermodynamic quantities [a] for the transfer of HBr from water to water–DMF mixtures at 25 °C

x [b] (wt%)	ΔG_t^0	$\Delta G_{t(el)}^0$	$\Delta G_{t(nonel)}^0$	ΔS_t^0	$\Delta S_{t(el)}^0$
10	−1395	30	−1425	−9.50	11.90
20	−2529	140	−2669	−5.80	14.20
40	−6025	1106	−7131	−40.00	−0.21
60	−6449	2686	−9135	3.72	−14.50

x [b] (wt%)	$\Delta S_{t(nonel)}^0$	ΔG_t^0	$\Delta H_{t(el)}^0$	$\Delta H_{t(nonel)}^0$	$T\Delta S_t^0$ (J mol^{-1})
10	−21.40	−3920	3876	−7796	−2525
20	−20.00	−4258	4374	−8632	−1729
40	−39.79	−18028	1043	−19071	−12003
60	18.22	−5340	−1637	−3703	1109

[a] Gibbs energy in J, entropy in J K^{-1} mol^{-1}, enthalpy in J.

[b] Weight% DMF.

where b_s and c_s and b_w and c_w are the coefficients from Table 3 for the solvent and water, respectively, and $K_w = 2R/F \ln(1000/18.016) = 6.92 \times 10^{-4}$; $K_s = 2R/F \ln(1000/M_{xy})$. The last term in eqn. (13) arises in the conversion of ${}_sE_m^0$ to ${}_sE_N^0$. $\Delta S_{t(el)}^0$ can be obtained by differentiating eqn. (12) with respect to temperature to give

$$\Delta S_{t(el)}^0 = -(Ne^2/2)\left(\frac{1}{r_{H^+}} + \frac{1}{r_{Br^-}}\right)\left(\frac{1}{D_S\theta_s} - \frac{1}{D_w\theta_w}\right) \tag{14}$$

where θ is a constant given by

$$\partial \ln \frac{D}{\partial T} = -\frac{1}{\theta}$$

and is a characteristic of the medium. θ has been evaluated from the slopes of the plots ln D against temperature for various water–DMF compositions.

The standard enthalpy of transfer, ΔH_t^0, was calculated from the equation

$$\Delta H_t^0 = \Delta G_t^0 + T\Delta S_t^0 \tag{15}$$

and $\Delta H_{t(el)}^0$ and $\Delta H_{t(nonel)}^0$ contributions were obtained using equations similar to eqn. (11). All these thermodynamic quantities on a mole fraction scale are given in Table 5. The ΔG_t^0 values are accurate to ±20 J and the expected errors in ΔS_t^0 and ΔH_t^0 are ±0.5 J K^{-1} and ±140 J, respectively.

It can be seen from Table 5 that ΔG_t^0 is negative in water–DMF mixtures and decreases with the addition of DMF to water. This suggests that the transfer of HBr from water to water–DMF mixtures is a favourable process. The variation of ΔG_t^0 with solvent composition, when examined in the light of eqn. (11) indicates that $\Delta G_{t(el)}^0$ becomes increasingly positive due to the decrease in the dielectric constant of the solvent with increasing amounts of DMF, whereas $\Delta G^0_{\mathrm{t(nonel)}}$ becomes increasingly negative under the same conditions. This indicates that the transfer of HBr from water to water–DMF mixtures is a favourable process as far as chemical interactions are considered, suggesting that water–DMF mixtures are more basic than water, which has also been observed in other aqueous dipolar aprotic solvent mixtures [11]. Das and Kundu [16] also arrived at a similar conclusion based on hydrogen bonded interactions in these solvent mixtures and also on the more basic nature of DMF compared to water. A comparison of $\Delta G^0_{\mathrm{t(el)}}$ and $\Delta G^0_{\mathrm{t(nonel)}}$ shows that $\Delta G^0_{\mathrm{t(nonel)}}$ predominates making the overall transfer process a favourable one.

Franks and Ives [17] and Feakins and Voice [18] have emphasised the importance of ΔH^0_{t} and ΔS^0_{t} in explaining the structural effects of solvents on the transfer process. The enthalpy change (ΔH^0_{t}) becomes increasingly negative up to 40 wt% DMF and then increases (becomes less negative). The entropy change (ΔS^0_{t}) is negative up to 40 wt% DMF and then becomes slightly positive at 60 wt% DMF.

The negative and decreasing values of ΔH^0_{t} and ΔS^0_{t} indicate that there is a breakdown of water structure on the transfer process [19]. The mixed solvent is then less associated than pure water. Hydrobromic acid thus breaks more structure in water than in the mixed solvent [20].

The changes in $\Delta H^0_{\mathrm{t(nonel)}}$ and $\Delta S^0_{\mathrm{t(nonel)}}$ with the solvent composition are generally similar after making allowance for the electrostatic contribution. However, they are affected somewhat by the values of radii chosen for the cation and the anion in eqn. (12).

$\Delta H^0_{\mathrm{t(nonel)}}$ is negative throughout the range of solvent composition which is in agreement with the conclusions of Feakins et al. [21] on the variation of *B* coefficients of viscosity of electrolytes in alcohol–water mixtures. The negative values of $\Delta H^0_{\mathrm{t(nonel)}}$ suggest structure making ion–solvent interactions in the mixed solvent.

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