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GIBBS ENERGIES OF TRANSFER OF INDIVIDUAL IONS FROM WATER INTO TETRAHYDROFURAN AND ITS AQUEOUS MIXTURES

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ABSTRACT

The standard Gibbs free energies of transfer (ΔG_t°) of halogen acids HX (X = Cl, Br or I) and alkali metal halides MX (M = Li, Na, K, Rb or Cs) as well as their constituent individual ions from water into tetrahydrofuran (THF) and its aqueous mixtures were determined from the e.m.f. measurements at 25 °C of the cells: glass electrode/HX, solvent/AgX, Ag; and glass electrode (M)/MX, solvent/AgX, Ag. The values of ΔG_t° of the individual ions on the molal, molar and mole fraction scales show the same trend of variation with solvent composition, i.e. they increase monotonically with increasing THF content in the solvent. The standard absolute potentials of different electrodes in these solvents as well as the radii of the solvated cations and the extent of their solvation in such media were computed. The results are briefly discussed in relation to ion–solvent interactions and ion solvation.

INTRODUCTION

Cationic glass electrodes have frequently been used to determine standard Gibbs energies of transfer (ΔG_t°) for electrolytes from water into several aqueous organic solvents [1–7]. However, relatively few electrochemical studies using glass electrodes have been made in aqueous mixtures of dipolar aprotic solvents, and no work seems to have been done on the determination of ΔG_t° values for any electrolyte from water into non-aqueous solvents.

Recently we have used [1] glass electrodes for the determination of ΔG_t° values for the halogen acids and alkali metal halides from water into aqueous acetone solvents containing up to 80 wt.% acetone. Our studies have been extended to the tetrahydrofuran (THF)–water system. Therefore, the

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present investigation was undertaken to determine Gibbs energies of transfer for the halogen acids HX (X = Cl, Br or I) and alkali metal halides MX (M = Li, Na, K, Rb or Cs) as well as their constituent individual ions from water into THF and its aqueous mixtures. Transfer quantities have been determined by e.m.f. measurements in THF–water solvents of the cells:

Glass electrode/HX, solvent/AgX, Ag Cell (i)

Glass electrode (M)/MX, solvent/AgX, Ag Cell (ii)

The standard absolute electrode potentials obtained in such aqueous dipolar aprotic media have been used to compute the Gibbs free energies of transfer for individual ions from water into each solvent, with a view to obtaining a comprehensive understanding of the ion–solvent interactions.

Smits et al. [5] used such cells and reported the values of ΔG_t° for the transfer of HCl as well as RbCl into several aqueous solvents containing THF up to 85 wt.%, and for NaCl into 10–50 wt.% THF–water solvents. However, comparisons show that agreement between the new values of ΔG_t° and those of Smits et al. [5] for aqueous THF solvents is generally good.

EXPERIMENTAL

THF (BDH grade) was further purified as reported previously [8]. AnalaR and Merck quality alkali metal salts were purified further, dried at 120 °C and kept in a dessicator over P_2O_5 [1,5]. Redistilled deionized water [1,8] was generally used in the preparation of the solutions. All solutions were freshly prepared before taking measurements. The compositions of the solvents were accurate to ±0.01 wt.%. The solutions were all stored in dark bottles under a nitrogen atmosphere.

The cell design, general experimental procedure and mathematical treatment of the results have been described previously [1]. The molality (m) of cell solutions was in the range 0.001–0.050 mol kg^{-1}. The values of m are accurate to approximately 0.01%. The incomplete dissociation of electrolytes in the THF-rich solvents (media with low dielectric constant) was avoided by working at lower salt concentrations [5]. Also, exposure of the cells to light was always avoided. All measurements were taken by three different electrodes for each solution. The cell measurements were made in triplicate, and the mean values of these observations recorded. The experimental set-up allowed the recording of cell potentials up to 0.1 mV, 0.3 mV and 0.5 mV for solvents containing up to 30%, 60% and 100% THF, respectively. However, these potential values correspond to the mean precision of the measurements. A large number of experiments should be carried out to reach an acceptable precision [5], especially for the THF-rich solvents. The temperature of the measuring cells was maintained at 25 ± 0.01 °C.

RESULTS AND DISCUSSION

For cells (i) or (ii) in water (w) and in aqueous or non-aqueous THF solvent (s), if the same glass electrode is used in each and the e.m.f. values are corrected for drift [1–3], we can define

$$\Delta E = {}^{w}E - {}^{s}E \tag{1}$$

and

$$\Delta G_t^\circ = F\Delta E_m^\circ \tag{2}$$

where F is the Faraday constant, m refers to the molal concentration scale and ΔG_t° is the standard molal Gibbs free energy of transfer of 1 mole of electrolyte from water into any solvent [1]. The values of ΔE were analyzed in the way previously described [1–3] to give ΔE_m° values in the respective solvents. These are collected in Table 1 for HCl, HBr, HI, LiCl, NaCl, KCl, RbCl and CsCl, in 20 THF–water solvents. Note that the behaviour of the electrodes was so satisfactory when used as described [1–3] that extrapolation of the individual ${}^{w}E$ or ${}^{s}E$ values to give the individual E_m° values was possible; ΔE_m° values obtained as the difference of these data agreed well with those obtained by extrapolation of ΔE. Generally, the values of ΔE_m° are precise to better than ± 0.1, ± 0.3 and ± 0.5 mV for solvents containing up to 30, 60 and 100 wt.% THF, respectively. The values of ΔG_t° for the transfer of HCl, HBr, HI, LiCl, NaCl, KCl, RbCl and CsCl from water into THF–water solvents, calculated on the molal scale from ΔE_m° values (Table 1) using Eqn. (2), are listed in Table 2. These are therefore precise to better than ± 0.01, ± 0.03 and ± 0.05 kJ mol^{-1} for solvents containing up to 30, 60 and 100 wt.% THF, respectively, based on the precision of the ΔE_m° values.

The values of E_m° of cells (i) and (ii), containing HCl, HBr, HI, LiCl, NaCl, KCl, RbCl and CsCl in water and in THF–water solvents, are recorded in Table 3. All the values of ${}^{w}E_m^\circ$ of the cells, determined using glass electrodes in the present investigation, agree very well with those obtained previously [1,9]. In THF–water solvents, the agreement between the values of ${}^{s}E_m^\circ$ obtained earlier using hydrogen electrodes [8] and the present values using glass electrodes is good (taking into account the combined precision limits of the measurements) up to 50 wt.% THF for HCl and to 55 wt.% THF for HBr; the differences in E_m° values tend to increase with increasing concentration of THF. However, previously, such comparisons [4] showed that agreement between the two types of electrode, hydrogen and glass, is generally good up to approximately 40 wt.% of organic solvent.

In order to verify the accuracy of our measurements, and to assess their reliability, a comparison of our results for the standard Gibbs free energies of transfer to THF–water solvents with those obtained earlier by previous investigators has been made. Smits et al. [5] reported their ΔG_t° values for

TABLE 1

Values of ΔE_m° (mV) for cells (i) and (ii) in tetrahydrofuran–water solvents at 25 °C

THF (wt.%)	Compound							
	HCl	HBr	HI	LiCl	NaCl	KCl	RbCl	CsCl
5	3.6	0.9	−1.1	7.7	9.0	9.2	8.8	8.3
10	6.9	2.2	−2.3	15.5	18.6	18.9	18.2	16.8
15	10.5	3.1	−3.5	23.6	28.2	28.5	28.0	25.6
20	14.1	4.4	−4.5	32.1	38.2	38.4	38.0	34.7
25	18.2	6.4	−5.1	40.9	48.1	48.3	48.2	44.1
30	22.7	9.1	−5.1	50.2	58.5	58.9	58.9	53.9
35	28.2	12.7	−4.3	60.0	69.1	69.7	69.8	64.1
40	33.6	16.8	−3.4	70.3	80.3	81.1	81.4	74.9
45	40.2	22.8	−1.2	81.3	92.2	93.6	94.0	86.5
50	48.2	29.0	2.2	93.1	105.2	107.2	107.7	98.9
55	58.1	35.4	7.3	106.0	119.2	121.4	122.2	112.4
60	69.3	44.5	13.9	120.2	134.9	138.2	139.2	127.2
65	82.9	56.0	22.8	136.1	152.0	156.1	157.6	143.8
70	99.7	71.0	35.1	154.0	172.0	177.7	180.0	162.8
75	120.2	89.9	51.0	174.9	196.3	204.4	207.8	185.5
80	146.3	114.5	72.5	199.9	225.9	236.6	241.5	213.5
85	182.1	148.4	103.8	230.5	263.3	279.3	286.5	248.6
90	225.0	189.0	142.0	268.1	311.1	334.5	345.3	292.0
95	270.6	232.5	183.0	313.4	366.1	396.4	412.3	343.8
100	313.6	273.4	221.3	367.0	425.6	466.3	487.4	404.0

HCl (17 values) and RbCl (17 values) on the molar scale (c) in kJ mol^{-1}, whereas those for NaCl (5 values) on the molal scale (m) in cal mol^{-1}. Thus, to avoid any approximations and to obtain a more precise and accurate comparison, all the ΔG_t° values are expressed on the molar scale and collected in Table 4. Values of ΔG_t° (m) on the molal scale were converted to the molar scale [10] using Eqn. (3);

$$\Delta G_t^\circ(\mathrm{c}) = \Delta G_t^\circ(\mathrm{m}) + 2RT \ln(d_w/d_s) \tag{3}$$

where d_w and d_s are the densities of water and THF–water solvent, respectively. The values of Smits et al. [5] were taken with all significant digits as they were originally given. In general, the agreement between our results and those of Smits et al. [5] is acceptable, practically always within the combined precision limits of their and our measurements.

Table 2 shows that the values of ΔG_t° of all electrolytes (except HI) are positive and increase with increasing THF concentration in the solvent. For HI, the value of ΔG_t° decreases negatively to a minimum at around 25–30 wt.% THF and thereafter continues to increase negatively until becoming positive, and increases with increasing THF content in the solvent. On the other hand, the values of E_m° of cells (i) and (ii) containing any electrolyte (except HI) decrease monotonically, whereas those of cell (i) containing HI

TABLE 2

Standard molal Gibbs free energies (kJ mol^{-1}) of transfer of halogen acids and alkali metal halides from water into tetrahydrofuran–water solvents at 25 °C

Compound	THF (wt.%)									
	10	20	30	40	50	60	70	80	90	100
HCl	0.67	1.36	2.19	3.24	4.65	6.69	9.62	14.12	21.71	30.25
HBr	0.21	0.42	0.88	1.62	2.80	4.29	6.85	11.05	18.23	26.38
HI	−0.23	−0.44	−0.49	−0.33	0.22	1.34	3.38	7.00	13.70	21.35
LiCl	1.49	3.10	4.84	6.78	8.99	11.60	14.86	19.29	25.87	35.41
LiBr	1.14	2.40	3.79	5.37	7.22	9.48	12.39	16.46	22.68	31.88
LiI	0.62	1.34	2.20	3.26	4.57	6.30	8.68	12.21	17.91	26.57
NaCl	1.79	3.69	5.64	7.75	10.15	13.01	16.60	21.80	30.01	41.06
NaBr	1.44	2.98	4.59	6.34	8.38	10.89	14.12	18.97	26.83	37.53
NaI	0.92	1.93	3.01	4.22	5.73	7.71	10.41	14.72	22.05	32.22
KCl	1.82	3.71	5.68	7.82	10.34	13.33	17.15	22.83	32.27	44.99
KBr	1.48	3.00	4.62	6.42	8.57	11.21	14.68	19.99	29.09	41.45
KI	0.96	1.95	3.04	4.30	5.93	8.03	10.96	15.75	24.31	36.14
RbCl	1.75	3.67	5.68	7.85	10.39	13.43	17.37	23.31	33.31	47.03
RbBr	1.40	2.96	4.62	6.44	8.63	11.31	14.89	20.48	30.13	43.49
RbI	0.88	1.91	3.04	4.32	5.98	8.13	11.18	16.23	25.35	38.18
CsCl	1.62	3.34	5.20	7.23	9.54	12.27	15.71	20.60	28.18	38.98
CsBr	1.27	2.64	4.14	5.82	7.77	10.15	13.23	17.77	24.99	35.44
CsI	0.75	1.59	2.56	3.71	5.12	6.97	9.52	13.52	20.22	30.13

TABLE 3

Values of standard e.m.f., E_m° (V), of cells (i) and (ii) in tetrahydrofuran–water solvents at 25 °C

Compound	THF(wt.%)										
	0	10	20	30	40	50	60	70	80	90	100
HCl	0.22236	0.2154	0.2082	0.1996	0.1888	0.1741	0.1530	0.1227	0.0761	−0.0027	−0.0912
HBr	0.07105	0.0689	0.0667	0.0620	0.0542	0.0421	0.0265	0.0000	−0.0435	−0.1179	−0.2024
HI	−0.15235	−0.1500	−0.1478	−0.1473	−0.1490	−0.1546	−0.1662	−0.1874	−0.2249	−0.2944	−0.3737
LiCl	3.2667	3.2512	3.2346	3.2165	3.1964	3.1735	3.1464	3.1126	3.0668	2.9986	2.8996
LiBr	3.1169	3.1051	3.0921	3.0777	3.0612	3.0421	3.0187	2.9885	2.9464	2.8818	2.7865
LiI	2.8923	2.8858	2.8784	2.8694	2.8585	2.8449	2.8270	2.8024	2.7657	2.7067	2.6169
NaCl	2.9352	2.9166	2.8970	2.8767	2.8549	2.8300	2.8003	2.7632	2.7093	2.6241	2.5096
NaBr	2.7854	2.7705	2.7545	2.7379	2.7197	2.6986	2.6726	2.6391	2.5889	2.5074	2.3965
NaI	2.5608	2.5512	2.5408	2.5296	2.5170	2.5014	2.4809	2.4529	2.4082	2.3322	2.2269
KCl	3.1472	3.1283	3.1088	3.0883	3.0661	3.0400	3.0090	2.9694	2.9106	2.8127	2.6809
KBr	2.9974	2.9821	2.9663	2.9495	2.9309	2.9085	2.8812	2.8453	2.7902	2.6959	2.5678
KI	2.7727	2.7629	2.7526	2.7413	2.7282	2.7113	2.6895	2.6591	2.6095	2.5208	2.3982
RbCl	3.1475	3.1293	3.1095	3.0886	3.0661	3.0398	3.0083	2.9675	2.9060	2.8022	2.6601
RbBr	2.9978	2.9832	2.9670	2.9498	2.9310	2.9083	2.8805	2.8434	2.7855	2.6855	2.5470
RbI	2.7731	2.7640	2.7533	2.7416	2.7283	2.7112	2.6889	2.6572	2.6049	2.5104	2.3774
CsCl	3.1454	3.1286	3.1107	3.0915	3.0704	3.0465	3.0182	2.9826	2.9318	2.8533	2.7414
CsBr	2.9956	2.9824	2.9682	2.9527	2.9353	2.9150	2.8904	2.8585	2.8114	2.7366	2.6283
CsI	2.7710	2.7632	2.7545	2.7444	2.7326	2.7179	2.6987	2.6723	2.6308	2.5614	2.4587

TABLE 4

Comparison of standard molar Gibbs free energies of transfer ΔG_t° (kJ mol^{-1}) from water into tetrahydrofuran–water solvents, obtained by Smits et al. [5] for HCl, NaCl and RbCl, with the corresponding new values

THF (wt.%)	HCl		NaCl		RbCl	
	Ref. 5	This work	Ref. 5	This work	Ref. 5	This work
5	0.36	0.35			0.86	0.86
10	0.68	0.69	1.8	1.81	1.77	1.77
15	1.03	1.05			2.74	2.74
20	1.37	1.41	3.7	3.73	3.71	3.71
25	1.77	1.82			4.74	4.72
30	2.23	2.28	5.73	5.73	5.77	5.76
35	2.74	2.82			6.85	6.84
40	3.31	3.37	7.87	7.88	7.99	7.98
45	4.05	4.04			9.25	9.23
50	4.85	4.84	10.3	10.34	10.6	10.58
55	5.88	5.83			12.0	12.01
60	7.02	6.95			13.7	13.69
65	8.34	8.29			15.5	15.50
70	9.99	9.95			17.7	17.70
75	12.0	11.97			20.4	20.42
80	14.5	14.53			23.7	23.72
85	18.0	18.04			28.1	28.11

are all negative, increase to a maximum at around 25–30 wt.% THF, and thereafter decrease, with increasing amounts of THF in the solvent (Table 3). Such features have been noticed earlier [9] in different solvent systems.

Absolute electrode potentials and Gibbs free energies

A new procedure for the determination of standard absolute electrode potentials in aqueous and non-aqueous, protic and aprotic solvents, as well as the thermodynamics of individual ions in these media, was described recently [11]. The procedure was applied successfully to the e.m.f. data of different cells, and the interest, validity and general applicability of the procedure to various solvent systems have been demonstrated [1,9,11]. According to this procedure, the oxidation potential of any electrode varies directly with the radius (r) of the solvated ion on the activity of which the potential depends. Therefore, the cell e.m.f. is related linearly to the radius of the solvated ion which is being varied in a series of electrolytes having a common ion. Thus, in any solvent, the plot of the standard e.m.f. (E_m°) values of cell (i), containing HCl, HBr and HI, against the radius of the solvated anion (r_-) should yield a straight line according to Eqn. (4), at any temperature [11].

$$E_m^\circ = a_1^\circ r_+ - a_1^\circ r_- \qquad (4)$$

TABLE 5

The least-squares results of applying Eqn. (4) to the E_m° values of cell (i) in tetrahydrofuran–water solvents at 25° C

Parameter		THF (wt.%)									
		10	20	30	40	50	60	70	80	90	100
$-$corr (10^{-2})		99.9999	99.9996	99.9994	99.9998	99.9998	99.9991	99.9987	99.9995	99.9984	99.9973
Δ (mV)	X = Cl	−0.2	+0.4	+0.4	+0.2	−0.2	+0.5	+0.5	+0.3	+0.6	+0.7
	Br	+0.2	−0.6	−0.7	−0.3	+0.4	−0.8	−0.9	−0.5	−1.0	−1.2
	I	−0.1	+0.2	+0.3	+0.1	−0.2	+0.3	+0.4	+0.2	+0.4	+0.5
a_1° (10^{10}Vm^{-1})		1.0440	1.0177	0.9915	0.9653	0.9390	0.9127	0.8865	0.8601	0.8340	0.8078
r_+ (10^{-10} m)		2.016	2.015	2.012	2.006	1.995	1.978	1.949	1.899	1.807	1.698
${}^{\text{ox}}_{\text{L}}E_m^\circ$ (V)		2.1049	2.0506	1.9947	1.9362	1.8735	1.8054	1.7278	1.6332	1.5075	1.3716
${}^{\text{ox}}_{\text{R}}E_m^\circ$ (V)	X = Cl	1.8896	1.8420	1.7947	1.7472	1.6996	1.6519	1.6045	1.5568	1.5095	1.4621
	Br	2.0358	1.9845	1.9335	1.8824	1.8311	1.7797	1.7286	1.6772	1.6263	1.5752
	I	2.2550	2.1982	2.1417	2.0851	2.0282	1.9713	1.9148	1.8578	1.8014	1.7448
ΔG_t°	H^+	5.18	10.42	15.81	21.46	27.51	34.08	41.57	50.70	62.83	75.93
(kJ mol^{-1})	Cl^-	4.55	9.14	13.72	18.29	22.89	27.49	32.06	36.67	41.23	45.80
	Br^-	4.90	9.85	14.78	19.71	24.66	29.61	34.54	39.50	44.41	49.34
	I^-	5.43	10.91	16.37	21.83	27.31	32.80	38.26	43.76	49.20	54.66

TABLE 6

Standard absolute potentials, ${}^{\mathrm{ox}}_{\mathrm{L}}E^{\circ}_{\mathrm{m}}$ (V), of M/M^+ electrodes, radii (r_+) of solvated cations and their solvation extent (S_e) in tetrahydrofuran–water solvents, and standard transfer Gibbs free energies (ΔG_t°) of individual cations from water into these solvents, at 25 °C

Parameter	M	THF (wt.%)									
		10	20	30	40	50	60	70	80	90	100
${}^{\mathrm{ox}}_{\mathrm{L}}E^{\circ}_{\mathrm{m}}$ (V)	Li	5.1409	5.0766	5.0111	4.9436	4.8731	4.7983	4.7172	4.6236	4.5081	4.3617
	Na	4.8063	4.7390	4.6713	4.6021	4.5296	4.4522	4.3677	4.2661	4.1337	3.9717
	K	5.0179	4.9508	4.8830	4.8133	4.7396	4.6609	4.5739	4.4674	4.3222	4.1430
	Rb	5.0190	4.9515	4.8833	4.8134	4.7394	4.6602	4.5720	4.4628	4.3118	4.1222
	Cs	5.0182	4.9527	4.8861	4.8176	4.7461	4.6701	4.5871	4.4886	4.3629	4.2035
r_+ (10^{-10} m)	Li	4.924	4.988	5.054	5.121	5.190	5.258	5.321	5.376	5.405	5.400
	Na	4.604	4.657	4.711	4.767	4.824	4.878	4.927	4.960	4.956	4.917
	K	4.806	4.865	4.925	4.986	5.047	5.107	5.160	5.194	5.183	5.129
	Rb	4.807	4.865	4.925	4.986	5.047	5.106	5.158	5.189	5.170	5.103
	Cs	4.807	4.867	4.928	4.991	5.054	5.117	5.175	5.219	5.231	5.204
S_e (10^{-10} m)	Li	4.32	4.39	4.45	4.52	4.59	4.66	4.72	4.78	4.81	4.80
	Na	3.65	3.71	3.76	3.82	3.87	3.93	3.98	4.01	4.01	3.97
	K	3.48	3.53	3.59	3.66	3.72	3.78	3.83	3.86	3.85	3.80
	Rb	3.33	3.39	3.45	3.51	3.57	3.63	3.68	3.71	3.69	3.62
	Cs	3.12	3.18	3.24	3.30	3.36	3.43	3.48	3.53	3.54	3.51
ΔG_t° (kJ mol^{-1})	Li	5.98	12.18	18.50	25.01	31.81	39.03	46.86	55.89	67.03	81.15
	Na	6.28	12.77	19.30	25.98	32.97	40.44	48.59	58.40	71.17	86.80
	K	6.31	12.79	19.33	26.05	33.16	40.76	49.15	59.43	73.43	90.72
	Rb	6.24	12.75	19.33	26.08	33.22	40.86	49.36	59.91	74.47	92.77
	Cs	6.10	12.42	18.85	25.46	32.36	39.70	47.70	57.20	69.34	84.71

This holds in various THF–water solvents, and the least-squares results at 25 °C are collected in Table 5. In all solvents perfect straight lines were obtained, and the extent of correlation is indicated by the correlation coefficient (corr) and the differences, Δ (mV), between the E°_m values obtained experimentally and those calculated by Eqn. (5),

$$E^\circ_m = {}^{ox}_{L}E^\circ_m - {}^{ox}_{R}E^\circ_m \qquad (5)$$

where ${}^{ox}_{L}E^\circ_m$ and ${}^{ox}_{R}E^\circ_m$ are the oxidation potentials of the left and right electrodes, respectively [1,9,11]. Thus, the standard absolute potential of the H_2/H^+ and Ag–AgX (X = Cl, Br or I) electrodes, the radius (r_+) of the solvated H^+ ion and thus its solvation extent (S_e), in the standard state, have been computed as before [1,9,11].

From the computed values of the standard absolute potential of the Ag–AgCl electrode in each solvent (Table 5), those of M/M^+ (where M = Li, Na, K, Rb or Cs) electrodes could be obtained (by Eqn. (5)) from the E°_m values of cell (ii) containing MCl, Table 3. The radii of the solvated cations and their solvation extent, in each solvent, were calculated as before [1,9,11]. All these results are collected in Table 6.

It is evident from Tables 5 and 6 that as the THF content of the solvent increases, the value of a_1° (which appears to be a universal constant for all electrodes, and dependent only on the medium, at any temperature [1,9,11]) decreases, the oxidation potentials of both left and right electrodes decrease, and the radius (r_+) of the solvated H^+ ion decreases (i.e. the extent of solvation of the protons decreases) whereas that of any solvated cation and thus its solvation extent increases to a maximum at around 80–90 wt.% THF and thereafter decreases. In any solvent, the extent of solvation of M^+ ions increases in the expected well-known order: $Cs^+ < Rb^+ < K^+ < Na^+ < Li^+$, and the Li^+ ion is always highly solvated. The standard absolute potentials of Ag–AgX electrodes decrease in the regular order: ${}^{ox}E^\circ_m$ (Ag–AgI) > ${}^{ox}E^\circ_m$ (Ag–AgBr) > ${}^{ox}E^\circ_m$ (Ag–AgCl), in any solvent, whereas the irregular order of variation of the standard absolute potentials of the alkali metal electrodes, from Li/Li^+ to Cs/Cs^+, is dictated by the extent of solvation of the alkali metal ions, and thus by the radii of solvated cations. These interesting features have been observed recently in several solvent systems [1,9,11].

Further, by coupling the standard absolute potentials (${}^{ox}_{L}E^\circ_m$) of M/M^+ (M = Li, Na, K, Rb or Cs) electrodes with those (${}^{ox}_{R}E^\circ_m$) of Ag–AgX (X = Br or I) electrodes, using Eqn. (5), the values of E°_m for cell (ii), containing MBr or MI, could be computed. Thus, all the values of E°_m of this cell in various THF–water solvents at 25 °C so computed are also included in Table 3. Furthermore, the values of ΔG_t° for the other alkali metal halides, MBr and MI, could also be obtained from the E°_m values of cell (ii) in water and in various THF–water solvents (Table 3) using Eqn. (2). These are also included in Table 2.

The standard free energy changes ($\Delta G_{\mathrm{E}}^{\circ}$) involved in the half-cell reactions are related to the standard absolute electrode potentials (${}^{\mathrm{ox}}_{\mathrm{E}}E_{\mathrm{m}}^{\circ}$) by the relation [1,9,11]:

$$\Delta G_{\mathrm{E}}^{\circ} = -F\,{}^{\mathrm{ox}}_{\mathrm{E}}E_{\mathrm{m}}^{\circ} \qquad (6)$$

Thus, the value of $\Delta G_{\mathrm{E}}^{\circ}$ can be computed on the molal scale using the ${}^{\mathrm{ox}}_{\mathrm{E}}E_{\mathrm{m}}^{\circ}$ values given in Tables 5 and 6.

The values for the standard Gibbs free energy $\Delta G_{\mathrm{t}}^{\circ}$ for the transfer of an individual ion from water to various THF–water solvents were calculated [1,9,11] on the molal scale from the standard absolute electrode potentials in water (${}^{\mathrm{w}}_{\mathrm{E}}E_{\mathrm{m}}^{\circ}$) and in the respective solvents (${}^{\mathrm{s}}_{\mathrm{E}}E_{\mathrm{m}}^{\circ}$), Tables 5 and 6, using Eqn. (7).

$$\Delta G_{\mathrm{t}}^{\circ} = F\left({}^{\mathrm{w}}_{\mathrm{E}}E_{\mathrm{m}}^{\circ} - {}^{\mathrm{s}}_{\mathrm{E}}E_{\mathrm{m}}^{\circ}\right) \qquad (7)$$

The values of $\Delta G_{\mathrm{t}}^{\circ}$ so calculated at 25 °C are also included in Table 6. These are accurate to better than 0.02, 0.05 and 0.09 kJ mol^{-1} for solvents containing up to 30, 60 and 100 wt.% THF, respectively.

The values of $\Delta G_{\mathrm{t}}^{\circ}$ for all ions show a qualitative resemblance to other solvent systems [1,9,11] in that all the values are positive and increase (i.e. ion transfer becomes increasingly less favourable) with rising THF content of the solvent. In general, free energies of transfer are dictated by ion–solvent interactions. So, these may be simply interpreted by assuming that the ions, which are hydrophilic, interact more strongly with water molecules than with co-solvent (THF) molecules in any solvent, without reference to any special structural properties of water or the co-solvent studied [11]. In any solvent, the relative order of non-spontaneity for the anions is $\Delta G_{\mathrm{t}}^{\circ}$ (Cl^-) < $\Delta G_{\mathrm{t}}^{\circ}$ (Br^-) < $\Delta G_{\mathrm{t}}^{\circ}$ (I^-). For the cations, there is a marked rise in $\Delta G_{\mathrm{t}}^{\circ}$ from H^+ through Li^+ and Na^+ to K^+ and a fall from Rb^+ to Cs^+ with a maximum (for K^+ in solvents of low THF content) that shifts (to Rb^+ in solvents of high THF content) as the proportion of THF is increased. This pattern is very similar to that found for transfers from water to several solvent systems [1,9,11], and the similarity in the profiles of $\Delta G_{\mathrm{t}}^{\circ}$ points to a common cause for the behaviour of these single ions in these solvent systems. However, this behaviour is extensively explained and discussed in terms of the acid–base theory of ionic solvation [12,13].

Increased desolvation of the proton (r_+ value decreases) and, on the other hand, increased solvation of the M^+ ions (r_+ values increase) with increasing amounts of THF in the solvent are observed. Nevertheless, the values of $\Delta G_{\mathrm{t}}^{\circ}$ for all (H^+ and M^+) ions are positive and increase with increasing THF concentration in the solvent. This presumably indicates, and proves again [1,9], that there is no relationship between $\Delta G_{\mathrm{t}}^{\circ}$ values and the solvation of ions.

The standard absolute oxidation potentials of the hydrogen and Ag–AgCl electrodes (as examples) on the molar (c) and on the mole fraction (x) scales

TABLE 7

The standard absolute oxidation potential, $E°$ (V), of the hydrogen and Ag–AgCl electrodes, and the transfer free energy, $\Delta G_t°$ (kJ mol^{-1}), of H^+ and Cl^- ions from water into tetrahydrofuran–water solvents, on the molal (m), molar (c) and mole fraction (x) scales at 25 °C

THF	Hydrogen electrode			Ag–AgCl electrode			$\Delta G_t°$ (H^+)			$\Delta G_t°$ (Cl^-)		
(wt.%)	$E_m°$	$E_c°$	$E_x°$	$E_m°$	$E_c°$	$E_x°$	(m)	(c)	(x)	(m)	(c)	(x)
0	2.1586	2.1585	2.0554	1.9368	1.9369	2.0400						
10	2.1049	2.1048	2.0037	1.8896	1.8898	1.9908	5.18	5.19	4.99	4.55	4.54	4.75
20	2.0506	2.0503	1.9516	1.8420	1.8424	1.9411	10.42	10.44	10.02	9.14	9.12	9.55
30	1.9947	1.9942	1.8981	1.7947	1.7952	1.8913	15.81	15.86	15.18	13.72	13.67	14.35
40	1.9362	1.9355	1.8422	1.7472	1.7480	1.8412	21.46	21.52	20.57	18.29	18.23	19.18
50	1.8735	1.8724	1.7824	1.6996	1.7007	1.7907	27.51	27.60	26.34	22.89	22.79	24.05
60	1.8054	1.8051	1.7176	1.6519	1.6523	1.7397	34.08	34.10	32.59	27.49	27.46	28.97
70	1.7278	1.7260	1.6437	1.6045	1.6063	1.6886	41.57	41.74	39.72	32.06	31.89	33.91
80	1.6332	1.6309	1.5535	1.5568	1.5590	1.6364	50.70	50.90	48.42	36.67	36.46	38.94
90	1.5075	1.5047	1.4331	1.5095	1.5123	1.5838	62.83	63.08	60.04	41.23	40.97	44.01
100	1.3716	1.3684	1.3041	1.4621	1.4654	1.5297	75.93	76.24	72.49	45.80	45.50	49.24

were computed at 25 °C with the help of Eqns. (8)–(11) [10,11] and these are recorded in Table 7.

$$ {}^{\mathrm{ox}}_{\mathrm{L}}E^{\circ}_{\mathrm{c}} = {}^{\mathrm{ox}}_{\mathrm{L}}E^{\circ}_{\mathrm{m}} + k \log d \tag{8}$$

$$ {}^{\mathrm{ox}}_{\mathrm{R}}E^{\circ}_{\mathrm{c}} = {}^{\mathrm{ox}}_{\mathrm{R}}E^{\circ}_{\mathrm{m}} - k \log d \tag{9}$$

$$ {}^{\mathrm{ox}}_{\mathrm{L}}E^{\circ}_{\mathrm{x}} = {}^{\mathrm{ox}}_{\mathrm{L}}E^{\circ}_{\mathrm{m}} - k \log(10^3/M_{\mathrm{s}}) \tag{10}$$

$$ {}^{\mathrm{ox}}_{\mathrm{R}}E^{\circ}_{\mathrm{x}} = {}^{\mathrm{ox}}_{\mathrm{R}}E^{\circ}_{\mathrm{m}} + k \log(10^3/M_{\mathrm{s}}) \tag{11}$$

where k is $(RT \ln 10)/F$, d is the density and M_{s} is the mean molar mass of the solvent. In all cases, the standard e.m.f. of the cell on the molal, molar and mole fraction scales, is equal to the difference between ${}^{\mathrm{ox}}_{\mathrm{L}}E^{\circ}$ and ${}^{\mathrm{ox}}_{\mathrm{R}}E^{\circ}$ as given by Eqn. (5) or similar equations [1,9,11].

Also, the values of $\Delta G_{\mathrm{t}}^{\circ}$ of H^+ and Cl^- ions (as examples) were computed at 25 °C on the molar (c) and on the mole fraction (x) scales using Eqns. (12)–(15) [10,11] and these are included in Table 7.

$$\Delta G_{\mathrm{t}}^{\circ}(\mathrm{H}^+)_{\mathrm{c}} = \Delta G_{\mathrm{t}}^{\circ}(\mathrm{H}^+)_{\mathrm{m}} + RT \ln(d_{\mathrm{w}}/d_{\mathrm{s}}) \tag{12}$$

$$\Delta G_{\mathrm{t}}^{\circ}(\mathrm{Cl}^-)_{\mathrm{c}} = \Delta G_{\mathrm{t}}^{\circ}(\mathrm{Cl}^-)_{\mathrm{m}} - RT \ln(d_{\mathrm{w}}/d_{\mathrm{s}}) \tag{13}$$

$$\Delta G_{\mathrm{t}}^{\circ}(\mathrm{H}^+)_{\mathrm{x}} = \Delta G_{\mathrm{t}}^{\circ}(\mathrm{H}^+)_{\mathrm{m}} - RT \ln(M_{\mathrm{s}}/M_{\mathrm{w}}) \tag{14}$$

$$\Delta G_{\mathrm{t}}^{\circ}(\mathrm{Cl}^-)_{\mathrm{x}} = \Delta G_{\mathrm{t}}^{\circ}(\mathrm{Cl}^-)_{\mathrm{m}} + RT \ln(M_{\mathrm{s}}/M_{\mathrm{w}}) \tag{15}$$

where d_{w} and d_{s} are the densities and M_{w} and M_{s} are the mean molar masses of water and solvent, respectively. In all cases, the standard Gibbs free energy of transfer of HCl, for example, is equal to the difference between those of H^+ and Cl^- ions, all are on the same concentration scale and are referred to the oxidation potential scale, Eqn. (16). As was evident previously [1,9,11], the potential scale to which a $\Delta G_{\mathrm{t}}^{\circ}$ value is referred to should be defined, and the oxidation potential scale should only be used for all treatments of e.m.f. data, whereas all relations based on the reduction potential scale cannot be used to obtain the thermodynamics of single ions.

$$\Delta G_{\mathrm{t}}^{\circ}(\mathrm{HX\ or\ MX}) = \Delta G_{\mathrm{t}}^{\circ}(\mathrm{H}^+\ \mathrm{or}\ \mathrm{M}^+) - \Delta G_{\mathrm{t}}^{\circ}(\mathrm{X}^-) \tag{16}$$

However, Table 7 shows that whatever the concentration scale used, the same trend of variation of standard absolute electrode potential as well as standard Gibbs free energy for the transfer of an individual ion with solvent composition is found, i.e. the trend of variation of $\Delta G_{\mathrm{t}}^{\circ}$ with THF wt.% is independent of the concentration scale used.

The maximum in E_{m}° values of cell (i) containing HI and the minimum in $\Delta G_{\mathrm{t}}^{\circ}(\mathrm{HI})$ values, at around 25–30 wt.% THF, can now be explained in view of Eqns. (5) and (16) respectively, where the net rate of variation of E_{m}° or $\Delta G_{\mathrm{t}}^{\circ}$ is determined by the difference between the rates of variation of two positive values with increasing THF content in the solvent.

Other $\Delta G_t°$ values for single ions

Wells et al. [14–17] determined the free energy of transfer of the proton, $\Delta G_t°(H^+)$, from water into water-rich mixtures of several co-solvents by the spectrophotometric solvent-sorting method using trace additions of 4-nitroaniline. In all cases the values for $\Delta G_t°(H^+)$ are negative, those for $\Delta G_t°(X^-)$ determined by combining $\Delta G_t°(H^+)$ values with values for $\Delta G_t°(HX)$ are normally positive and $\Delta G_t°(M^+)$, determined by combining $\Delta G_t°(X^-)$ with values for $\Delta G_t°(MX)$, are normally negative [14–17]. For the water–THF mixtures [15], the same broad dispersion of values for $\Delta G_t°(i)$ has been found, $\Delta G_t°(i)$ is negative for i = cations and positive for i = anions, with a minimum in $\Delta G_t°(H^+)$ and a maximum in $\Delta G_t°(Cl^-)$ at around 30 wt.% THF, for example. However, one should point out that, if the $\Delta G_t°(H^+)$ values were negative as given by Wells et al. [14–17], those of $\Delta G_t°(X^-)$ would also all be negative, because the value of $\Delta G_t°$ for an electrolyte should be given by the difference between (and not the sum of [14–17]) the values for the constituent ions [11]. This well-proven and important point has been discussed at length in our recent papers [1,9,11]. Further, Wells et al. [16] reported that their results are in contrast to expectations from purely electrostatic considerations in a dielectric continuum having a dielectric constant less than that of water of positive values for $\Delta G_t°(i)$ for all i ions irrespective of the sign of the charge. Furthermore, other comments, which are of major importance and should be taken into account, are also included, such as the following. (1) Although their investigations [14–17] are restricted to water-rich mixtures to avoid other net effects resulting from the transfer of H^+_{aq} between water and the mixtures, uncertain extrapolations of the ΔG_2 curves are usually made, e.g. from 37.26 to 50 wt.% THF [15] and from 54.26 to 65 wt.% ethanol [17]. (2) Their values of ΔG(Born), 167.6 $(D_s^{-1} - D_w^{-1})$ kJ mol^{-1} [14,16], must be corrected and recalculated as 16.76 $(D_s^{-1} - D_w^{-1})$ kJ mol^{-1}, i.e. divided by 10, and thus all the values of $\Delta G_t°(H^+)$ should be recalculated. However, this mistake has been noticed elsewhere [18]. After dividing by 10, ΔG(Born) forms only a very small part of the total $\Delta G_t°(H^+)$. In fact, comparably, the electrostatic contribution to the standard transfer free energy for the individual ions, calculated on the basis of the corrected Born equation [11], is 0.7–1.6% of the total $\Delta G_t°$ value for an ion in aqueous solvent containing up to 90 wt.% ethylene glycol. (3) Again, the potential scale to which the value of $\Delta G_t°$ is referred to should be defined [11]. The free energy of transfer of the proton $\Delta G_t°(H^+)$ from water into any mixture has been calculated by Wells et al. [14–17] using the equation

$$\Delta G_t°(H^+) = [\Delta G(\text{Born}) + \Delta G_2]_c + RT\ \ln(d_s M_w / d_w M_s) \qquad (17)$$

Equation (17) gives values of $\Delta G_t°(H^+)$ on the oxidation potential scale, whereas both the values of ΔG_2 and ΔG(Born), which is inversely related to

r [11], are based on the reduction potential scale. Therefore, the second term on the right-hand side must be rewritten as $RT\ \ln(d_w M_s/d_s M_w)$ to give $\Delta G_t^\circ(H^+)$ values on the reduction potential scale. (4) The use of organic indicators implies assumptions regarding the entropy effect and the hydrophobic effect, too, especially in mixtures of organic solvent with water [19]. The values obtained by working with indicators are strongly dependent on the kind of indicator, especially regarding the extrema of ΔG_t°, pH or H_0 at mean concentrations of organic solvents [19].

Moreover, the determination of the medium ionic activity coefficients, and thus the transfer free energies of single ions, from solubility products of salts can be erroneous if the salt is incompletely dissociated or if the solubility product is determined for a solid solvate of the salt [20]. The selection of salts is therefore crucial [20]. The difference in Gibbs free energy of transfer for single ions determined using potentiometric and solubility measurements amounts to 3.0 kJ mol^{-1} (30 mV) [20].

Interestingly, though, values of ΔG_t° for BPh_4^- and TAB^+ (triisoamylbutylammonium ion) are not equal and differ from those for Ph_4P^+ and Ph_4As^+, although the assumption of their mutual equality has been used as another basis for the resolution of ΔG_t° values for salts into the values for separate ions [17,21]. Similarly, $\Delta G_t^\circ(Ph_4As^+)$ is also not equal to $\Delta G_t^\circ(BPh_4^-)$ in several solvent systems [14,17].

Finally, for the methanol–water solvent system, which is one of the most frequently used solvent systems for thermodynamic and kinetic studies of electrolytes, Abraham et al. [21] have pointed out the quite different (negative and positive) single-ion ΔG_t° values reported for transfer of univalent ions from water into methanol–water solvents based on some particular extra-thermodynamic assumption; such differences are magnified for the M^{2+} ions. Therefore, Schwabe and Queck [19] prefer potentiometric measurements to obtain thermodynamic values of single ions for their reported reasons. This may be justified because cells contain the electrolyte and the solvent only.

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