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ABSOLUTE ELECTRODE POTENTIALS IN DIMETHYL SULPHOXIDE–WATER MIXTURES AND TRANSFER FREE ENERGIES OF INDIVIDUAL IONS

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ABSTRACT

The standard potentials of $H_2|H^+$, $M|M^+$ (M = Li, Na, K, Rb and Cs) and $Ag|AgX$ (X = Cl, Br and I) electrodes in seven aqueous solutions of dimethyl sulphoxide (DMSO), containing up to 60 wt.% DMSO, have been determined from EMF measurements of cells of the type: $Ag|AgX|MX$ (m), $S|M(Hg)|MX$ (m), $W|AgX|Ag$, or a variant of it, at 25°C by our recently reported procedure. The interest, validity and general applicability of this procedure in both aqueous protic and aprotic solvents have been demonstrated. The radii of solvated cations and their solvation extent in these media have been calculated. The standard Gibbs free energies of transfer of halogen acids and alkali metal halides as well as their constituent individual ions from water to each of the DMSO–water mixtures have been also computed. The results are interpreted and discussed.

INTRODUCTION

The energetics of ion solvation in the aqueous dipolar aprotic solvents have received increasing attention recently [1–6]. These are fundamentally important in that they constitute the basis of theories of ion–solvent interactions and provide an insight into the structural aspects of these solvents [3]. However, relatively little is known of ion–solvent interactions in such solvents. The thermodynamic basis of these interactions in many of the aqueous dipolar aprotic solvents, including dimethyl sulphoxide (DMSO)–water mixtures, is not yet established [2]. Thus, Khoo [3] reported free energies of transfer, ΔG_t^0 of X^- (X = Cl, Br and I) and H^+ ions from water to some aqueous DMSO solutions, evaluated from studies on the

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TABLE 1

Values of ΔE_m^0 (mV) for cells (A) in dimethyl sulphoxide–water mixtures at 25 °C, and previously reported [1,2,4] values, for comparison

DMSO (wt.%)		LiCl	NaCl	KCl	KBr	KI	RbCl	CsCl
5	This work	2.7	5.2	5.5	2.7	0.7	5.4	5.0
	[4]	2.6	5.3	5.3	–	–	5.3	4.1
10	This work	5.6	10.6	11.2	6.4	1.5	11.1	10.2
	[1]	5.3	10.4	10.8	6.5	1.4	11.0	10.3
	[2]	5.7	12.3	11.5	–	–	11.0	10.9
	[4]	5.5	10.7	11.2	–	–	11.2	8.3
20	This work	13.2	23.4	25.0	16.4	3.8	24.3	23.1
	[1]	13.6	23.4	24.1	–	–	23.7	23.1
	[2]	12.7	21.0	26.2	–	–	25.3	24.6
	[4]	11.9	22.5	24.9	–	–	24.3	19.0
30	This work	22.2	38.8	41.0	28.2	6.4	40.7	38.7
	[4]	19.6	37.3	41.5	–	–	40.8	33.2
40	This work	32.0	58.3	61.7	41.5	9.0	61.4	59.2
	[1]	32.0	58.1	61.7	–	–	59.7	59.3
	[2]	34.7	58.4	64.9	–	–	61.3	56.9
	[4]	28.6	55.0	61.6	–	–	61.6	51.5
50	This work	42.7	81.2	85.7	55.5	11.6	86.0	83.6
	[4]	38.6	76.3	85.8	–	–	84.1	74.5
60	This work	53.7	104.1	111.3	71.3	14.2	113.6	110.0
	[1]	–	104.3	–	–	–	–	–
	[2]	53.8	103.0	111.5	–	–	113.5	110.1
	[4]	51.4	100.6	114.2	–	–	114.8	100.0

standard potentials of Ag | AgX | X^- electrodes in these solvents. Smits et al. [4] determined ΔG_t^0 values of the alkali metal chlorides, MCl (M = Li, Na, K, Rb and Cs), from water to several DMSO–water mixtures, by EMF measurements using glass electrodes. The values of ΔG_t^0 of MCl were also reported by Das and Kundu [2], from water to aqueous solutions of DMSO containing 10, 20, 40 and 60 wt.% DMSO, and by Feakins et al. [1] to 40% DMSO, of NaCl to 60% DMSO and of KBr and KI to the 10% mixture. All these EMF measurements were at 25 °C.

Although the EMF data reported by Feakins et al. [1] and Das and Kundu [2] were obtained by amalgam electrode measurements, the agreement is less satisfactory. Discrepancies between the reported EMF values (ΔE_m^0) were generally noted (see Table 1); e.g. there is as much as 3.2 mV difference for KCl in 40% DMSO. Further, the data obtained by amalgam electrodes [1,2] are in poor agreement with those by glass electrodes [4]. For

LiCl, the ΔE_m^0 values are 34.7 mV [2], 32.0 mV [1] and 28.6 mV [4], and for CsCl are 56.9 mV [2], 59.3 mV [1] and 51.5 mV [4], in 40% DMSO.

Recently, we reported [7,8] a new procedure to obtain the standard absolute potentials of $H_2|H^+$, $M|M^+$ and $Ag|AgX$ electrodes in aqueous and non-aqueous protic solvents, as well as the thermodynamics of individual ions, without any extrathermodynamic assumption. As far as electrochemical methods are concerned, amalgam electrodes have been considered for a long time as the most reliable means for the determination of alkali metal ion activity in solution [1,8]. Thus, in order to resolve the discrepancies noted, and as a continuation of previous investigations [6–9] in both aqueous and non-aqueous solvents, EMF measurements were made at 25 °C on the double cell

$$Ag\,|\,AgX\,|\,MX\ (m),\ S\,|\,M(Hg)\,|\,MX\ (m),\ W\,|\,AgX\,|\,Ag \qquad (A)$$

or a variant of it [1]; where M = Li, Na, K, Rb and Cs for X = Cl and M = K for X = Br and I. S is mixed solvent, W is water and m is molality, which varies from 0.02 to 0.20 mol kg^{-1}. In the present paper, the new procedure [8] is applied to the EMF data of cell (A) to verify its use in such aqueous dipolar aprotic media, and to obtain the absolute potentials of $H_2|H^+$, $M|M^+$ and $Ag|AgX$ electrodes in seven DMSO–water mixtures containing up to 60 wt.% DMSO, and the transfer free energies of halogen acids and alkali metal halides as well as their constituent individual ions from water to the respective DMSO–water solvent mixtures.

EXPERIMENTAL

DMSO and other materials used were as before [1,6,8]. For the EMF measurements the procedure was generally as described previously [1,8], with the modifications reported by Feakins et al. [1] for the solvents containing $\geqslant$ 30% DMSO, because of the solubility of the silver halide from the electrodes. The temperature of the measuring cell was carefully maintained at 25 ± 0.05 °C. Experimental details and mathematical treatment of the results have been described earlier [1,8]. Attempts at measurements with cell (A), where X = Br and I, in $\geqslant$ 70% DMSO failed; poorly reproducible EMF values were obtained. As reported [1,3], this may be due to the relatively high solubility of these silver halides in such solvents.

RESULTS AND DISCUSSION

The EMF values of cell (A) were treated as before [1,8] to give the standard EMF values, ΔE_m^0, which are collected in Table 1. These values are accurate to ± 0.2 mV or better. Table 1 also includes values of ΔE_m^0

TABLE 2

Values of E_m^0 (V) of cells (B) and (C) in dimethyl sulphoxide–water mixtures at 25°C, and those of Feakins et al. [1] in the 10% DMSO mixture

DMSO (wt.%)	HCl	LiCl	NaCl	KCl	KBr	KI	RbCl	CsCl
0	0.22236	3.2667	2.9352	3.1472	2.9974	2.7727	3.1475	3.1454
5	0.22162	3.2640	2.9300	3.1417	2.9947	2.7720	3.1421	3.1404
10	0.22104	3.2611	2.9246	3.1360	2.9910	2.7712	3.1364	3.1352
Feakins et al. [1]	0.2210	3.2614	2.9248	3.1364	2.9909	2.7713	3.1365	3.1351
20	0.21998	3.2535	2.9118	3.1222	2.9810	2.7689	3.1232	3.1223
30	0.21900	3.2445	2.8964	3.1062	2.9692	2.7663	3.1068	3.1067
40	0.21773	3.2347	2.8769	3.0855	2.9559	2.7637	3.0861	3.0862
50	0.21564	3.2240	2.8540	3.0615	2.9419	2.7611	3.0615	3.0618
60	0.21176	3.2130	2.8311	3.0359	2.9261	2.7585	3.0339	3.0354

reported earlier [1,2,4], for comparison. As would be expected, the best agreement is between the present results and those obtained with amalgam electrodes [1,2]. Good agreement is also observed between the two sorts of electrodes in several places. For CsCl, the ΔE_m^0 values obtained with glass electrodes [4] are appreciably lower than those of amalgam electrodes; Smits et al. [4] reported that their data for this electrolyte (CsCl) are also poorly reproducible. All the precautions taken over the dissolution of silver and other halides make ours the more reliable data.

The value of ΔE_m^0 is the difference between the E_m^0 values of cell (B)

$$\mathrm{M} \,|\, \mathrm{MX,S} \,|\, \mathrm{AgX} \,|\, \mathrm{Ag} \qquad \text{(B)}$$

in water and in the DMSO–water solvent mixture, i.e.,

$$\Delta E_m^0 = {}^{\mathrm{w}}E_m^0 - {}^{\mathrm{s}}E_m^0 \qquad (1)$$

The values of ${}^{\mathrm{w}}E_m^0$ of cell (B) have been obtained recently [8], and thus, those of ${}^{\mathrm{s}}E_m^0$ could be computed in each of the DMSO–water mixtures for cell (B) containing MX = LiCl, NaCl, KCl, KBr, KI, RbCl and CsCl. These are recorded in Table 2, together with earlier results [6] for HCl in DMSO–water mixtures, obtained from EMF measurements on cell (C).

$$\mathrm{Pt} \,|\, \mathrm{H_2}\ (\mathrm{g,\ 1\ atm}) \,|\, \mathrm{HX,\ S} \,|\, \mathrm{AgX} \,|\, \mathrm{Ag} \qquad \text{(C)}$$

The new procedure [7,8] can be applied to the E_m^0 values of cells (B), containing KCl, KBr and KI, in each solvent (Table 2). This procedure depends on the fact that there are generally two possibilities (I and II) for the variation of the electrode potential with the radius of the solvated ion, r, on whose activity the potential depends, i.e., either the oxidation potential varies directly with r (case I), or the reduction potential varies inversely with r (case II). Therefore the standard EMF (E_m^0) of a cell, which is the difference between two oxidation or reduction potentials, is given as either

$$E_m^0 = {}^{\mathrm{ox}}_{\mathrm{L}}E_m^0 - {}^{\mathrm{ox}}_{\mathrm{R}}E_m^0 = a_1^0 r^+ - a_1^0 r^- \qquad (2\text{-I})$$

or

$$E_m^0 = {}^{\mathrm{red}}_{\mathrm{R}}E_m^0 - {}^{\mathrm{red}}_{\mathrm{L}}E_m^0 = a_2^0/r^- - a_2^0/r^+ \qquad (2\text{-II})$$

where r^+ and r^- are the radii of solvated cations and anions, respectively, and all the symbols have their usual significance [7,8]. Therefore, the cell EMF (E_m^0) is proportional to the radius of the solvated ion which is being varied in a series of electrolytes having a common ion [7,8].

Standard absolute electrode potential

According to eqns. (2-I) and (2-II), the plot of E_m^0 of cells (B), containing KCl, KBr and KI, against r^- (method I) or against $1/r^-$ (method II) gave almost perfect straight lines, in each solvent. The least-squares results of applying eqns. (2-I) and (2-II) to the E_m^0 values of cells (B) in DMSO–water solvent mixtures at 25 °C, are summarized in Tables 3 and 4, respectively. As previously [7,8], the standard absolute potential of the $\mathrm{K}|\mathrm{K}^+$ (${}_{\mathrm{L}}E_m^0$) and $\mathrm{Ag}|\mathrm{AgX}$ (${}_{\mathrm{R}}E_m^0$) electrodes, the radius of the solvated K^+ ion (r^+) and thus its solvation extent (S_e), in the standard state, have been computed by both methods I and II. As expected [7,8], different values based on different, oxidation or reduction, potential scales are obtained. Of course, only one set of data should be credited. However, it is evident [7–9] that method I should be applied to the EMF data for the determination of absolute electrode potentials as well as thermodynamics of individual ions in solution, and thus its set of data should be credited. All previous results [7–9] gave evidence that the plots of standard transfer free energy or entropy against $1/r^-$, used earlier [1–3] to obtain the thermodynamic properties of individual ions, cannot be accepted. Nevertheless, the results of calculations by both methods I and II are considered in the present work, in order to provide further proof for these conclusions.

Using the known computed values of the standard absolute potential of the $\mathrm{Ag}|\mathrm{AgCl}$ electrode, in each solvent (Tables 3 and 4), those of $\mathrm{H_2}|\mathrm{H}^+$, $\mathrm{Li}|\mathrm{Li}^+$, $\mathrm{Na}|\mathrm{Na}^+$, $\mathrm{Rb}|\mathrm{Rb}^+$ and $\mathrm{Cs}|\mathrm{Cs}^+$ electrodes, containing HCl, LiCl, NaCl, RbCl and CsCl, respectively, could be obtained from the E_m^0 values of cells (C) and (B) (Table 2). Thus, the radii of the solvated cations (r^+) and their solvation extent (S_e), as well as the individual ionic contributions to ΔG_t^0 values of electrolytes, in each solvent, were calculated as before [7,8]. These are included in Tables 3 and 4.

The results in Tables 3 and 4 reflect the following interesting features.

(1) In all solvents, eqn. (2-I) fits better than eqn. (2-II), as indicated by the correlation coefficients (corr). Further, the differences (Δ, mV), between

TABLE 3

The least-squares results of applying eqn. (2-I) to the E_m^0 values of cells (B) in dimethyl sulphoxide–water mixtures at 25 °C, ΔG_t^0 values on the molal scale

		DMSO (wt.%)							
		5	10	10 [1]	20	30	40	50	60
$-$Corr (10^{-2})		99.9996	99.9996	99.9999	100.0000	99.9994	99.9995	99.9998	99.9989
Δ (mV)	KCl	-0.3	-0.4	-0.2	0.0	$+0.4$	$+0.3$	-0.2	-0.5
	KBr	$+0.6$	$+0.6$	$+0.4$	$+0.1$	-0.7	-0.6	$+0.4$	$+0.8$
	KI	-0.2	-0.2	-0.1	0.0	$+0.3$	$+0.2$	-0.1	-0.3
a_1^0 (10^{10} V m^{-1})		1.0566	1.0426	1.0433	1.0095	0.9708	0.9191	0.8585	0.7930
r^+ (10^{-10} m)	H	2.020	2.022	2.022	2.028	2.036	2.047	2.061	2.077
	Li	4.899	4.938	4.936	5.033	5.152	5.329	5.565	5.862
	Na	4.583	4.615	4.613	4.694	4.794	4.940	5.134	5.380
	K	4.784	4.818	4.816	4.903	5.009	5.167	5.376	5.639
	Rb	4.784	4.818	4.816	4.904	5.010	5.168	5.376	5.636
	Cs	4.782	4.817	4.815	4.903	5.010	5.168	5.376	5.638
S_c (10^{-10} m)	Li	4.30	4.34	4.34	4.43	4.55	4.73	4.97	5.26
	Na	3.63	3.67	3.66	3.74	3.84	3.99	4.18	4.43
	K	3.45	3.49	3.49	3.57	3.68	3.84	4.05	4.31
	Rb	3.30	3.34	3.34	3.42	3.53	3.69	3.90	4.16
	Cs	3.09	3.13	3.12	3.21	3.32	3.48	3.69	3.95

${}^{\mathrm{ox}}_{\mathrm{L}}E^{0}_{m}$ (V)	H	2.1341	2.1082	2.1095	2.0471	1.9761	1.8813	1.7695	1.6471
	Li	5.1765	5.1483	5.1499	5.0806	5.0016	4.8983	4.7779	4.6483
	Na	4.8425	4.8118	4.8133	4.7389	4.6535	4.5405	4.4079	4.2664
	K	5.0545	5.0235	5.0251	4.9494	4.8629	4.7487	4.6156	4.4717
	Rb	5.0546	5.0236	5.0250	4.9503	4.8639	4.7497	4.6154	4.4692
	Cs	5.0529	5.0224	5.0236	4.9494	4.8638	4.7498	4.6157	4.4707
${}^{\mathrm{ox}}_{\mathrm{R}}E^{0}_{m}$ (V)	Cl	1.9125	1.8872	1.8885	1.8271	1.7571	1.6636	1.5539	1.4353
	Br	2.0604	2.0331	2.0345	1.9685	1.8930	1.7922	1.6741	1.5464
	I	2.2823	2.2521	2.2536	2.1805	2.0968	1.9853	1.8544	1.7129
ΔG^{0}_{t} (J mol^{-1})	H	2332	4831	4707	10723	17580	26723	37508	49320
	Li	2586	5307	5152	11839	19461	29428	41045	53549
	Na	2875	5837	5693	12871	21111	32014	44807	58460
	K	2779	5770	5615	12919	21265	32284	45126	59010
	Rb	2769	5760	5625	12832	21169	32187	45145	59251
	Cs	2740	5683	5567	12726	20985	31985	44923	58913
	Cl	2311	4754	4628	10544	17306	26327	36910	48347
	Br	2490	5121	4987	11360	18645	28364	39765	52087
	I	2758	5673	5524	12584	20653	31418	44048	57696

TABLE 4

The least-squares results of applying eqn. (2-II) to the E_m^0 values of cells (B) in dimethyl sulphoxide-water mixtures at 25°C, ΔG_t^0 values on the molal scale

		DMSO (wt.%)							
		5	10	10 [1]	20	30	40	50	60
Corr (10^{-2})		99.8646	99.8638	99.8699	99.8765	99.8950	99.8933	99.8677	99.8538
Δ (mV)	KCl	−6.2	−6.2	−6.0	−5.7	−5.0	−4.8	−5.0	−4.8
	KBr	+11.1	+11.1	+10.8	+10.2	+9.0	+8.6	+9.0	+8.7
	KI	−4.9	−4.9	−4.8	−4.5	−4.0	−3.8	−4.0	−3.9
a_2^0 (10^{-10} V m)		4.1438	4.0890	4.0920	3.9594	3.8083	3.6056	3.3670	3.1097
r^+ (10^{-10} m)	H	2.004	2.006	2.006	2.012	2.020	2.032	2.047	2.064
	Li	4.252	4.081	4.089	3.714	3.339	2.901	2.469	2.080
	Na	6.469	6.144	6.162	5.467	4.806	4.075	3.388	2.794
	K	4.827	4.630	4.641	4.211	3.781	3.283	2.791	2.351
	Rb	4.860	4.661	4.673	4.232	3.798	3.296	2.803	2.363
	Cs	4.869	4.667	4.680	4.236	3.798	3.295	2.802	2.361
S_c (10^{-10} m)	Li	3.65	3.48	3.49	3.11	2.74	2.30	1.87	1.48
	Na	5.52	5.19	5.21	4.52	3.86	3.12	2.44	1.84
	K	3.50	3.30	3.31	2.88	2.45	1.95	1.46	1.02
	Rb	3.38	3.18	3.19	2.75	2.32	1.82	1.32	0.88
	Cs	3.18	2.98	2.99	2.55	2.11	1.61	1.11	0.67

$-{}^{\mathrm{red}}_{\mathrm{L}}E^0_m$ (V)	H	−2.0678	−2.0381	−2.0398	−1.9675	−1.8850	−1.7743	−1.6446	−1.5063
	Li	0.9746	1.0020	1.0006	1.0660	1.1405	1.2427	1.3638	1.4949
	Na	0.6406	0.6655	0.6640	0.7243	0.7924	0.8849	0.9938	1.1130
	K	0.8585	0.8831	0.8816	0.9404	1.0072	1.0983	1.2063	1.3227
	Rb	0.8527	0.8773	0.8757	0.9357	1.0028	1.0941	1.2013	1.3158
	Cs	0.8510	0.8761	0.8743	0.9348	1.0027	1.0942	1.2016	1.3173
${}^{\mathrm{red}}_{\mathrm{R}}E^0_m$ (V)	Cl	2.2894	2.2591	2.2608	2.1875	2.1040	1.9920	1.8602	1.7181
	Br	2.1250	2.0969	2.0985	2.0305	1.9530	1.8490	1.7266	1.5947
	I	1.9184	1.8930	1.8944	1.8331	1.7631	1.6692	1.5588	1.4397
ΔG^0_t (J mol^{-1})	H	2237	5105	4941	11909	19872	30555	43073	56411
	Li	1977	4622	4488	10795	17984	27844	39531	52182
	Na	1697	4101	3958	9772	16344	25267	35777	47280
	K	2364	4733	4597	10261	16713	25499	35921	47150
	Rb	1803	4178	4025	9811	16286	25094	35440	46489
	Cs	1832	4255	4083	9917	16469	25296	35662	46827
	Cl	2836	5760	5598	12666	20724	31529	44249	57961
	Br	2631	5347	5197	11757	19236	29266	41072	53800
	I	2376	4827	4691	10614	17366	26420	37079	48569
$a^0_2/a^0_1(10^{-20}$ m^2)		3.9218	3.9218	3.9220	3.9223	3.9230	3.9229	3.9219	3.9214

the original E_m^0 values and those calculated by eqn. (2), reflect the extent of this correlation. Thus, although only three points are available, the correlation coefficients and values of Δ always indicate [7–9] that the variables are very closely related in the wider range ($r^- = 1.81–2.16$) of case I than in the narrower range ($1/r^- = 0.463–0.552$) of case II.

(2) The ratio (a_2^0/a_1^0) is constant (3.922 ± 0.001) and independent of the solvent type and composition; the same result has been obtained in several solvent systems [7–9] including both protic and aprotic, partially aqueous and non-aqueous solvents. Thus, a_1^0 and a_2^0 appear to be universal constants for all electrodes, dependent only on the temperature and the medium. The values of these constants decrease with increasing either the temperature or the organic content of the solvent system [7–9].

(3) While the radius of the solvated proton calculated by both methods I and II ($r_{\mathrm{I}}^+ > r_{\mathrm{II}}^+$, in any solvent) increases with increasing DMSO content in the solvent, the radii of the solvated alkali metal cations and thus their solvation extent calculated by method I increase, but those calculated by method II decrease. As the water content of the solvent decreases, the water molecules in the solvation sheath around the ion are gradually replaced by the larger more polar DMSO molecules [2]. Therefore, the increasing values of r^+ and S_e, obtained by method I, are as expected. This may be so in view of the results obtained by Cowie and Toporowski [10], on the basis of viscometric, densimetric, heat of mixing and refractive index measurements, indicating that there is a greater degree of association in DMSO–water mixtures than in water alone. This is explained in terms of the polar sulphoxide group, in which the negatively charged oxygen should form hydrogen bonds with the water molecules, and therefore the hydrogen bonds between H_2O and DMSO in the mixtures are stronger than the H_2O–H_2O bonds [10]. Also, NMR measurements [11] indicate that the stronger H_2O–DMSO interactions are present in the water-rich mixtures. The results in Table 3 (r^+ and S_e values) are confirmed by these observations [10,11]. These results lend further support to the validity and general applicability of method I in aqueous mixtures of dipolar aprotic solvents. Thus, the protons have to be more solvated in the mixed solvent than in water, and much more solvated by increasing DMSO content in the solvent, as indicated by the results of both methods I and II. The solvation of protons in aqueous aprotic solvents could be compared with that in aqueous protic solvents, where the protons become gradually less solvated (r^+ values decrease) on the successive addition of methanol [7] or glycols [8,9] to the aqueous medium; minimum solvation is always [7–9] reached in the non-aqueous media.

(4) The successive substitution of water dipoles by the larger sized DMSO dipoles in the solvation sheath, on gradual addition of DMSO to the solvent, is further supported by another very interesting feature seen in Table 3. In any solvent, the extent of solvation increases in the expected

order: $\mathrm{Cs^+} < \mathrm{Rb^+} < \mathrm{K^+} < \mathrm{Na^+} < \mathrm{Li^+}$, and the $\mathrm{Li^+}$ ion is always highly solvated. On the other hand, results of method II (Table 4) show that the expected order is inverted for $\mathrm{Li^+}$ and $\mathrm{Na^+}$ ions. As it is well known [12,13], this is not the case. Similar results were also obtained for the alkali metal ions in methanol- [7] and glycol–water [8,9] solvent systems. These results shed more light on the inapplicability of method II for such calculations, and should confer extra confidence in the validity and, hence, greater reliability of the data evaluated by method I.

(5) As the DMSO content of the solvent increases, the oxidation potentials of both left and right electrodes decrease, whereas the reduction potentials decrease positively for the right electrode and negatively for the left one, as indicated by the results of methods I and II in Tables 3 and 4, respectively. In any solvent, as would be expected [7–9], the standard absolute oxidation potentials calculated by method I increase in the order: $^{\mathrm{ox}}E_m^0$ (Ag | AgCl) < $^{\mathrm{ox}}E_m^0$ (Ag | AgBr) < $^{\mathrm{ox}}E_m^0$ ($\mathrm{H_2}$ | $\mathrm{H^+}$) < $^{\mathrm{ox}}E_m^0$(Ag | AgI), whereas the standard absolute reduction potentials calculated by method II decrease in the same order. On the other hand, the irregular order of variation of the standard absolute potentials of the alkali metal electrodes, from Li | $\mathrm{Li^+}$ to Cs | $\mathrm{Cs^+}$ in any solvent, is dictated by the extent of solvation of the alkali metal ions, and thus by the radii of solvated cations.

Further, the standard free energy change associated with any electrode (half-cell) reaction could be obtained as $-{}_{\mathrm{E}}E_m^0 F$, where F is the faraday and ${}_{\mathrm{E}}E_m^0$ is the standard absolute electrode potential. By coupling the

TABLE 5

Values of E_m^0 (V) of cells (C) in dimethyl sulphoxide–water mixtures at 25°C, and those reported earlier [1,3,5]

	DMSO (wt.%)						
	5	10	20	30	40	50	60
HCl							
This work	0.2216	0.2210	0.2200	0.2190	0.2177	0.2156	0.2118
[1]	–	0.2210	–	–	–	–	–
[3]	–	0.2210	0.2199	–	0.2177	–	0.2117
[5]	–	–	0.2205	–	0.2185	–	–
HBr							
This work	0.0737	0.0751	0.0787	0.0831	0.0891	0.0954	0.1007
[1]	–	0.0750	–	–	–	–	–
[3]	–	0.0736	0.0765	–	0.0896	–	0.1040
HI							
This work	−0.1482	−0.1439	−0.1333	−0.1208	−0.1040	−0.0848	−0.0658
[1]	–	−0.1441	–	–	–	–	–
[3]	–	−0.1436	−0.1343	–	−0.1059	–	−0.0653

TABLE 6

Standard transfer free energies (J mol^{-1}) of halogen acids and alkali metal halides from water to dimethyl sulphoxide–water mixtures at 25°C

	DMSO (wt.%)							
	5	10	10 [1]	20	30	40	50	60
HCl	21	77	79	179	274	396	598	973
HBr	−158	−290	−280	−637	−1065	−1641	−2257	−2767
HI	−426	−842	−817	−1861	−3073	−4695	−6540	−8376
LiCl	275	553	524	1295	2155	3101	4135	5202
LiBr	96	186	165	479	816	1064	1280	1462
LiI	−172	−366	−372	−745	−1192	−1990	−3003	−4147
NaCl	564	1083	1065	2327	3805	5687	7897	10113
NaBr	385	716	706	1511	2466	3650	5042	6373
NaI	117	164	169	287	458	596	759	764
KCl	468	1016	987	2375	3959	5957	8216	10663
KBr	289	649	628	1559	2620	3920	5361	6923
KI	21	97	91	335	612	866	1078	1314
RbCl	458	1006	997	2288	3863	5860	8235	10904
RbBr	279	639	638	1472	2524	3823	5380	7164
RbI	11	87	101	248	516	769	1097	1555
CsCl	429	929	939	2182	3679	5658	8013	10566
CsBr	250	562	580	1366	2340	3621	5158	6826
CsI	−18	10	43	142	332	567	875	1217

standard absolute potentials of $H_2|H^+$ or $M|M^+$ electrodes with those of $Ag|AgX$ electrodes, using eqn. (2-I), the values of E_m^0 for cells (C) or (B), containing HX or MX electrolytes, respectively, could be computed. The values so computed at 25°C for HX acids, for example, are given in Table 5, together with those calculated from the data of Feakins et al. [1] for the 10% DMSO mixture and the earlier reported values [3,5], for comparison. Agreement is generally seen in several places. This supports the general applicability of the new procedure [8] to the EMF data of cells (A), and hence the reliability of the evaluated results (Tables 2, 3, 5 and 6).

However, it should be pointed out that Khoo [3] determined E_m^0 values of cell (C) for X = Br or I by plotting $(E_{HX} - E_{HCl})$ against m, where E_{HX} and E_{HCl} are the EMF's of buffered cells with X = Br or I and X = Cl, respectively, at the same value of m. The linear plots were extrapolated to $m = 0$ to obtain $(E^0_{m,HX} - E^0_{m,HCl})$. Then, using known values of $E^0_{m,HCl}$, those of $E^0_{m,HX}$ were calculated [3]. However, the errors in such values may increase in the successive steps of treatment of EMF data. Thus, taking into account the combined precision limits of the results of Khoo [3], the agreement between his E_m^0 values and the new ones is fairly close in several places. The assumption that the activity coefficient term varies linearly with m was made by Khoo [3] in order to obtain E_m^0 values of cell (C) for X = Br and I. Since our new E_m^0 values are obtained in various DMSO–water mixtures, without any assumptions, these should be preferred.

In Table 5, it is notable that while the value of E_m^0 for HCl decreases, that for HBr or HI increases with increasing DMSO content in the solvent. Nevertheless, the standard absolute potentials of the $H_2|H^+$ or Ag|AgX electrodes all decrease in the same direction. Since the value of E_m^0 is the difference between those of $_{L}E_m^0$ and $_{R}E_m^0$ (eqn. 2-I), the rate of variation of each will determine the net rate of variation of E_m^0 with solvent composition. This may explain the maximum observed at around 60% DMSO for the E_m^0 values of HBr obtained by Khoo [3].

Standard transfer Gibbs free energies of individual ions

Assessment of ΔG_t^0 for the individual ion is necessary in order to draw meaningful conclusions from these results and hence about ion-solvent interactions in these solvents. Individual ion values of ΔG_t^0 are given in Tables 3 and 4. These are accurate to $\leqslant 40$ J mol^{-1}, and show a qualitative resemblance to other mixed solvent systems [7–9] in that all the values are positive and increase, i.e., ion transfer becomes less favourable with increasing organic content of the solvent.

Although the transfer free energies calculated by method I are based on the oxidation potential scale, whereas those calculated by method II are based on the reduction potential scale, the transfer free energies of ions from water to mixed solvents show the same trend with increasing proportions of DMSO in the solvent. For any ion, absence of any break at least within the present limit of solvent composition indicates [2] that either no appreciable structural changes of the solvents occur within this range during the transfer process of the ions, as observed for other properties [2], or if any, these are compensated in a property such as ΔG_t^0.

In any mixed solvent, the values of ΔG_t^0 for cations do not follow such a regular order. As in the methanol–water mixtures [7], ΔG_t^0 values, calculated by method I (Table 3), rise somewhat sharply from H^+ through Li^+ to Na^+ and fall from Rb^+ to Cs^+ with a maximum between Na^+ and Rb^+ depending on the solvent composition. While the shifting of the maximum to Rb^+ occurs at around 90% methanol in the methanol–water system, it occurs as early as 50% DMSO in the DMSO–water system. Nevertheless, the essential similarity in the profiles of ΔG_t^0 against S_e points to a common cause for the resulting behaviour of these simple ions in the two solvent systems. On the other hand, although the behaviour of ΔG_t^0 values calculated by method II in the methanol–water system [7] is opposite where there is a minimum between Na^+ and Rb^+, depending on solvent composition, characteristic behaviour is generally seen for ΔG_t^0 values evaluated by method II (Table 4) in the DMSO–water system. Two minima at Na^+ and Rb^+ and a maximum at K^+, are observed in all solvents, except the 60% DMSO solvent where a minimum is observed at Rb^+. This irregular trend of variation of ΔG_t^0 values may lend further proof against the validity and applicability of method II for calculations of the thermodynamics of individual ions.

For anions, in any solvent, the values of ΔG_t^0 calculated by method I increase in the order: ΔG_t^0 $(Cl^-) < \Delta G_t^0$ $(Br^-) < \Delta G_t^0$ (I^-), whereas those calculated by method II decrease in that order. Similar behaviour was observed in several solvent systems [7–9].

Standard transfer Gibbs free energies of halogen acids and alkali metal halides

The values of ΔG_t^0 for halogen acids, as well as alkali metal halides, could be obtained by coupling the transfer free energies of cations with those of anions, i.e., from the differences between those for the ion constituents, both based on the same type of oxidation or reduction potential scale [7–9], in any solvent. The values of ΔG_t^0 so calculated from the results of method I at 25°C, by eqn. (3), in various DMSO–water mixtures, are collected in Table 6.

$$\Delta G_t^0(\text{HX or MX}) = \Delta G_t^0(\text{H}^+ \text{ or M}^+) - \Delta G_t^0\,(\text{X}^-) \qquad (3)$$

It is interesting to note from Table 6 that while ΔG_t^0 values for HCl become increasingly positive, those for HBr and HI become increasingly negative as the proportion of DMSO increases. Also, for the alkali metal halides, the ΔG_t^0 values for LiI become increasingly negative (and a slight negative minimum is observed for CsI at around 5% DMSO) whilst those for the rest become increasingly positive, with increasing the DMSO content in the solvent. Further, the ΔG_t^0 values become increasingly negative in the order HCl, HBr, HI for transfer to any solvent. This behaviour is reflected in eqn. (3), since the values of ΔG_t^0 for the halide ion increases from Cl^- through Br^- to I^-. The decreasing order of ΔG_t^0 values from MCl through MBr to MI, in any solvent, can thus be explained in the same manner. However, in view of eqn. (3), it is notable that the usual tests of additivity of free energies made by Feakins et al. [1,13] could be performed between our results for potassium halides, for example, and those for halogen acids, in any solvent. The difference $\Delta G_t^0(KX) - \Delta G_t^0(HX)$, or $\Delta G_t^0(K^+) - \Delta G_t^0(H^+)$, is constant within the experimental error.

The net value of ΔG_t^0 of HX or MX is determined by the rate of increasing positive values of ΔG_t^0, of both positive and negative ions, with increasing DMSO concentration in the solvent. For the alkali metal halides, the ΔG_t^0 values for the transfer of LiI are all negative and decrease, while for transfers of all other MX they are all positive (except a negative minimum for CsI at around 5% DMSO) and increase with increasing proportion of

TABLE 7

The least-squares results of applying eqn. (2) to the previous EMF data in DMSO–water mixtures at 25°C reported by Khoo [3], ΔG_t^0 (J mol^{-1})

	DMSO (wt.%)				
	0	10	20	40	60
Results of method I					
− Corr (10^{-2})	99.9992	99.9988	99.9985	99.9989	99.9919
Δ (mV)					
HCl	−0.5	−0.6	−0.7	+0.5	+1.2
HBr	+0.9	+1.0	+1.1	−0.9	−2.0
HI	−0.4	−0.4	−0.4	+0.4	+0.8
a_1^0 (10^{10} V m^{-1})	1.0701	1.0411	1.0114	0.9251	0.7926
r^+ (10^{-10} m)	2.017	2.022	2.027	2.046	2.079
${}^{\text{ox}}_{\text{L}}E_m^0$ (V)	2.1587	2.1048	2.0498	1.8926	1.6475
${}^{\text{ox}}_{\text{R}}E_m^0$ (V)					
X = Cl	1.9368	1.8844	1.8306	1.6744	1.4346
Br	2.0866	2.0302	1.9721	1.8039	1.5456
I	2.3114	2.2488	2.1845	1.9982	1.7120
$\Delta G_t^0(\text{H}^+)$	–	5199	10511	25675	49323
$\Delta G_t^0(\text{X}^-)$					
X = Cl	–	5055	10255	25322	48459
Br	–	5446	11048	27281	52207
I	–	6033	12238	30219	57829
Results of method II					
Corr (10^{-2})	99.8974	99.9012	99.9041	99.8540	99.8075
Δ (mV)					
HCl	+5.5	+5.2	+5.0	+5.7	+5.6
HBr	−9.8	−9.4	−9.0	−10.1	−10.0
HI	+4.4	+4.2	+4.0	+4.5	+4.4
a_2^0 (10^{-10} V m)	4.1980	4.0846	3.9679	3.6276	3.1069
r^+ (10^{-10} m)	2.007	2.012	2.017	2.037	2.072
${}^{\text{red}}_{\text{L}}E_m^0$ (V)	2.0915	2.0305	1.9673	1.7809	1.4992
${}^{\text{red}}_{\text{R}}E_m^0$ (V)					
X = Cl	2.3193	2.2567	2.1922	2.0042	1.7165
Br	2.1528	2.0947	2.0348	1.8603	1.5933
I	1.9435	1.8910	1.8370	1.6794	1.4384
ΔG_t^0 (H^+)	–	5885	11977	29970	57141
$\Delta G_t^0(\text{X}^-)$					
X = Cl	–	6044	12264	30407	58166
Br	–	5610	11384	28224	53990
I	–	5065	10277	25480	48741
a_2^0/a_1^0 (10^{-20} m^2)	3.9231	3.9233	3.9234	3.9214	3.9199

DMSO in the solvent. However, this behaviour indicates that the combined effects of the solvent and solute properties disfavour the transfer of HCl or any MX (except LiI to any solvent and CsI to 5% DMSO) while they increasingly favour the transfer of HBr, HI and LiI. This behaviour is quite different from that observed for transfers of the halogen acids and LiI from water to other aqueous organic solvents [1–9], and is reported earlier [3].

Petrella et al. [14] summarized reports on the structural properties of DMSO–water mixtures, and showed that there is no general agreement on the structural characteristics of these solvents. Results of some measurements indicate that DMSO is only weakly hydrophobic and scarcely affects water structure, while to the contrary, others show that DMSO in water forms strong structures; contrasting results suggest that DMSO breaks structure in water [14]. If the transfer behaviour of the individual ions is compared with that in methanol–water mixtures [7] at the corresponding solvent composition, the smaller positive values of ΔG_t^0 obtained in methanol–water solvents [7] suggest that the ion affinity of these solvents is greater than in DMSO–water solvents. The transfer behaviour of HX or MX shows a different trend. The larger positive values of ΔG_t^0 for HX or MX, obtained in methanol–water solvents [7], show that the affinity of these solvents for the electrolytes is smaller than that in DMSO–water solvents.

The new procedure and previous EMF data in DMSO–water mixtures

The new procedure of determination of absolute electrode potential, as well as transfer free energies of individual ions, has also been applied to previous EMF data for the halogen acids in DMSO–water mixtures, reported by Khoo [3]. The least-squares results of applying eqns. (2-I) and (2-II) to the EMF data [3] are recorded in Table 7. However, the same interesting features and trends seen in Tables 3 and 4 are again observed, leading to the same conclusions. Thus, there is every reason that method I should be applied to the EMF data for determination of absolute electrode potentials as well as thermodynamic properties of individual ions in various aqueous solutions of both protic and aprotic solvents, and that its set of data should be credited. Further, the interest, validity and general applicability of the new procedure [7,8] in various solvents are demonstrated.

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REFERENCES

1 D. Feakins, B.E. Hickey and P.J. Voice, J. Chem. Soc., Faraday Trans. 1, 75 (1979) 907.
2 A.K. Das and K.K. Kundu, J. Chem. Soc., Faraday Trans. 1, 70 (1974) 1452.
3 K.H. Khoo, J. Chem. Soc. A, (1971) 1177, 2932.
4 R. Smits, D.L. Massart, J. Juillard and J.P. Morel, Electrochim. Acta, 21 (1976) 437.
5 J.P. Morel, Bull. Soc. Chim. Fr., (1967) 1405.
6 M.M. Elsemongy and I.M. Kenawy, Z. Phys. Chem. Neue Folge, 130 (1982) 37.
7 M.M. Elsemongy, Thermochim. Acta, 80 (1984) 239.
8 M.M. Elsemongy and F.M. Reicha, Thermochim. Acta, 103 (1986) 371; 106 (1986) 309.
9 M.M. Elsemongy, Thermochim. Acta, 103 (1986) 387; 108 (1986) 133.
10 J.M.G. Cowie and P.M. Toporowski, Can. J. Chem., 39 (1961) 2240.
11 K.J. Packer and D.J. Tomlinson, Trans. Faraday Soc., 67 (1971) 1302.
12 R.G. Bates, in J.F. Coetzee and C.D. Ritchie (Eds.), Solute–Solvent Interactions, Dekker, New York, 1969.
13 D. Feakins, in F. Franks (Ed.), Physico-Chemical Processes in Mixed Aqueous Solvents, Heinemann, London, 1969, and references therein.
14 G. Petrella, M. Petrella, M. Castagnolo, A. Dell' Atti and A. De Giglio, J. Solution Chem., 10 (1981) 129.